

# Synthesis, Structure, and Reactivity of Ruthenium(II) Terminal Imido Complexes

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The reactions of  $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$  and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  with  $\text{LiNH-R}$  ( $\text{R} = 2,6\text{-diisopropylphenyl (Ar)}, 2,6\text{-dimethylphenyl (Ar')}, 2,4,6\text{-tri-tert-butylphenyl (Ar'*)}$ ) lead to a number of different products depending on the nature of ligands employed. The addition of 2 equiv of  $\text{LiNHAr}$  to  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  gives the amido complex  $(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{NHAr})$ . Reaction of 4 equiv of the lithium amides with the ruthenium complex  $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$  or  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  yields imido complexes. The steric bulk of the substituents on either the  $\eta^6\text{-arene}$  or nitrogen influence the structure of the final product. Large ligands such as the  $\eta^6\text{-C}_6\text{Me}_6$  or the  $\text{Ar}^*$  group prevent the formation of bridged complexes, while combinations of ligands which have smaller steric requirements give dimeric compounds. The structures of  $(\eta^6\text{-cymene})\text{RuCl}_2(\text{NH}_2\text{Ar})$ ,  $(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{NHAr})$ , and  $[(\eta^6\text{-cymene})\text{Os}(\text{NAr})]_2$  are presented and discussed in relation to the previously reported structures of  $[(\eta^6\text{-cymene})\text{Ru}(\text{NAr})]_2$  and  $(\eta^6\text{-cymene})\text{Ru}(\equiv\text{NAr}^*)$ .

## Introduction

The number of transition metal imido complexes has grown dramatically in recent years<sup>1,2</sup> with one notable exception, low-valent terminal imido compounds. Transition metal complexes that contain terminal imido ligands with d-electron counts other than  $d^{0-4}$  are represented by only a few examples.<sup>3</sup> Complexes of this type tend to be reactive, displaying nucleophilic behavior at the imido carbon. Thus, many of the  $d^6$  imido complexes react with small molecules that contain multiple bonds. In particular the reaction of  $\text{Cp}^*\text{Ir}(\equiv\text{N-}t\text{-Bu})$  with  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$  in which the  $\text{Ir}\equiv\text{N}$  bond is cleaved to form an  $\eta^4\text{-pyrrole}$  is intriguing.

It is possible reactions of this type could be extended to other substrates by varying the transition metal or the nature of the imido and ancillary ligands. Extending the chemistry of these complexes in this fashion has proved difficult. The second-row analogues of the known complexes have not been reported. Terminal imido complexes of rhodium are poorly characterized,<sup>4</sup> and until recently<sup>5</sup> only a single well-characterized example of a  $d^4$  ruthenium terminal imido complex was known.<sup>6</sup> The ruthenium analogue of the  $d^6$  osmium complexes appeared to form bridged complexes.<sup>7</sup>

Previous work has shown that the preference for bridged or monomeric imido complexes can be controlled by adjusting the steric requirements of the ancillary ligands or the organic group on the imido ligand.<sup>8</sup> Using a more sterically demanding imido ligand, it is possible to isolate complexes that contain monomeric imidos.<sup>7</sup> Here we report the synthesis and structures of  $d^6$  ruthenium imido complexes. Portions of this work have been communicated previously.<sup>5</sup>

## Experimental Section

**General Considerations.** Unless otherwise noted all reactions and manipulations were performed under an inert atmosphere in a Innovative Technologies drybox. Nuclear magnetic resonance spectroscopy was performed at 6.34 T on a JEOL GX270W spectrometer operating at 270 MHz for  $^1\text{H}$ .  $^1\text{H}$  NMR spectra were referenced to benzene at 7.15 ppm, and  $^{13}\text{C}$  NMR were referenced to benzene at 128 ppm. Elemental analysis was carried out at the microanalytical laboratory of the University of Otago, Dunedin, New Zealand. Infrared spectra were recorded on a BIO-RAD FTS-40 spectrophotometer as a thin film of Nujol mull between KBr disks. Benzene, toluene, and THF were distilled from sodium/benzophenone. Pentane, hexane, and hexamethyldisiloxane were distilled from sodium/potassium alloy, and deuterated benzene was distilled from sodium/benzophenone. Lithium amides were prepared from the freshly distilled anilines by treatment with  $n\text{-butyllithium}$  in benzene.  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$ ,  $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$ ,<sup>9</sup> and 2,4,6-tri-tert-butylaniline<sup>10</sup> were prepared from literature methods. Unless otherwise noted, all other reagents were used as received from commercial suppliers.

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**$[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\mu\text{-NAr}')]_2$ .** A solution of  $\text{LiNHAr}'$  (75 mg, 0.6 mmol) in THF (5 mL) was added to a THF (10 mL) suspension of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  (100 mg, 0.150 mmol). This mixture was stirred at room temperature for 12 h after which it was black color. The THF was removed *in vacuo* and the dark solid extracted with benzene and filtered through Celite. Evaporation of the benzene gave 33 mg of a brown product in 29% yield. The product can be recrystallized from pentane at  $-35^\circ\text{C}$ . Anal. Calcd: C, 62.80; H, 7.11; N, 3.66. Found: C, 62.11; H, 7.62; N, 3.73.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.30 (d,  $J = 7.3$ , 2H,  $\text{Me}_2\text{C}_6\text{H}_3$ ), 7.17 (t,  $J = 7.3$ , 1H,  $\text{Me}_2\text{C}_6\text{H}_3$ ), 2.45 (s, 6H,  $\text{Me}_2\text{C}_6\text{H}_3$ ), 2.11 (s, 18H,  $\text{C}_6\text{Me}_6$ ).  $^{13}\text{C}$  NMR:  $\delta$  166.4 ( $\text{Me}_2\text{C}_6\text{H}_3$ ), 125.7 ( $\text{Me}_2\text{C}_6\text{H}_3$ ), 124.0 ( $\text{Me}_2\text{C}_6\text{H}_3$ ), 121.1 ( $\text{Me}_2\text{C}_6\text{H}_3$ ), 89.6 ( $\text{C}_6\text{Me}_6$ ), 19.6 ( $\text{Me}_2\text{C}_6\text{H}_3$ ), 18.2 ( $\text{C}_6\text{Me}_6$ ).

