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A Dinuclear Ruthenium(II) Chelating Amido Complex: Synthesis, Characterization, and Coupling Reaction with Carbon Monoxide

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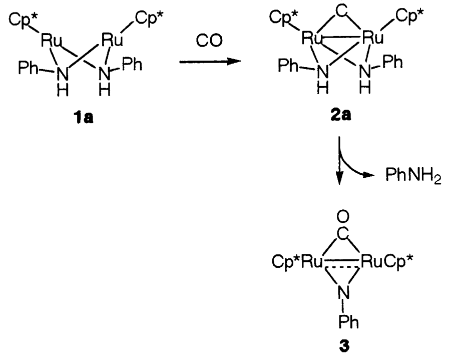
Summary: [Cp*RuCl]$_4$ (Cp* = η^5-C_5Me_5) reacts with 2 equiv of dilithium 2,3-naphthalenediamide to afford the dinuclear bridging amido complex [(Cp*Ru)$_2$\{μ_2-$(NH)_2$-$C_{10}H_6$\}] (**1b**) in moderate yield. Treatment of **1b** with CO (1 atm) resulted in the incorporation of three molecules of CO into the diruthenium core to give the carbamoyl amido bis(carbonyl) complex [Cp*Ru(μ_2-CO)-\{μ_2-2,3-(CONH)(NH)$C_{10}H_6$\}RuCp*(CO)] (**4**).

Amido complexes of low-valent late transition metals have received considerable attention, primarily because of their implication in many important catalytic processes.[1−20] It has been shown that amido ligands in this class of complexes not only behave as coordinated bases or nucleophiles[21−28] but also undergo migratory insertion[27,29−32] and reductive elimination[28,33−36] reactions relevant to those elucidated for alkyl, aryl, and hydride ligands. Work in our laboratories has focused on the preparation and reactivities of dinuclear amido derivatives of Cp*M fragments (M = Ru, Rh, Ir; Cp* = η^5-C_5Me_5).[37−39] Recently, we studied the reactions of the dimeric Ru(II) anilido complex [Cp*Ru(μ_2-NHPh)]$_2$ (**1a**;

Scheme 1



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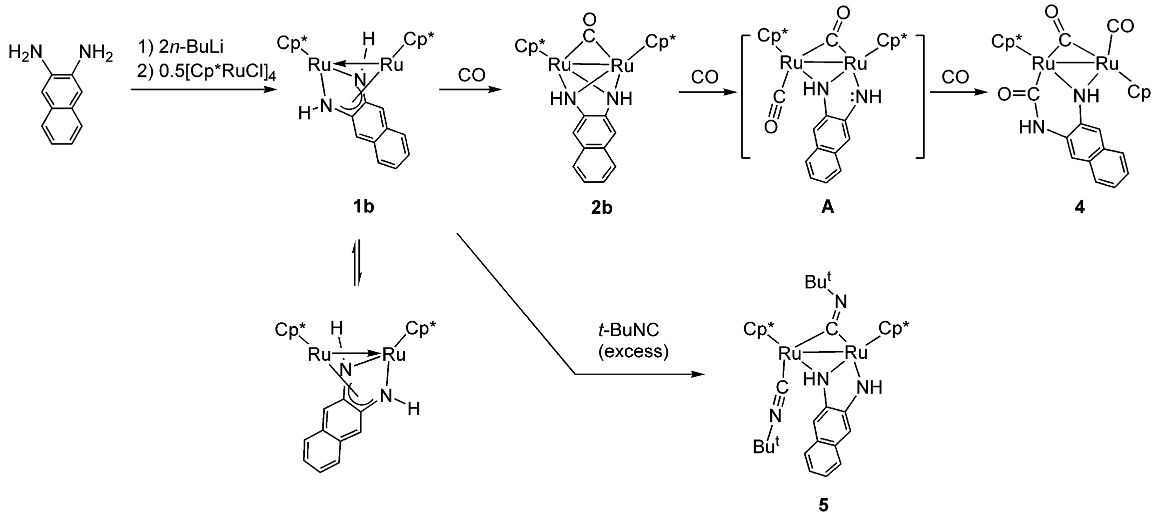
Scheme 2



