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Investigating intermediates in the CCC–NHC pincer ligand metalation/transmetalation to Rh sequence, an improved stoichiometric synthesis of CCC–NHC pincer Rh complexes

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ABSTRACT

The metalation/transmetalation strategy using [$Zr(NMe_2)_4$] as initial metalating reagent offers an efficient approach to the synthesis of CCC–NHC pincer complexes. Many CCC–NHC pincer complexes have been prepared via this methodology. As efficient as this methodology is, many questions remained as to the mechanism for the process, particularly the requirement of two equivalents of Rh per proligand for good yields. Previously, no intermediates have been reported to shed light on the mechanism. In the process of investigating an intermediate and the mechanism of the metalation/transmetalation methodology, a new mixed valent bimetallic CCC–NHC pincer Rh complex with two chloro ligands bridged between a [(CCC–NHC)Rh(III)] and a [Rh(I)(COD)] fragment was isolated and fully characterized. The investigation of the Rh(III)/Rh(I) bimetallic intermediate in the CCC–NHC pincer metalation/transmetalation methodology led to an improved stoichiometric synthesis of CCC–NHC pincer Rh complexes. It was found that switching the proligand from iodide to chloride counterion obviated the need for an extra equivalent of Rh. The iodide bridged Rh(III)/Rh(I) intermediate was much more stable and prevented further reaction in comparison to the chloride congener. When it was switched to only chloride present the reaction quickly gave efficient, complete transmetalation with only a 1:1 ratio of proligand:Rh.

1. Introduction

After more than a century of research [1–5], stable, free carbenes only became recognized in 1988 when Bertrand's group reported the "push-pull" carbenes [6,7]. A few years later, the stable, crystalline N-heterocyclic carbenes (NHCs), were reported by Arduengo [8–10]. Particularly important was the discovery that these were strong two electron σ-donors to transition metals [11–15], which led to widespread application in transition metal complexes and catalysts. Especially noteworthy was the incorporation of a NHC into a Ru metathesis catalyst, the, so called, Grubbs II catalyst that inspired widespread industrial application [16–18]. The isolation of stable carbenes, particularly access to NHCs, initiated the development of numerous ligands, complexes, and a wide variety of catalytic and other applications of these unique molecules ushering in the present age of stable carbenes [2,11,19-22].

The incorporation of NHCs into pincer ligand frameworks has received considerable attention recently [22–31]. The strong σ-donating ability, stability, general ease of synthesis, combined with the ability to fine tune the steric and electronic properties made NHC pincer ligands highly attractive for the preparation of transition metal complexes [24,29,32-36]. Many different pincer complexes containing NHCs have been reported and have been demonstrated to be efficient catalysts for C–H activation [37], CO_2 reduction [38,39], hydroamination [40], hydrosilylation [41], hydroboration [42], to name a few [19,26,29,43-47].

An efficient preparation of CCC–NHC pincer proligands was first reported in 2003 [48]. An efficient metalation/transmetalation strategy to tris-activate the bisimidazolium salt proligand for the preparation of the CCC–NHC pincer complexes was reported in 2005 [49]. This strategy exploited the unique properties of [$Zr(NMe_2)_4$]. Namely, the basicity of the amido group and the Lewis acidity (i.e., electrophilicity) of the electron deficient Zr center. These combined with the reversibility of the metalation under the reaction conditions provided efficient and quantitative access to the CCC–NHC pincer Zr complexes [40]. Having achieved concur-

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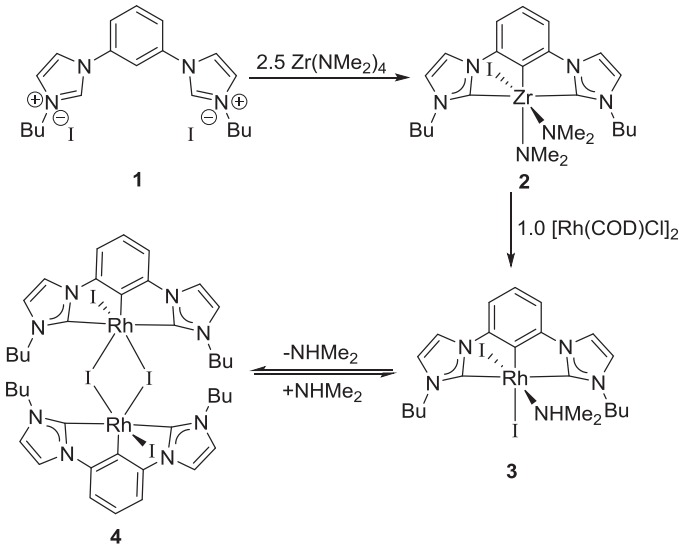