**$(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\equiv\text{NAr}^*$ .** A solution of  $\text{LiNHAr}^*$  (165 mg, 0.617 mmol) in THF (5 mL) was added to a THF (10 mL) suspension of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  (100 mg, 0.150 mmol). This mixture was stirred at room temperature for 12 h after which it was a deep-green color. The THF was removed *in vacuo* and the black-green solid extracted with benzene and filtered through Celite. Evaporation of the benzene gave 63 mg of a deep green product in 40% yield. The product can be recrystallized from pentane at  $-35^\circ\text{C}$ . Anal. Calcd: C, 68.93; H, 9.06; N, 2.68. Found: C, 68.48; H, 9.79; N, 3.39.  $^1\text{H}$  NMR:  $\delta$  7.20 (s, 2H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 2.11 (s, 18H,  $\text{C}_6\text{Me}_6$ ), 1.81 (s, 18H,  $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ), 1.27 (s, 9H,  $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ).  $^{13}\text{C}$  NMR:  $\delta$  146.9 ( $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ), 128.7 ( $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ), 128.4 ( $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ), 121.6 ( $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ), 89.2 ( $\text{C}_6\text{Me}_6$ ), 38.2 ( $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ), 31.3 ( $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ), 30.9 ( $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ), 30.6 ( $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ), 18.2 ( $\text{C}_6\text{Me}_6$ ).

**$(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{NHAr})$ .** A solution of  $\text{LiNHAr}$  (54 mg, 0.28 mmol) in THF (5 mL) was added to a THF (10 mL) suspension of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  (100 mg, 0.150 mmol). This mixture was stirred at room temperature for 12 h after which it was a dark red color. The THF was removed *in vacuo* and the dark red solid then extracted with toluene and filtered through Celite. Removal of the toluene to a minimal volume and cooling to  $-35^\circ\text{C}$  gave 93 mg of a red crystalline solid in 65% yield. Anal. Calcd: C, 60.67; H, 7.64; N, 2.95. Found: C, 60.07; H, 7.81; N, 3.06.  $^1\text{H}$  NMR:  $\delta$  10.18 (s, 1H,  $\text{NH}$ ), 7.26 (d,  $J = 7.0$ , 2H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 7.18 (t,  $J = 7.0$ , 1H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 3.63 (sept,  $J = 6.6$ , 2H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 1.69 (s, 18H, e,  $\text{C}_6\text{Me}_6$ ), 1.16 (d,  $J = 7.0$ , 12H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ).  $^{13}\text{C}$  NMR:  $\delta$  152.5 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 142.6 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 124.7 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 122.2 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 88.0 ( $\text{C}_6\text{Me}_6$ ), 28.3 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 28.1 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 15.8 ( $\text{C}_6\text{Me}_6$ ).

**$(\eta^6\text{-C}_6\text{Me}_6)\text{RuN}(\text{Ph})\text{C}(\text{O})\text{N}(\text{Ar})$ .** A solution of  $(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{NHAr})$  (100 mg, 0.210 mmol) in benzene (10 mL) was added to a solution of phenyl isocyanate (26 mg, 0.218 mmol) in benzene (5 mL). This mixture was stirred at room temperature for 12 h after which it was a yellow color. The benzene was removed *in vacuo*, and the yellow solid was extracted with toluene and filtered through Celite. Reduction in volume of the toluene gave 67 mg of a yellow product in 57% yield. The product can be recrystallized from a toluene pentane solution at  $-35^\circ\text{C}$ . IR (KBr): 2965 (m), 2925 (m), 2292 (m), 1777 (s), 1718 (s), 1596 (s), 1500 (s), 1443 (s), 1385 (m), 932 (w), 768 (m)  $\text{cm}^{-1}$ . Anal. Calcd: C, 66.75; H, 7.23; N, 5.02. Found: C, 66.14; H, 7.42; N, 5.13.  $^1\text{H}$  NMR:  $\delta$  7.30 (m, 5H, Ph), 7.18 (t,  $J = 7.7$ , 1H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 7.07 (d,  $J = 8.1$ , 2H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 3.13 (br s, 2H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 2.08 (s, 18H,  $\text{C}_6\text{Me}_6$ ), 1.17 (d,  $J = 6.2$ , 12H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ).  $^{13}\text{C}$  NMR:  $\delta$  170.4 (CO), 152.4 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 140.2 ( $\text{C}_6\text{H}_5$ ), 129.0 ( $\text{C}_6\text{H}_5$ ), 127.4 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 127.2 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 125.6 ( $\text{C}_6\text{H}_5$ ), 123.9 ( $\text{C}_6\text{H}_5$ ), 120.8 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 89.4 ( $\text{C}_6\text{Me}_6$ ), 25.9 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 25.1 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 18.0 ( $\text{C}_6\text{Me}_6$ ).