Cp* = η^5-C_5Me_5), originally reported by Tilley et al.,[40] with small organic molecules such as CO, *tert*-butyl isocyanide, the sulfur ylide $Ph_2S{=}CH_2$, and diphenylacetylene.[39] Complex **1a** readily reacted with CO to form initially the μ_2-carbonyl adduct $[(Cp^*Ru)_2(\mu_2\text{-}CO)(\mu_2\text{-}NHPh)_2]$ (**2a**), which was detected in solution and spontaneously eliminates 1 equiv of aniline to give the bridging imido complex $[(Cp^*Ru)_2(\mu_2\text{-}CO)(\mu_2\text{-}NPh)]$ (**3**) (Scheme 1). This observation motivated us to investigate a related dinuclear amidoruthenium system containing a bidentate diamido ligand. Herein we describe the preparation and characterization of the dinuclear 2,3-naphthalenediamido complex $[(Cp^*Ru)_2\{\mu_2\text{-}(NH)_2C_{10}H_6\}]$ (**1b**) together with its reactions with CO and *tert*-butyl isocyanide.

The results are summarized in Scheme 2. Treatment of $[Cp^*RuCl]_4$ with 2 equiv of dilithium 2,3-naphthalenediamide in THF resulted in the quantitative formation of blue **1b**, which was isolated in 43% yield as dark blue plates after recrystallization from diethyl ether and has been characterized by elemental analysis, ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy, and single-crystal X-ray diffraction.[41] An ORTEP drawing of **1b** is given in Figure 1, showing an unsymmetrically bridged dinuclear structure where one of the Cp*Ru units is coordinated not only by the amido nitrogen atoms but also by the C(2) and C(3) atoms of the naphthalene moiety. The Ru−N bond lengths for the κ^2N,N′-bonded Ru atom (Ru(1)) are typical Ru−N single σ-bond lengths (2.085(17) and 2.097(18) Å). The η^4-bonded Ru atom (Ru(2)) is almost equally separated from the amido nitrogen and ipso naphthalene carbon atoms, and the Ru−N and Ru−C bond lengths (2.235 Å (average)) are much longer than the Ru(1)−N bond lengths. The relatively short C−N bond lengths (1.39(2) and 1.35(2) Å) indicate the presence of N−C π-bonds. These structural features suggest that the 2,3-naphthalenediamido ligand is acting as a 4e σ-donor ligand to Ru(1) and a 6e π-bound ligand to Ru(2). A similar κ^2:η^4 bonding mode has been observed for the dinuclear ruthenium diazadiene complexes $[Ru_2(CO)_5(\mu_2\text{-}RN{=}CHCH{=}NR)]$ (R = *i*-Pr, cyclohexyl)[42] and, more recently, for the *o*-phenylenediamido complex $[Ru_2\{\mu_2\text{-}(NH)_2C_6H_4\}(\mu_2\text{-}dppm)(CO)_2(PPh_3)_2][PF_6]_2$.[43] The Ru−Ru distance for **1b** (2.961(2) Å) is comparable to that of the anilido complex **1a** (2.945(4) Å),[40] for which the absence of a Ru−Ru bonding interaction has been proposed. As for **1b**, the intermetallic separation is most likely ascribed to a dative interaction from Ru(2) to Ru(1), since it allows both of the Ru atoms to adopt an 18e configuration.

In contrast to the solid-state structure, the ^{1}H NMR spectrum of **1b** in solution (C_6D_6 or toluene-d_8) displays only one Cp* resonance at 20 °C. When the temperature was lowered, the signal became broadened and finally split into two distinct singlets ($T_c = -60$ °C). Over the temperature range of +20 to −80 °C, the $^{13}C\{^1H\}$ NMR spectrum of **1b** exhibits a characteristic resonance at δ 121 assignable to the coordinated naphthalene carbon atoms, which is shifted upfield by 15 ppm relative to that of the free diamine. These spectroscopic features are fully consistent with a dynamic behavior that involves a fast site exchange between the two Ru centers (Scheme 2).