Scheme 1. Previously reported *in situ* metalation/transmetalation sequence showing equilibrium between Rh amine complex **3** and dimer **4**. The Zr complex **2** was formed *in situ* [49].

rent activation of the three desired C–H bonds, the CCC–NHC pincer Zr complex was found to transmetalate providing access to late transition metal complexes of Rh and Ir [49,50]. Achieving transmetalation of the CCC–NHC pincer Zr complex (**2**→**3**, Scheme 1) ran contrary to the prevailing dogma at the time that both NHCs and the tridentate pincers were non-dissociating ligands [11,51-53].

The metalation/transmetalation methodology to prepare CCC–NHC pincer complexes of the late transition metals has become well-established for many metals including Pt [54], Co [55,56], Ir[50], Rh [49], and Ni [57]. Initial contributions focused on syntheses of the pincer complexes of Rh or Ir, and highlighted their catalytic activity in hydroamination [50], hydroboration [58], and hydrosilylation [41]. However, the mechanism of the transmetalation has not been addressed. For example, the optimized *in situ* transmetalation step required two atom equivalents of Rh per proligand, **1** (Rh:proligand::2:1) as illustrated in Scheme 1 for the conversion of **1** to **3** via **2**. With loss of $HNMe_2$ during crystallization dimer **4** was obtained as x-ray quality crystals [49]. Specifically, when only a 1:1 ratio of Rh:proligand **1**, was used during the *in situ* metalation/transmetalation, only about 50% conversion of the CCC–NHC pincer Zr complex **2** to Rh pincer **3** was observed by ^{13}C NMR spectroscopy [49]. Therefore, a ratio of one proligand to one $[Rh(COD)Cl]_2$ dimer was reported for quantitative *in situ* transmetalation and to achieve improved yields of the CCC–NHC pincer Rh complex (Scheme 1) [49,58].

The nature of the transmetalation step and its mechanism were not clarified [49], and no intermediates were identified in typical synthetic procedures. If an intermediate generated during the transmetalation step could be isolated, it would provide crucial insight to understand the reaction mechanism and to guide improvements. Additionally, it would perhaps more significantly provide understanding into NHC ligand dissociation from transition metals [59–61].

We report herein the investigation of a Rh(III)/Rh(I) bimetallic intermediate in the CCC–NHC pincer $Zr(NMe_2)_4$-based metalation/transmetalation methodology. It led to an improved transmetalation to Rh that required only the minimum one atom equivalent. The results indicated that switching the proligand salt **1** from iodide to the chloride as counterion obviated the need for an extra equivalent of Rh. Thus, the atom efficiency and yield of the metalation/transmetalation methodology were significantly improved.

2. Experimental

2.1. General considerations

All syntheses were carried out under an inert atmosphere of N_2. Reagents were purchased from standard sources. The $Zr(NMe_2)_4$ was sublimed before use. All solvents were dried and degassed using an anhydrous, anaerobic solvent purification system. All reactions involving organometallic reagents were carried out in a nitrogen filled glovebox. All workups were done on the benchtop. NMR solvents were passed through basic alumina with 4 Å molecular sieves plug. Bisimidazolium dichloride salt **6** and pincer Zr complex **9** were synthesized following literature procedures [40,62].

2.2. Synthesis

2.2.1. Synthesis of 2-(1,3-bis(N-butylimidazol-2-ylidene)phenylene)-(1,5-cyclooctadiene)(chloro)bis(μ–chloro) Rh(III)-Rh(I), 7: in-situ metalation/transmetalation