**$(\eta^6\text{-cymene})\text{Ru}\equiv\text{NAr}^*$ .** A solution of  $\text{LiNHAr}^*$  (179 mg, 0.669 mmol) in THF (5 mL) was added to a THF (10 mL) suspension of  $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$  (100 mg, 0.163 mmol). This mixture was stirred at room temperature for 12 h after which it was a deep-green color. The THF was removed *in vacuo*, and the green solid was extracted with benzene and filtered

through Celite. Evaporation of the benzene gave 76 mg of a green product in 47% yield. The product can be recrystallized from pentane at  $-35^\circ\text{C}$ . Anal. Calcd: C, 67.98; H, 8.76; N, 2.83. Found: C, 67.38; H, 8.66; N, 2.70.  $^1\text{H}$  NMR:  $\delta$  (s, 2H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 5.11 (d,  $J = 6.2$ , 2H,  $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 5.03 (d,  $J = 6.2$ , 2H,  $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 2.65 (sept,  $J = 6.8$ , 1H,  $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 2.01 (s, 3H,  $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 1.87 (s, 18H,  $(\text{CMe}_3)_2\text{C}_6\text{H}_2\text{CMe}_3$ ), 1.26 (s, 9H,  $(\text{CMe}_3)_2\text{C}_6\text{H}_2\text{CMe}_3$ ), 1.19 (d,  $J = 6.9$ , 6H,  $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR:  $\delta$  157.9 ( $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ), 148.1 ( $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ), 145.6 ( $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ), 121.7 ( $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ), 102.4 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 90.3 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 79.4 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 77.4 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 38.0 ( $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ), 35.5 ( $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ), 32.9 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 31.5 ( $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ), 31.2 ( $\text{CMe}_3\text{C}_6\text{H}_2(\text{CMe}_3)_2$ ), 23.9 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 20.8 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ).

**$(\eta^6\text{-cymene})\text{RuCl}_2(\text{NH}_2\text{Ar})$ .** A solution of  $\text{NH}_2\text{Ar}$  (73 mg, 0.412 mmol) in toluene (5 mL) was added to a toluene (10 mL) suspension of  $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$  (250 mg, 0.204 mmol). This mixture was stirred at room temperature for 12 h. The toluene was then removed *in vacuo* leaving 150 mg of a yellow product in 76% yield. The product can be recrystallized from a toluene-pentane solution at  $-35^\circ\text{C}$ . Anal. Calcd: C, 54.65; H, 6.88; N, 2.90. Found: C, 54.38; H, 6.61; N, 2.97. IR (KBr): 3300 (w), 3252 (w), 1605 (w), 1580 (w), 1169 (w), 1029 (m), 877 (w), 800 (m), 760 (w), 719 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  (d,  $J = 0.8$ , 2H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 7.27 (t,  $J = 0.8$ , 1H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 4.96 (d,  $J = 6.2$ , 2H,  $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 4.82 (d,  $J = 6.2$ , 2H,  $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 4.76 (br s, 2H,  $\text{NH}_2$ ), 3.44 (sept,  $J = 6.7$ , 2H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 2.91 (sept,  $J = 7.0$ , 1H,  $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 2.09 (s, 3H,  $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 1.32 (d,  $J = 6.9$ , 12H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 1.28 (d,  $J = 7.0$ , 6H,  $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR:  $\delta$  139.0 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 123.5 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 123.4 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 105.3 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 94.3 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 82.8 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 77.0 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 31.0 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 27.7 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 22.4 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 22.1 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 17.7 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ).

**$[(\eta^6\text{-cymene})\text{Ru}(\mu\text{-NAr})]_2$ . Method a.** A solution of  $\text{LiNHAr}$  (122 mg, 0.666 mmol) in THF (5 mL) was added to a THF (10 mL) suspension of  $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$  (100 mg, 0.163 mmol). This mixture was stirred at room temperature for 12 h after which it was a deep-green color. The THF was removed *in vacuo* and the green-black solid extracted with benzene and filtered through Celite. Evaporation of the benzene gave 50 mg of a green-black product in 37% yield. The product can be recrystallized from pentane at  $-35^\circ\text{C}$ . Anal. Calcd: C, 64.36; H, 7.61; N, 3.41. Found: C, 64.53; H, 7.82; N, 3.54.  $^1\text{H}$  NMR: ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.33 (d,  $J = 1.8$ , 2H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 7.20 (t,  $J = 0.9$ , 1H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 4.74 (d,  $J = 5.9$ , 2H,  $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 4.55 (d,  $J = 5.9$ , 2H,  $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 3.61 (br s, -, 2H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 2.52 (sept,  $J = 6.8$ , 1H,  $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 1.76 (s, 3H,  $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 1.43 (d,  $J = 6.6$ , 12H,  $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 1.03 (d,  $J = 6.6$ , 6H,  $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR: ( $\text{C}_6\text{D}_6$ ):  $\delta$  167.7 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 128.7 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 123.3 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 122.9 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 102.1 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 90.8 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 77.7 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 77.6 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 30.8 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 26.7 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 26.5 ( $(\text{Me}_2\text{CH})_2\text{C}_6\text{H}_3$ ), 24.0 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ), 19.1 ( $\text{MeC}_6\text{H}_4\text{CHMe}_2$ ).

**Method b.** A solution of potassium bis(trimethylsilyl)amide (83 mg, 0.416 mmol) in benzene (5 mL) was added to a benzene (10 mL) suspension of  $(\eta^6\text{-cymene})\text{RuCl}_2(\text{NH}_2\text{Ar})$  (100 mg, 0.207 mmol). This mixture was stirred at room temperature for 12 h after which to give deep-green color. The benzene was removed *in vacuo*, and the green-black solid was extracted with toluene and filtered through Celite. Evaporation of the toluene and recrystallization from pentane at  $-35^\circ\text{C}$  gave 58 mg of a green-black product (in 68% yield) that had spectroscopic properties identical to those of the compound isolated in method a.