The hemilabile nature of the naphthalene carbon atoms is reflected in the high reactivity of **1b** toward electron donors such as CO and *tert*-butyl isocyanide. Treatment of **1b** with CO (1.5 equiv) resulted in the rapid formation of the μ_2-carbonyl complex $[(Cp^*Ru)_2(\mu_2\text{-}CO)\{\mu_2\text{-}2,3\text{-}(NH)_2C_{10}H_6\}]$ (**2b**), which was isolated in 57% yield and has been characterized by elemental analysis and standard spectroscopic methods. The

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[41] Crystallographic data for **1b**: $C_{30}H_{38}N_2Ru_2$; $M_r = 628.76$, monoclinic, space group $P2_1/c$, $a = 11.483(15)$ Å, $b = 15.91(2)$ Å, $c = 16.02(2)$ Å, $\beta = 105.74°$, $V = 2817(6)$ Å^3, $Z = 4$, $T = 296$ K, μ(Mo Kα) = 1.092 mm^{-1}, 21 148 reflections measured, 4884 unique ($R_{int} = 0.2949$), R1 = 0.1406, wR2 = 0.3696, GOF = 1.076. Crystallographic data for **4**·2CH$_2$Cl$_2$: $C_{35}H_{42}N_2O_3Cl_4Ru_2$; $M_r = 882.65$, triclinic, space group $P\bar{1}$, $a = 11.634(5)$ Å, $b = 12.399(5)$ Å, $c = 13.935(8)$ Å, $\alpha = 105.730(18)°$, $\beta = 105.74°$, $\gamma = 95.60(2)°$, $V = 1882.8(15)$ Å^3, $Z = 2$, $T = 296$ K, μ(Mo Kα) = 1.121 mm^{-1}, 18 159 reflections measured, 8259 unique ($R_{int} = 0.0321$), R1 = 0.0414, wR2 = 0.1146, GOF = 1.034. Crystallographic data for **5**·MeCN: $C_{42}H_{59}N_3Ru_2$; $M_r = 836.08$, monoclinic, space group $P2_1/c$, $a = 11.510(3)$ Å, $b = 16.845(5)$ Å, $c = 22.298(7)$ Å, $\beta = 105.30°$, $V = 4170(2)$ Å^3, $Z = 4$, $T = 296$ K, μ(Mo Kα) = 1.040 mm^{-1}, 40 012 reflections measured, 9535 unique ($R_{int} = 0.0364$), R1 = 0.0399, wR2 = 0.0993, GOF = 1.068.

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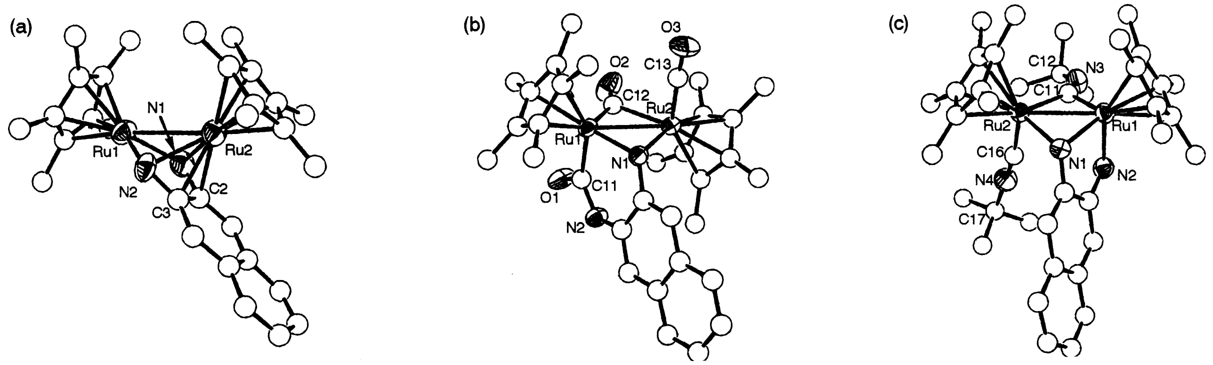

Figure 1. Molecular structures of (a) the diamido complex **1b**, (b) the carbamoyl amido bis(carbonyl) complex **4**, and (c) the bis(isocyanide) adduct **5**. Ellipsoids are drawn at the 50% probability level. Carbon atoms are drawn with arbitrary circles, and hydrogen atoms are omitted for clarity.

marked stability of **2b** contrasts strikingly with the high lability of its monodentate analogue **2a**, which rapidly releases aniline to form the bridging imido complex **3** (vide supra).