A sample of 1,3-bis(1-butylimidazole)benzene dichloride, **6** (0.100 g, 0.253 mmol), $Zr(NMe_2)_4$ (0.101 g, 0.379 mmol), and dry THF (10 mL) were stirred for 1 h at room temperature affording a yellow solution. A sample of $[Rh(COD)Cl]_2$ (0.125 g, 0.253 mmol) was added producing an orange solution. Stirring was continued for 15 min. The volatiles were removed under reduced pressure. The resulting solid was washed with pentane (3 × 10 mL). Dichloromethane (15 mL) was added to the solid, and the resulting mixture was filtered through Celite® and concentrated to dryness. The crude product was triturated with acetone (5 mL) and the light-yellow solid was collected by filtration. It was washed with acetone (3 × 5 mL) and dried under vacuum. The product was recrystallized from a saturated solution of DCM by addition of hexane (0.079 g, 58%, 0.106 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 1.8 Hz, 2H), 7.13 (d, J = 1.8 Hz, 2H), 7.10 (t, J = 8.1 Hz, 1H), 7.00 (d, J = 7.7 Hz, 2H), 5.14 – 4.98 (m, 4H), 4.31 (s, 2H), 3.75 (s, 2H), 2.53 – 2.27 (m, 8H), 1.85 – 1.58 (m, 8H), 1.15 (t, J = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.52 (d, J = 36.8 Hz, $C_{carbene\text{-}Rh}$), 147.91 (d, J = 28.0 Hz, $C_{aromatic\text{-}Rh}$), 146.17 (s), 124.11 (s), 120.98 (s), 115.73 (s), 108.57 (s), 79.23 (d, J = 13.9 Hz, $C_{COD\text{-}Rh}$), 77.96 (d, J = 13.5 Hz, $C_{COD\text{-}Rh}$), 50.28 (s), 34.44 (s), 30.86 (s), 30.72 (s), 20.42 (s), 14.12 (s). Anal Calcd for $C_{28}H_{37}Cl_3N_4Rh_2 \bullet 0.3CH_2Cl_2$: C, 44.30; H, 4.94; N, 7.30. found C, 44.67; H, 4.99; N, 7.53. HRMS (ESI-TOF) Calcd for $C_{28}H_{37}Cl_2N_4Rh_2$ $[M\text{-}Cl]^+$ = 705.0500, obs m/z = 705.0516; Calcd for $[M\text{-}Cl{+}CH_3CN]^+$ = 746.0765, obs m/z = 746.0805; Calcd for $[M\text{-}2Cl\text{-}Rh(COD)]^+$ = 459.0817, obs m/z = 459.0795

2.2.2. Synthesis of 2-(1,3-bis(N-butylimidazol-2-ylidene)phenylene)-(1,5-cyclooctadiene)(chloro)bis(μ–chloro) Rh(III)-Rh(I), 7: direct transmetalation from isolated Zr complex 9

A sample of 2-(1,3-bis(N-butylimidazol-2-ylidene)-phenylene)(dimethylamido)bis(chloro)zirconium (IV), **9** (0.100 g, 0.190 mmol) was stirred in THF (15 mL) at room temperature for 15 mins affording a pale-yellow suspension. A sample of $[Rh(COD)Cl]_2$ (0.093 g, 0.190 mmol) was added, instantly yielding a red solution. The solution was stirred for 15 min. The volatiles were removed under reduced pressure. The resulting solid was washed with pentane (3 × 10 mL). Dichloromethane (15 mL) was added to the solid and the resulting suspension was filtered through Celite® and concentrated to dryness. The crude product was triturated with acetone (5 mL) and the pale-yellow solid was collected by filtration. It was washed with acetone (3 × 5 mL) and dried under vacuum. Yield (0.089 g, 63%, 0.120 mmol). Crystals

suitable for x-ray analysis were grown by vapor diffusion of hexane into a DCM solution of the pale-yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, J = 2.0 Hz, 2H), 7.13 (d, J = 2.0 Hz, 2H), 7.12 – 7.07 (m, 1H), 7.00 (d, J = 7.3 Hz, 2H), 5.14 – 4.97 (m, 4H), 4.31 (d, J = 3.1 Hz, 2H), 3.75 (d, J = 3.0 Hz, 2H), 2.50 – 2.29 (m, 8H), 1.86 – 1.60 (m, 8H), 1.15 (t, J = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.52 (d, J = 36.8 Hz, $C_{carbene\text{-}Rh}$), 147.91 (d, J = 28.0 Hz, $C_{aromatic\text{-}Rh}$), 146.17 (s), 124.11 (s), 120.98 (s), 115.73 (s), 108.57 (s), 79.23 (d, J = 13.9 Hz, $C_{COD\text{-}Rh}$), 77.96 (d, J = 13.5 Hz, $C_{COD\text{-}Rh}$), 50.28 (s), 34.44 (s), 30.86 (s), 30.72 (s), 20.42 (s), 14.12 (s). HRMS (ESI-TOF) Calcd for $C_{28}H_{37}Cl_2N_4Rh_2$ $[M\text{-}Cl]^+$ = 705.0500, obs m/z = 705.0505; Calcd for $[M\text{-}Cl{+}CH_3CN]^+$ = 746.0765, obs m/z = 746.0789; Calcd for $[M\text{-}2Cl\text{-}Rh(COD)]^+$ = 459.0817, obs m/z = 459.0806