**$[(\eta^6\text{-cymene})\text{Ru}(\mu\text{-NAr}')]_2$ .** A solution of  $\text{LiNHAr}'$  (85 mg, 0.669 mmol) in THF (5 mL) was added to a THF (10 mL) suspension of  $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$  (100 mg, 0.163 mmol). This

**Table 1. Crystal Data for ( $\eta^6$ -cymene)RuCl<sub>2</sub>(NH<sub>2</sub>Ar), ( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)RuCl(NHAr), and [( $\eta^6$ -cymene)Os(NAr)]<sub>2</sub>**

identification code	( $\eta^6$ -cymene)RuCl <sub>2</sub> (NH <sub>2</sub> Ar)	( $\eta^6$ -C <sub>6</sub> Me <sub>6</sub> )RuCl(NHAr)	[( $\eta^6$ -cymene)Os(NAr)] <sub>2</sub>
empirical formula	C <sub>22</sub> H <sub>33</sub> Cl <sub>2</sub> NRu	C <sub>24</sub> H <sub>35</sub> ClNRu	C <sub>44</sub> H <sub>62</sub> N <sub>2</sub> Os <sub>2</sub>
fw	483.46	474.05	999.36
temp, K	291(2)	168(2)	183(2)
wavelength, Å	0.710 73	0.710 73	0.710 73
cryst system	monoclinic	monoclinic	monoclinic
space group	Cc (No. 9)	P2 <sub>1</sub> /c (No. 14)	P2 <sub>1</sub> /c (No. 14)
a, Å	19.865(4)	9.699(7)	19.733(7)
b, Å	6.930(4)	14.095(14)	10.254(2)
c, Å	33.57(2)	16.758(10)	19.378(4)
α, deg	90	90	90
β, deg	98.47(3)	100.82(8)	99.38(3)
γ, deg	90	90	90
V, Å <sup>3</sup>	4571(4)	2250(3)	3869(2)
Z	8	4	4
D(calcd), Mg/m	1.405	1.399	1.716
abs coeff, mm <sup>-1</sup>	0.926	0.824	6.595
F(000)	2000	988	1968
cryst size, mm	0.70 × 0.70 × 0.50	0.64 × 0.20 × 0.06	0.41 × 0.45 × 0.11
θ range for data colln, deg	1.23–24.99	2.14–18.00	1.05–24.98
index ranges	0 ≤ h ≤ 23, 0 ≤ k ≤ 8, –39 ≤ l ≤ 39	–10 ≤ h ≤ 0, 0 ≤ k ≤ 15, –17 ≤ l ≤ 17	–23 ≤ h ≤ 23, –12 ≤ k ≤ 0, 0 ≤ l ≤ 23
no. of colcd reflns	4149	1665	7012
indepdt reflns	4149 (R <sub>int</sub> = 0.0000)	1547 (R <sub>int</sub> = 0.1763)	6786 (R <sub>int</sub> = 0.0837)
refinement method	full-matrix least squares of F <sup>2</sup>	full-matrix least squares of F <sup>2</sup>	full-matrix least squares of F <sup>2</sup>
data/restraints/params	4144/2/481	1539/132/239	6786/0/433
goodness-of-fit on F <sup>2</sup>	1.061	1.059	1.032
final R indices [I > 2σ(I)]	R1 = 0.0262, wR2 = 0.0842	R1 = 0.0825, wR2 = 0.1584	R1 = 0.0374, wR2 = 0.1006
R indices (all data)	R1 = 0.0371, wR2 = 0.0977	R1 = 0.1579, wR2 = 0.1945	R1 = 0.0524, wR2 = 0.1091
largest diff peak and hole, e <sup>-</sup> Å <sup>-3</sup>	0.503 and –0.413	0.764 and –0.669	1.936 and –1.931

mixture was stirred at room temperature for 12 h after which it was a brown color. The THF was removed *in vacuo*, and the brown solid was extracted with toluene and filtered through Celite. Removal of the toluene to minimal volume and cooling to –35 °C gave 44 mg of a brown crystalline product in 38% yield. Anal. Calcd: C, 60.99; H, 6.54; N, 3.95. Found: C, 60.43; H, 6.51; N, 4.14. <sup>1</sup>H NMR: (C<sub>6</sub>D<sub>6</sub>): δ 7.33 (d, J = 7.3, 2H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 7.17 (t, J = 7.3, 1H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 4.37 (d, J = 6.0, 2H, MeC<sub>6</sub>H<sub>4</sub>CHMe<sub>2</sub>), 4.26 (d, J = 5.9, 2H, MeC<sub>6</sub>H<sub>4</sub>CHMe<sub>2</sub>), 2.35 (s, 6H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 2.20 (sept, J = 6.9, 1H, MeC<sub>6</sub>H<sub>4</sub>CHMe<sub>2</sub>), 1.73 (s, 3H, MeC<sub>6</sub>H<sub>4</sub>CHMe<sub>2</sub>), 0.97 (d, J = 7.0, 6H, MeC<sub>6</sub>H<sub>4</sub>CHMe<sub>2</sub>). <sup>13</sup>C NMR: δ 169.7 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 127.7 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 126.0 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 121.6 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 100.6 (MeC<sub>6</sub>H<sub>4</sub>CHMe<sub>2</sub>), 89.2 (MeC<sub>6</sub>H<sub>4</sub>CHMe<sub>2</sub>), 81.8 (MeC<sub>6</sub>H<sub>4</sub>CHMe<sub>2</sub>), 79.2 (MeC<sub>6</sub>H<sub>4</sub>CHMe<sub>2</sub>), 31.7 (MeC<sub>6</sub>H<sub>4</sub>CHMe<sub>2</sub>), 23.7 (MeC<sub>6</sub>H<sub>4</sub>CHMe<sub>2</sub>), 19.6 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 19.1 (MeC<sub>6</sub>H<sub>4</sub>CHMe<sub>2</sub>).

## X-Ray Experimental Section

**General Methods.** Crystallographic data are summarized in Table 1, and all other relevant data are available as Supporting Information. Scattering factors are included in SHELX-93. The positions of the Ru or Os atoms were determined from a Patterson synthesis. Calculations were carried out using a IBM-compatible 486 computer and SHELX-93.<sup>11</sup> The remaining non-hydrogen atoms were located by application of a series of alternating least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the structure factor calculations at idealized positions but were not subsequently refined.

