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Synthesis and Molecular Structure of the Amido-Bridged Dinuclear Rhodium Complex $[Cp^*Rh\{\mu_2\text{-}(NH)_2C_{10}H_6\text{-}2,3\}(\mu_2\text{-}Cl)RhCp^*][PF_6]$ ($Cp^* = \eta^5\text{-}C_5Me_5$)

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Synthesis and Molecular Structure of the Amido-Bridged Dinuclear Rhodium Complex $[Cp^*Rh\{\mu_2\text{-}(NH)_2C_{10}H_6\text{-}2,3\}(\mu_2\text{-}Cl)RhCp^*][PF_6]$ ($Cp^* = \eta^5\text{-}C_5Me_5$)

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Reaction of $[Cp^*RhCl_2]_2$ (**1**) with $(LiNH)_2C_{10}H_6$-2,3 gives the mononuclear species $Cp^*Rh(NH)_2C_{10}H_6$-2,3 (**3**), which is selectively converted to the amido-bridged dinuclear Rh(III) complex $[Cp^*Rh\{\mu_2\text{-}(NH)_2C_{10}H_6\text{-}2,3\}(\mu_2\text{-}Cl)RhCp^*]PF_6$ (**4**; $Cp^* = \eta^5\text{-}C_5Me_5$) upon treatment with **1**/$AgPF_6$ in acetone. The molecular structure of **4** has been determined by X-ray crystallography.

Keywords: dinuclear complex; rhodium; bridging amido ligand; X-ray structure

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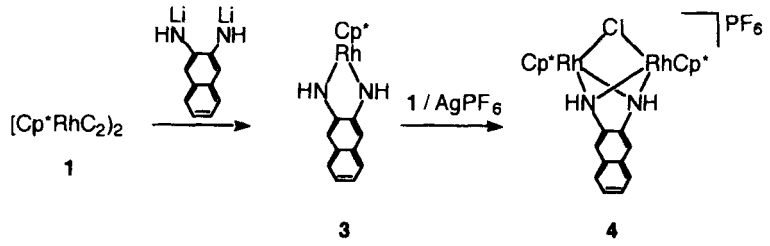
INTRODUCTION

Although the chemistry of amido complexes of early transition metals has been extensively investigated [1], that of late transition elements has been relatively less developed [2, 3]. We have recently shown that $[Cp^*MCl_2]_2$ ($Cp^* = \eta^5$-C_5Me_5; **1a**, M = Rh; **1b**, M = Ir;) directly reacts with $(LiNH)_2C_{10}H_6$-1,8 to give the amido-bridged dinuclear complex $[Cp^*M\{\mu_2\text{-}(NH)_2C_{10}H_6\text{-}1,8\}(\mu_2\text{-}Cl)MCp^*]Cl$ (**2a**, M = Rh; **2b**, M = Ir) in good to excellent yield [4, 5]. Here we wish to describe preparation of the related 2,3-diamidonaphthalene-bridged dinuclear Rh(III) complex via the mononuclear precursor. The molecular structure of **4** has been unambiguously determined by X-ray diffraction study.

RESULTS AND DISCUSSION

Treatment of **1a** with $(LiNH)_2C_{10}H_6$-2,3 did not afford the corresponding amido-bridged dinuclear species, but quantitatively produced a mononuclear species $Cp^*Rh(NH)_2C_{10}H_6$-2,3 (**3**) [6]. We have now found that **3** can be selectively converted to the amido-bridged dinuclear complex $[Cp^*Rh\{\mu_2\text{-}(NH)_2C_{10}H_6\text{-}2,3\}(\mu_2\text{-}Cl)RhCp^*][PF_6]$ (**4**) upon treatment of a mixture of **1**/$AgPF_6$ in acetone (Scheme 1). Complex **4** was isolated as an orange microcrystalline solid in 67%

Scheme 1



yield and both spectroscopically and crystallographically characterized. The ^{1}H NMR spectrum of **4** shows signals due to Cp* and NH protons at δ 1.37 and 4.00, respectively, together with three sets of resonances due to the naphthyl group. These features suggest the triply bridged structure of **4** shown in Scheme 1, which has been unequivocally confirmed by X-ray diffraction analysis.

An ORTEP drawing of a cationic portion of **4** shown in Figure 1 clearly indicates a dinuclear structure in which the two Cp*Rh units are triply bridged by the diamidonaphthalene and the Cl ligands. Two Cp* moieties are almost parallel (dihedral angle 2.41°) and are in a staggered conformation. The intramolecular distance between the two Rh atoms (3.04 Å) indicates the absence of a metal-metal bonding interaction. The related triply bridged complex [Cp*Rh{μ_2-(NH)$_2$C$_{10}$H$_6$-1,8}(μ_2-Br)BrCp*]Cl (**2c**) has been structurally defined [5], in which two Cp* moieties are almost parallel (dihedral angle 4.61°), but are in an eclipsed conformation.