2.2.3. Synthesis of 2-((1,3-bis(N-butylimidazol-2-ylidene)phenylene)-(dimethylamido)bis(chloro)rhodium(III), **8**

i) *From in situ metalation/transmetalation, ligand:Rh ratio of 1:1*: A sample of 1,3-bis(1-butylimidazole)benzene dichloride **6** (0.120 g, 0.303 mmol), $Zr(NMe_2)_4$ (0.122 g, 0.455 mmol), and THF (15 mL) were combined in a vial. The reaction was stirred at room temperature for 1 hour affording a yellow solution. A sample of $[Rh(COD)Cl]_2$ (0.076 g, 0.152 mmol) was added to the reaction and stirring was continued for 8 h. Deionized water (5 drops) was added to the reaction and stirred for 10 min or until a white precipitate formed. The resulting mixture was filtered, and the solvent was removed in vacuo. The crude product was dissolved in a minimum of dichloromethane (1 mL), and hexane (15 mL) was added yielding a precipitate. The yellow solid was collected by filtration, giving **8** in 87% yield (0.142 g, 0.263 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 1.9 Hz, 2H), 7.18 (dd, J = 8.3, 7.3 Hz, 1H), 7.08 (d, J = 7.8 Hz, 2H), 7.05 (d, J = 1.9 Hz, 2H), 5.08 – 5.00 (m, 2H), 4.87 – 4.79 (m, 2H), 3.72 (s, 1H), 1.99 (dtd, J = 20.9, 14.1, 6.0 Hz, 4H), 1.68 (d, J = 5.5 Hz, 6H), 1.54 (dq, J = 15.0, 7.4 Hz, 4H), 1.01 (t, J = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.84 (d, J = 39.1 Hz), 155.51 (d, J = 29.5 Hz), 145.96 (s), 123.85 (s), 120.86 (s), 115.60 (s), 108.61 (s), 49.84 (s), 45.52 (s), 33.66 (s), 20.04 (s), 13.96 (s).

ii) *From in situ metalation/transmetalation, ligand:Rh ratio of 1:2*. A sample of 1,3-bis(1-butylimidazole)benzene dichloride **6** (0.030 g, 0.076 mmol), $Zr(NMe_2)_4$ (0.030 g, 0.114 mmol), and THF (10 mL) were combined in a vial. The reaction was stirred at room temperature for an hour affording a yellow solution. A sample of $[Rh(COD)Cl]_2$ (0.037 g, 0.076 mmol) was added and stirring was continued for 8 h. Deionized water (5 drops) was added to the reaction, and it stirred open to air for approximately 10 min providing a precipitate and a yellow supernatant. The mixture was filtered and concentrated to dryness. The crude product was dissolved in a minimum dichloromethane (1 mL) and hexane (15 mL) was added yielding a precipitate. The precipitate was collected by filtration and recrystallized from dichloromethane/hexane (3:1) giving **8** (bright yellow crystals) in 51% yield (0.021 mg, 0.039 mmol). The ^{1}H NMR spectroscopy in $CDCl_3$ was consistent with **8**.

iii) *Direct transmetalation from **11***. A sample of 2-(1,3-bis(N-butylimidazol-2-ylidene)-phenylene)bis(dimethylamido) (chloro) zirconium (IV) **11** (0.013 g, 0.024 mmol) was dissolved in THF (2.0 mL) affording a yellow solution. A sample of $[Rh(COD)Cl]_2$ (0.006 g, 0.012 mmol) was added, and the reaction was stirred at room temperature for 8 h. Deionized water (5 drops) was added, and the suspension was stirred for 10 min. The resulting suspension was filtered, and the solvent was removed in vacuo. A minimum of dichloromethane (1.0 mL) was added, and petroleum ether (10 mL) was added to precipitate the product that was collected by filtration affording **8** in 85% yield (0.011 g, 0.020 mmol). It was analyzed by ^{1}H NMR spectroscopy in $CDCl_3$, which indicated the formation of **8** as the main product.