Single crystals of ( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)RuCl(NHAr) were grown by the evaporation of a benzene solution. A red plate was secured to the end of a glass fiber with silicone grease and then placed in a cold stream of nitrogen. Some difficulties were encountered with mounting as significant crystal deterioration was noted before the crystal was placed in the cold stream. Intensity data were collected using a Siemens P4 diffractometer. The data were corrected for Lorentz and polarization effects. Systematic monitoring of three check reflections

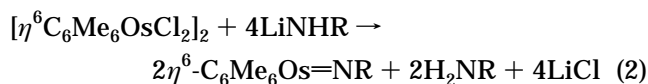
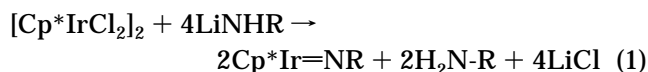
showed crystal decay of 35%, and a linear correction was applied. No correction for extinction was applied.

Single crystals of ( $\eta^6$ -cymene)RuCl<sub>2</sub>(NH<sub>2</sub>Ar) were grown by the evaporation of a benzene solution. A orange cubic shaped crystal was secured to the end of a glass fiber with epoxide. Crystallographic data are summarized in Table 1, and all other relevant data are available as Supporting Information. Intensity data were collected using an Enraf-Nonius CAD-4 diffractometer. The data were corrected for Lorentz, polarization, and X-ray absorption effects, the last by an empirical method based on azimuthal scan data (*T*<sub>max</sub>:*T*<sub>min</sub> = 0.9754:0.5636). No correction for extinction was applied.

Single crystals of [( $\eta^6$ -cymene)Os(*u*-NAr)]<sub>2</sub> were grown by the evaporation of a benzene solution. A dark purple hexagonal-shaped crystal was secured to the end of a glass fiber with silicone grease and then placed in a cold stream of nitrogen. Crystallographic data are summarized in Table 1, and all other relevant data are available as Supporting Information. Intensity data were collected using an Enraf-Nonius CAD-4 diffractometer. The data were corrected for Lorentz, polarization, and X-ray absorption effects, the last by an empirical method based on azimuthal scan data (*T*<sub>max</sub>:*T*<sub>min</sub> = 0.9357:0.6366). No correction for extinction was applied.

## Results

The general route for the synthesis of d<sup>6</sup> imido complexes is given in eqs 1 and 2.



This procedure has been shown to be useful in the synthesis of ruthenium compounds, but the yields are somewhat lower and the products from initial studies were clearly dimeric.<sup>7</sup> The ability to influence the preference for imido ligand bridging has been demon-

(11) Sheldrick, G. M. SHELXL-93, Institut für Anorganische Chemie der Universität Göttingen, Germany, 1993.

strated a number of times and appears to be strongly dependent upon the steric requirements of the groups on the imido.<sup>8</sup> In the synthesis of  $d^6$  terminal imido complexes of ruthenium both the size of the  $\eta^6$ -arene and the organic group on the imido can be changed to adjust the steric pressure at the metal center. It should be noted that all of the X-ray structures of the monomeric  $d^6$  terminal imido complexes presently known have either  $\eta^5$ -Cp\* or  $\eta^6$ -C<sub>6</sub>Me<sub>6</sub> as the ancillary ligand. The analogous ruthenium complex contained only an  $\eta^6$ -benzene ligand and was dimeric. It is reasonable to consider that if the  $\eta^6$ -C<sub>6</sub>Me<sub>6</sub> ligand was employed in the synthesis of ruthenium imidos, monomeric species would be much more likely.

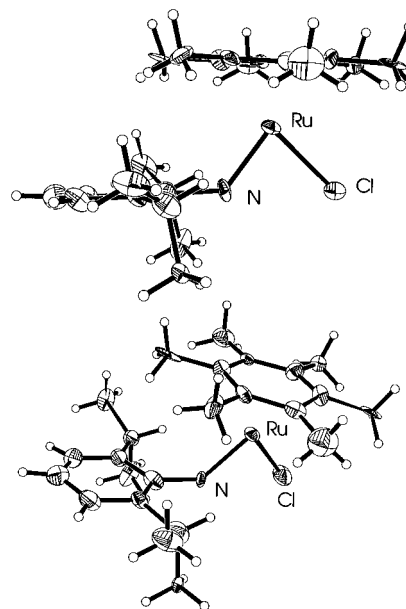
The reaction of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  with 4 equiv of LiNHAr' gives a black solution which upon workup yields a very reactive dark powder which analyses correctly for  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\equiv\text{NAr}'$ . Although, the structure cannot be easily determined, it is most likely to be dimeric, due to the relatively small size of the 2,6-dimethylphenyl group.

The use of larger anilines should reduce the possibility of forming dimeric species. Thus, the reaction of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  with 4 equiv of LiNHAr over a period of 12 h gives a very dark green solution that decomposes to an unidentifiable mixture. Any attempt at workup accelerates the decomposition preventing characterization. However, if the reaction is halted after only 1 h, a small amount of a red crystalline compound can be isolated. The <sup>1</sup>H NMR of this compound indicates the presence of both the  $\eta^6$ -C<sub>6</sub>Me<sub>6</sub> ligand and the 2,6-diisopropylphenyl group, in a 1:1 ratio. The only other resonance present is a 1 proton signal that appears at 10.18 ppm. These data combined with the elemental analysis provide a formulation of  $(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{NHAr})$ . This compound can be obtained in better yield by reacting 1.8 equiv of LiAr with  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$ .

This amido complex is highly reactive and decomposes slowly even under argon at low temperature. However, on one occasion single crystals suitable for X-ray diffraction were obtained. These crystals were extremely unstable, but a rapid collection of X-ray data was carried out and the structure determined (Table 1).

The structure (Figure 1) shows the coordination about the ruthenium as a two-legged piano-stool. The aryl group of the amido ligand occupies a geometry which places the aromatic ring almost parallel to the  $\eta^6$ -C<sub>6</sub>Me<sub>6</sub> ring. The mean planes of each of the rings are tilted at an angle of 5(1)° to each other. The isopropyl groups are bent away to minimize any steric interactions with the methyl's of the  $\eta^6$ -arene.