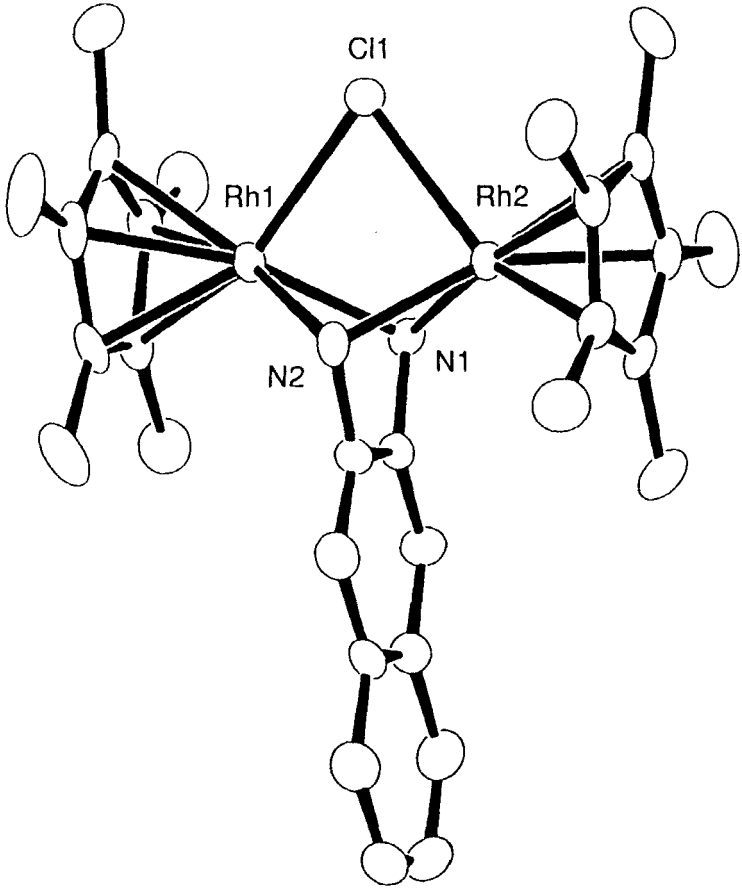


FIGURE. 1. An ORTEP drawing of a cationic part of **4** at the 50% probability level. Selected bond distances (Å) and angles (°): Rh(1)•••Rh(2), 3.04(1); Rh(1)-N(1), 2.144(4); Rh(1)-N(2), 2.149(4); Rh(1)-Cl(1), 2.433(1); Rh(2)-N(1), 2.150(4); Rh(2)-N(2), 2.148(4); Rh(2)-Cl(1), 2.426(1); N(1)-Rh(1)-N(2), 67.8(1); Cl(1)-Rh(1)-N(1), 83.8(1); Cl(1)-Rh(1)-N(2), 84.2(1); N(1)-Rh(2)-N(2), 67.7(1); Cl(1)-Rh(2)-N(1), 83.9(1); Cl(1)-Rh(2)-N(2), 84.4(1); Rh(1)-N(1)-Rh(2), 90.1(1); Rh(1)-N(2)-Rh(2), 90.0(2); Rh(1)-Cl(1)-Rh(2), 77.42(4).

EXPERIMENTAL

Preparation of **4**

To a mixture of **1** (206 mg, 0.333 mmol) and $AgPF_6$ (168 mg, 0.666 mmol) in acetone (20 ml) was added a violet solution of **3** (263 mg, 0.666 mmol) in acetone (20 ml), and the reaction mixture was stirred overnight at room temperature. The resultant red suspension was filtered off. After the solvent was removed from the filtrate, the remaining red solid was washed with THF (3 ml, five times) to afford **4** as an orange microcrystalline solid (367 mg, 67%). ^1H NMR (acetone-d_6) d 7.29, 7.03(m, 2H each, aryl), 6.66(s, 2H, aryl), 4.00(brs, 2H, NH), 1.37(s, 30H, Cp*). Anal. Calcd for $C_{39}H_{38}ClF_6N_2PRh_2$: C, 44.33; H, 4.71; N, 3.45. Found: C, 43.80; H, 4.71; N, 3.55. Single crystals suitable for X-ray diffraction study was obtained by recrystallization from acetone/hexane.

Structural Analysis of **4**

Data collection was made on a Rigaku RAXIS-II diffractometer. $C_{33}H_{44}ClF_6N_2OPRh_2$, $P2_12_12_1$ (orthorhombic), a = 15.054(2) Å, b = 15.3366(3) Å, c = 15.3021(4) Å, V = 3533.0(3) $Å^3$, Z = 4, D = 1.637 g/cm^{-3}; Graphite monochromated Mo Kα radiation (λ = 0.71069Å); R(Rw) = 0.044(0.044) for 3918 reflections ($I > 3\sigma(I)$) collected with $5.0 < 2\theta < 55.1°$ at 298K.

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[6] Preparation and structure of the related complex $Cp^*RhX_2C_6H_4$ (X = O, N) was reported. See, P. Espinet, P. M. Bailey, P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1542 (1979).