2.2.4. Synthesis of bis(2-(1,3-bis(N-butylimidazol-2-ylidene) phenylene))bis(μ–chloro) dirhodium(III), **10**

i) *Synthesis using Zr:Rh ratio of 1:1*. A sample of 2-(1,3-bis(N-butylimidazol-2-ylidene)-phenylene) (dimethylamido)bis(chloro) zirconium (IV) **9** (0.030 g, 0.057 mmol) was stirred with THF (2 mL) at room temperature for 15 mins affording a pale-yellow suspension. A sample of $[Rh(COD)Cl]_2$ (0.014 g, 0.028 mmol) was added yielding a red solution and stirring was continued for 18 h. Deionized water (5 drops) was added, and the suspension was stirred for 10 min. The resulting suspension was filtered, and the solvent was removed in vacuo yielding a yellow solid. A minimum of dichloromethane (1 mL) was added to this solid, and hexane was added to precipitate a pale-yellow solid that was collected by filtration. The crude product was triturated with acetone affording **10** as a pale-yellow microcrystalline solid (67%, 0.038 g, 0.038 mmol). The soluble portion was concentrated to dryness, and the residue was analyzed by ^{1}H NMR spectroscopy in chloroform, and it was consistent with complex **8** (33% yield, 0.010 g, 0.019 mmol).

ii) *Synthesis using Zr:Rh ratio of 1:2*. A sample of 2-(1,3-bis(N-butylimidazol-2-ylidene)-phenylene) (dimethylamido)bis(chloro) zirconium (IV) **9** (0.100 g, 0.190 mmol) and THF (15 mL) were stirred at room temperature for 15 mins affording a pale-yellow suspension. A sample of $[Rh(COD)Cl]_2$ (0.094 g, 0.190 mmol) was added yielding a red solution, and stirring was continued for 8 h. The volatiles were removed under reduced pressure. The resulting solid was washed with pentane (3 × 10 mL). Dichloromethane (15 mL) was added to the solid, and the resulting mixture was filtered. The filtrate was concentrated to dryness and recrystallized at room temperature from a saturated solution of DCM/Hexane (3:1 v/v), giving **10** as pale-yellow solid (63%, 119 mg, 0.120 mmol). Crystals suitable for x-ray analysis were grown by vapor diffusion of hexane into a saturated DCM solution. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.72 (d, J = 1.9 Hz, 4H), 7.25 (dd, J = 8.4, 7.0 Hz, 2H), 7.16 (d, J = 7.9 Hz, 4H), 7.15 (d, J = 1.9 Hz, 4H), 4.84 (ddd, J = 13.3, 9.7, 5.6 Hz, 4H), 3.52 (ddd, J = 13.2, 9.3, 6.5 Hz, 4H), 1.75 (ddd, J = 16.3, 11.0, 6.4 Hz, 4H), 1.67 (ddd, J = 13.5, 9.8, 6.7 Hz, 4H), 1.19 – 1.11 (m, 8H), 0.75 (t, J = 7.4 Hz, 12H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 181.85 (d, J = 37.0 Hz), 151.65 (d, J = 27.7 Hz), 146.55 (s), 124.15 (s), 120.99 (s), 116.55 (s), 108.97 (s), 49.61 (s), 33.49 (s), 20.30 (s), 13.70 (s). HRMS (ESI-TOF) Calcd for $C_{40}H_{50}Cl_3N_8Rh_2$ $[M\text{-}Cl]^+$ = 953.1329, obs m/z = 953.1331; Calcd for $[M\text{-}Cl{+}CH_3CN]^+$ = 994.1594, obs m/z = 994.1599; Calcd for $[M\text{-}2Cl]^{2+}$ = 459.0817, obs m/z = 459.0779.