This complex is effectively an imido precursor as treatment with base removes HCl to afford the putative imido complex  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\equiv\text{NAr})$ . Thus, treatment of a solution of  $(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{NHAr})$  with either NEt<sub>3</sub> or KN(TMS)<sub>2</sub> causes an immediate color change from red to green black. Once again it is not possible to isolate any compounds from the resulting solution. However, if the reaction with base is carried out in the presence of a species that can react with a coordinated imido ligand, such as PhNCO, a stable complex is obtained. The yellow crystalline solid obtained analyses correctly for  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{NArCONPh})$ . The carbonyl group produces a very strong absorption in the IR spectrum at 1718 cm<sup>-1</sup> and is apparent in the <sup>13</sup>C NMR



**Figure 1.** Structure of  $(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{NHAr})$  with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å): Ru-N, 1.94, Ru-Cl, 2.383(7).

as a signal at 170.4 ppm. This is a reasonable indication of the presence of a terminal imido complex such as  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\equiv\text{NAr})$ .

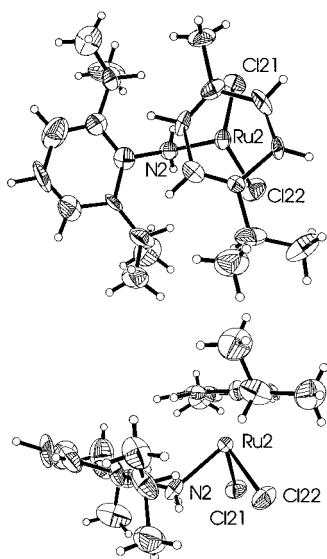
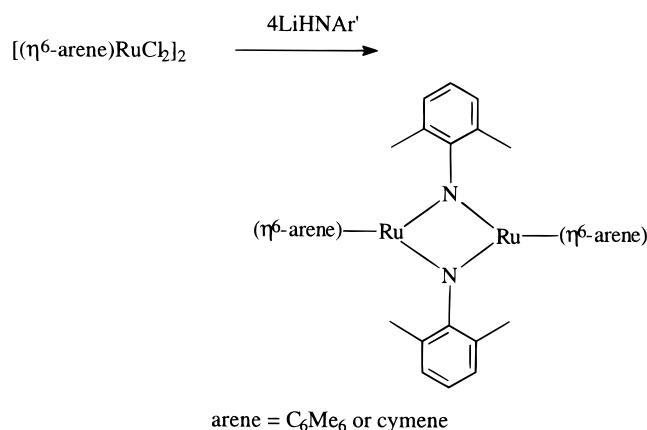
If a larger imido ligand is employed, a more stable complex can be obtained. This compound analyses for  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\equiv\text{NAr}^*)$ , and due to the bulky nature of the ligands we believe it to be a monomeric complex shown in Scheme 3. It was not possible to obtain crystals of  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\equiv\text{NAr}^*)$  suitable for X-ray diffraction. Treatment with proton sources such as alcohols or water results in decomposition and the isolation of only H<sub>2</sub>NAr\*. While this combination of ligands enables the isolation of a relatively stable complex, the steric constraints they impose limit the reactivity of the imido ligand. The  $\eta^6$ -cymene ligand is less sterically demanding than hexamethylbenzene, but previous work<sup>7a,b</sup> indicated that it should provide enough protection to enable the isolation of monomeric complexes. Therefore, the use of cymene as an ancillary ligand was investigated.

The reaction of  $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$  with 4 equiv of LiNHAr' gives a green solution which gives a dark green solid upon workup. As with the hexamethylbenzene analogue, it is not possible to determine the precise structure of the complex  $(\eta^6\text{-cymene})\text{Ru}\equiv\text{NAr}'$ . However the structure is most likely dimeric as shown in Scheme 1. The reaction of  $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$  with 4 equiv of LiNHAr also gives a dark green solid in 37% yield that correctly analyses for  $(\eta^6\text{-cymene})\text{Ru}\equiv\text{NAr}$ . An alternative synthesis of  $(\eta^6\text{-cymene})\text{Ru}\equiv\text{NAr}$  proved to be higher yielding (51% overall). Treatment of  $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$  with 2,6-diisopropylaniline gives  $(\eta^6\text{-cymene})\text{RuCl}_2(\text{NH}_2\text{Ar})$  in 76% yield. This complex crystallized as small yellow cubes suitable for X-ray diffraction.

The structure of  $(\eta^6\text{-cymene})\text{RuCl}_2(\text{NH}_2\text{Ar})$  shown in Figure 2 (Table 2) has similarities to  $(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{NHAr})$  in that the orientation of the 2,6-diisopropylphenyl group is effectively parallel to the plane of the  $\eta^6$ -arene. The mean planes of each of the rings are tilted at an angle of 18.4(3)° to each other. The N-Ru

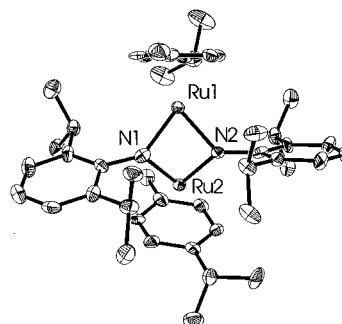
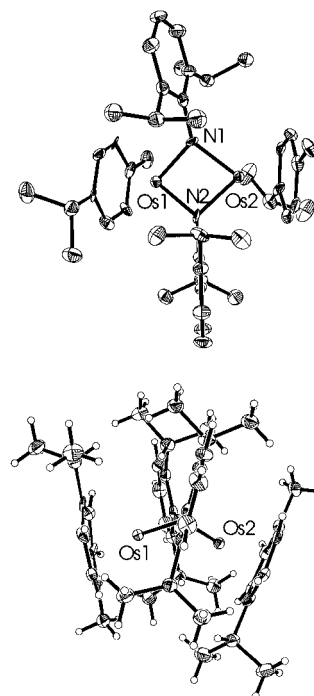
**Table 2. Summary of Ru–N Bond Lengths**