Prolonged bubbling of CO into a THF solution of **1b** induced C−N bond formation between amido and CO ligands. Three molecules of CO were incorporated into the diruthenium center to give the carbamoyl amido bis(carbonyl) complex **4**, which was isolated in 74% yield after chromatography on activated alumina and has been fully defined by spectroscopic, analytical, and crystallographic methods (Scheme 2, Figure 1).[44] It is worth noting that one of the CO molecules has inserted into the Ru−N bond to form the carbamoyl ligand. Two other CO ligands occupy terminal and bridging coordination sites. Although the insertion of CO into metal−amido bonds is important as a model for the metal-catalyzed synthesis of ureas by oxidative carbonylation of amines,[1,15−20,45] direct observations of this insertion reaction are still limited in number.[27,29,30] Complex **4** would be produced via the intermediate **A** (Scheme 2), whose structure has been indirectly supported by its isocyanide analogue **5** (vide infra). The C−N bond-forming step probably involves a nucleophilic attack of the terminal amido ligand in **A** to the coordinated CO.[46] Subsequent coordination of the third molecule of CO would afford the product **4**.

Treatment of **1b** with *tert*-butyl isocyanide (2.5 or 10 equiv) resulted in the quantitative formation of the bis(isocyanide) complex **5**, which was isolated as brown needles in 46% yield after recrystallization from THF−acetonitrile and has been fully characterized by elemental analysis, NMR and IR spectroscopy, and an X-ray diffraction study (Scheme 2, Figure 1). The molecular structure of **5** features the presence of terminal and bridging isocyanide ligands. The two amido nitrogen atoms also occupy the terminal and bridging coordination sites. The vicinal cis orientation of the terminal amido and isocyanide ligands evokes an idea that complex **5** would serve as a structural model of the bis(carbonyl) intermediate **A** that is likely to be formed during the reaction of **1b** with excess CO (vide supra).

In summary, we have succeeded in synthesizing a novel dinuclear 2,3-naphthalenediamido derivative of the Cp*Ru fragment, **1b**. The bidentate structure of the diamido ligand appears to enforce the coordination of a part of the naphthalene moiety to one of the Ru centers, resulting in a slightly modified and more stabilized structure of the diruthenium core as compared to that of its monodentate analogue. The chelation also plays a crucial role in preventing the Ru_2N_2 core from undergoing the amine elimination pathway observed for **1a** (Scheme 1). Despite these stabilizing effects, the diamido complex is still highly reactive toward CO, allowing us to observe a sequential reaction that leads to the carbonylation of the amido ligand at the well-defined diruthenium site. Further studies on the reactivity of the amido complexes **1a**,**b** and their derivatives are now in progress.

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Supporting Information Available: Text, tables, and figures giving experimental, spectroscopic, and crystallographic details; full crystallographic data are given as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(44) In contrast to the clean formation of **4** from **1b** and CO, treatment of the anilido complex **1a** with excess CO afforded a mixture of several complexes, including the Ru(I) carbonyl complex $[Cp^*Ru(CO)_2]_2$ (10% as judged by ^1H NMR). Two nitrogen-containing products were detected by ^1H NMR and FAB-MS spectrometry, which could be formulated as the carbamoyl amido bis(carbonyl) complex $[Cp^*Ru(CONHPh)(\mu_2\text{-}CO)(\mu_2\text{-}NHPh)RuCp^*(CO)]$ (55%) and the hydrido amido bis(carbonyl) complex $[Cp^*Ru(CO)(\mu_2\text{-}H)(\mu_2\text{-}NHPh)RuCp^*(CO)]$ (25%). The former probably possesses a structure similar to that of **4**. Full characterization of these products will be reported in due course.

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(46) Such an intramolecular nucleophilic attack of amido ligand at coordinated CO has previously been proposed to occur in the reaction of dirhodium amido/imido complexes with CO.[30]