compd	Ru–N (Å)	ref	compd	Ru–N (Å)	ref
( $\eta^6$ -cymene)RuCl <sub>2</sub> (NH <sub>2</sub> Ar)	2.18(1)		[( $\eta^6$ -C <sub>6</sub> H <sub>6</sub> )Ru(NAr)] <sub>2</sub>	1.974(8)	7
( $\eta^6$ -C <sub>6</sub> Me <sub>6</sub> )RuCl(NHAr)	1.94(2)		( $\eta^6$ -cymene)Ru( $\equiv$ NAr*)	1.753(3)	5
[( $\eta^6$ -cymene)Ru(NAr)] <sub>2</sub>	1.974(8)	5			

**Figure 2.** Structure of molecule 2 of ( $\eta^6$ -cymene)RuCl<sub>2</sub>(NH<sub>2</sub>Ar) with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å): Ru(2)–N(2), 2.15(1), Ru(2)–Cl(21), 2.429(4), Ru(2)–Cl(22), 2.418(5).**Scheme 1**

distance at 2.188(12) Å is significantly longer than the Ru–N distance of 1.94(2) Å observed in the structure of ( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)RuCl(NHAr).

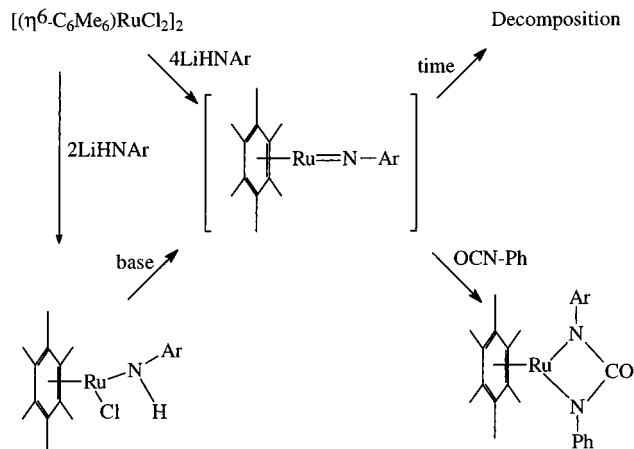
Treatment of ( $\eta^6$ -cymene)RuCl<sub>2</sub>(NH<sub>2</sub>Ar) with base yields ( $\eta^6$ -cymene)Ru $\equiv$ NAr in 68% yield. The structure<sup>5</sup> is shown in Figure 3 and confirms that in the solid state the complex exists as the dimeric species [( $\eta^6$ -cymene)Ru( $\mu^2$ -NAr)]<sub>2</sub>. The structure is very similar to that of the previously reported complex [( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)Ru( $\mu^2$ -NAr)]<sub>2</sub>,<sup>8</sup> in that there is a distinct deformation of the ruthenium–nitrogen plane. The nitrogen atoms are bent some 1.132(7) Å above an ideal “flat” ruthenium–nitrogen plane. Also the ruthenium–ruthenium distance, 2.814(1) Å, is short and falls within the range of known Ru–Ru bonds. This is more likely due to the geometry imposed by the bridging imido ligands than the presence of a Ru–Ru bond. This is supported by the appearance of only one signal for the isopropyl groups on the  $\mu$ -NAr

**Figure 3.** Structure of [( $\eta^6$ -cymene)Ru(NAr)]<sub>2</sub>. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)–N(1), 1.959(8), Ru(1)–N(2), 1.977(7), Ru(2)–N(1), 1.985(8), Ru(2)–N(2), 1.976(8), Ru(1)–Ru(2), 2.7515(12); Ru(1)–N(1)–Ru(2), 88.5(3), Ru(1)–N(2)–Ru(2), 88.2(3), N(1)–Ru(1)–N(2), 78.5(3), N(1)–Ru(2)–N(2), 77.9(3).**Figure 4.** Structure of [( $\eta^6$ -cymene)Os(NAr)]<sub>2</sub>. The hydrogen atoms have been omitted, from the top view, for clarity. Selected bond lengths (Å) and angles (deg): Os(1)–N(1), 1.978(6), Os(1)–N(2), 1.986(6), Os(2)–N(1), 1.980(6), Os(2)–N(2), 1.970(6), Os(1)–Os(2), 2.8142(7); Os(1)–N(1)–Os(2), 90.6(2), Os(1)–N(2)–Os(2), 90.7(2), N(1)–Os(1)–N(2), 77.2(2), N(1)–Os(2)–N(2), 77.5(2).

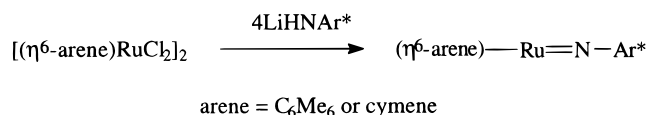
ligands, indicating rapid inversion of the butterfly structure in solution.

The dimeric nature of complex made us curious as to why the analogous osmium complex, ( $\eta^6$ -cymene)Os $\equiv$ NAr, is monomeric. To answer this we prepared ( $\eta^6$ -cymene)Os $\equiv$ NAr using the published procedure,<sup>3c</sup> and crystals were grown from benzene solution. The X-ray diffraction study (Table 1, Figure 4) proved that the ruthenium and osmium complexes are effectively isostructural. The structure of imido [( $\eta^6$ -cymene)Os–

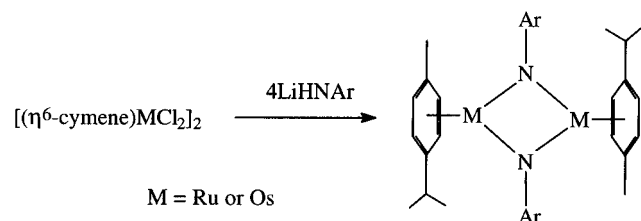
## Scheme 2



## Scheme 3

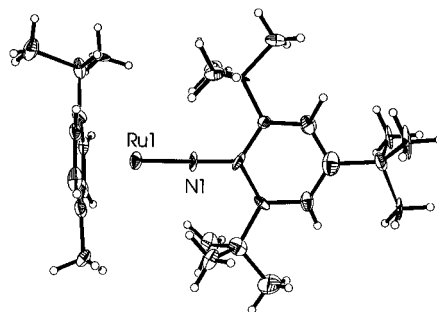


## Scheme 4



$(\mu^2\text{-NAr})_2$  is very similar to the imido complex  $[(\eta^6\text{-cymene})\text{Ru}(\mu^2\text{-NAr})]_2$ . There is a deformation of the osmium–nitrogen plane, and there is a short osmium–osmium distance, 2.7515(12) Å. In the solid state these complexes are clearly dimeric. For these compounds to crystallize as dimers they must exist as dimeric complexes in solution; however this does not rule out the possibility of a monomer–dimer equilibrium. A variable temperature NMR study<sup>3c</sup> has been previously carried out on  $[(\eta^6\text{-cymene})\text{Os}(\mu^2\text{-NAr})]_2$ , and the low-temperature NMR data reported are consistent with the X-ray structure. However, more work is required to precisely determine the nature of the solution species.

While  $\text{-NAr}$  is generally considered a sterically demanding ligand,  $\text{-NAr}^*$  is more demanding still. The reaction of 4 equiv of  $\text{LiHNAr}^*$  with  $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$  in THF once again yields a deep-green colored solution and a complex that has the formulation  $(\eta^6\text{-cymene})\text{Ru}(\text{=NAr}^*)$  (Scheme 2). The only conclusive method for determining the structure of this compound was single-crystal X-ray analysis.<sup>5</sup> The molecular geometry, shown in Figure 5, clearly indicates that  $(\eta^6\text{-cymene})\text{Ru}(\text{=NAr}^*)$  is a monomeric complex containing a terminal imido ligand. The averaged  $\text{Ru-N-C}$  angle is approximately linear at  $177.8(4)^\circ$ . The averaged  $\text{Ru-N}$  distance, at 1.753(3) Å, is consistent with the multiple-bond character expected of a terminal imido ligand<sup>1,2</sup> and compares well with the only other structurally characterized terminal imido complex of ruthenium,  $\text{Ru}(\text{=NAr})_2(\text{PMe}_3)_2$ , at 1.785(6) Å.<sup>6</sup> The  $\text{Ru-N}$  distance is also



**Figure 5.** Structure of  $(\eta^6\text{-cymene})\text{Ru}(\text{=NAr}^*)$ , molecule one. Selected bond lengths (Å) and angles (deg):  $\text{Ru}(1)\text{-N}(1)$ , 1.751(14),  $\text{N}(1)\text{-C}(121)$ , 1.39(2);  $\text{Ru}(1)\text{-N}(1)\text{-C}(121)$ , 178.5(12).

similar to that observed in the related osmium complex  $(\eta^6\text{-C}_6\text{Me}_6)\text{Os}(\text{=N-}t\text{-Bu})$  at 1.737(3) Å.<sup>3</sup> Table 2 lists all the  $\text{Ru-N}$  bonds for the structures presented and shows a clear progression as the type of bond changes from simple coordination in  $(\eta^6\text{-cymene})\text{RuCl}_2(\text{NH}_2\text{Ar})$  through to the imido bond in  $(\eta^6\text{-cymene})\text{Ru}(\text{=NAr}^*)$ .<sup>12</sup>

## Conclusion

We have shown that it is possible to isolate  $d^6$  terminal imido complexes of ruthenium. Steric factors can be used to dominate the propensity for these complexes to dimerize and allow the isolation of a monomeric compound. Complexes with combinations of the less sterically demanding ligands such as  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{NAr})]_2$ ,<sup>7</sup>  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{NAr}^*)]_2$ ,  $[(\eta^6\text{-cymene})\text{Ru}(\text{NAr}^*)]_2$ , and  $[(\eta^6\text{-cymene})\text{Ru}(\text{NAr})]_2$ <sup>5</sup> form dimeric species. The use of more sterically demanding ligands enables the isolation of terminal imido complexes such as  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{NAr}^*)$  and  $(\eta^6\text{-cymene})\text{Ru}(\text{NAr}^*)$ .<sup>5</sup> Unfortunately, the need to provide steric protection to the terminal imido also limits their reactivity. A compromise between the need for protection and the desire for reactivity can be reached if the correct combination of ligands is employed. Such an example is found with the complexes  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{NAr})$  and  $(\eta^6\text{-cymene})\text{Ru}(\text{NAr}^*)$ , which are both monomeric and reactive toward small molecules.<sup>12</sup> We are continuing to explore different combinations of ligands in an attempt to find the correct balance of complex stability and imido ligand reactivity.

**Acknowledgment.** We are grateful for support of this work from the Massey University Research Fund and the New Zealand Lottery Grants Board.

**Supporting Information Available:** For compounds  $(\eta^6\text{-cymene})\text{RuCl}_2(\text{NH}_2\text{Ar})$ ,  $(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{NHAr})$ , and  $[(\eta^6\text{-cymene})\text{Os}(\text{NAr})]_2$ , tables of crystal data, fractional atomic coordinates and  $U$  values, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and  $U$  values (24 pages). Ordering information is given on any current masthead page.

OM9609473

(12) The cycloaddition chemistry of  $(\eta^6\text{-cymene})\text{Ru}(\text{=NAr}^*)$  has recently been reported: Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1996**, 19, 3771–3778.