2.3. X-ray structure determination

A single crystal of appropriate dimensions (0.08×0.04×0.02 mm^3 for **5**; 0.096×0.109×0.128 mm^3 for **7**; 0.130×0.153×0.174 mm^3 for **8**; 0.237×0.277×0.658 mm^3, **10**) was mounted on a cryoloop using an oil cryoprotectant. The X-ray intensity data were measured at low temperature (T = 100 K), using a three circles goniometer Kappa geometry with a fixed Kappa angle at = 54.74 deg on a Bruker AXS D8 Venture, equipped with a

Photon 100 CMOS active pixel sensor detector. A monochromatized Cu X-ray radiation (λ = 1.54178 Å) (**7** and **8**) or Mo X-ray radiation (λ = 0.71073 Å) (**5** and **10**) was selected for the measurement. All frames were integrated with the aid of the Bruker SAINT software using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-Scan method implemented in the program [63]. Using the Bruker SHELXT Software Package [64,65], refinement of the structure was carried out by least squares procedures on weighted F^2 values using the SHELXTL-2018/3 [65] included in the APEX3 v2019, 11.0, AXS Bruker program. Hydrogen atoms were localized on difference Fourier maps but then introduced in the refinement as fixed contributors in idealized geometry with an isotropic thermal parameter fixed at 20% higher than the carbon atoms to which they were connected.

3. Results and discussion

3.1. Synthesis and characterization: in situ *metalation/transmetalation proligand: Rh ratio of 1:2*

In previous reports reaction intermediates pertinent to the metalation/transmetalation were not fully described. In this report, we isolate and characterize a di-Rh intermediate relevant to optimizing the synthesis of CCC–NHC pincer Rh complexes. It explains the requirement of an extra equivalent of Rh during the transmetalation with $[Rh(COD)Cl]_2$ when starting with the diiodide salt of the proligand. Shortly after the initial publication of the metalation/transmetalation methodology, a recrystallization of the orange CCC–NHC Rh amine adduct, **3**, contained a random light red crystal. A crystal structure was obtained and along with confirmation by EDS data the Rh(III)/Rh(I) bimetallic complex, **5**, illustrated in Fig. 1 was confirmed. It contained a Rh(III) center with one CCC–NHC ligand with halogens bridging to a [Rh(I)(COD)] fragment. Despite numerous attempts the results were not consistently repeatable until recently.

3.1.1. Avoiding halogen mixtures

To avoid the problems of halogen scrambling and the resulting complicated spectra, the proligand counterion was switched from iodide to chloride in the metalation/transmetalation sequence. It was performed quantitatively by allowing a 1:1.5 mr (mole ratio), of bis(imidazolium) dichloride salt **6** and $[Zr(NMe_2)_4]$ in THF to react at room temperature for 1 h as illustrated in Scheme 2 Path A. The observable changes in the ^1H NMR spectrum were the disappearance of the imidazolium protons singlet (2H) at 11.96 ppm, and the aryl C–H singlet (1H) at 9.21 ppm of salt **6**. Signals observed in the aromatic region were shifted upfield. Additionally, the triplet signal at 4.43 ppm assigned to the methylene protons alpha to the nitrogen of the butyl chain in salt **6** became diastereotopic and were observed in the region 4.09–4.59 ppm as multiplets consistent with formation of a C_s-symmetric CCC–NHC pincer Zr complex. The identity of this Zr complex was established as the chloride congener of iodo Zr complex, **2**. It was more thoroughly characterized by ^1H and ^{13}C NMR spectroscopy in a separate experiment (Complex **11**, Scheme S4 p. S6 and Figure SI 23 p. S17).

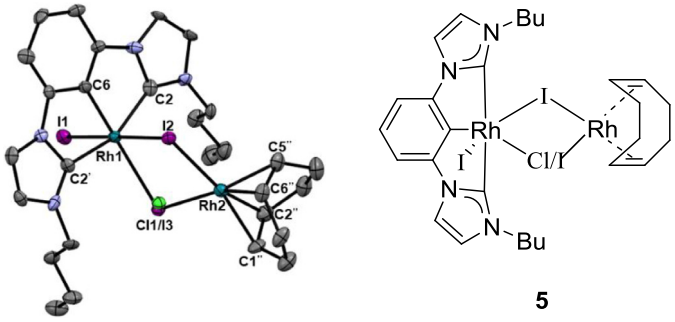


Fig. 1. ORTEP plot and chemdraw structure of early crystal of Rh(III)/Rh(I) obtained serendipitously. The ligands Cl1/I3 were present at 50/50 ratio in one position of the bridging halides.

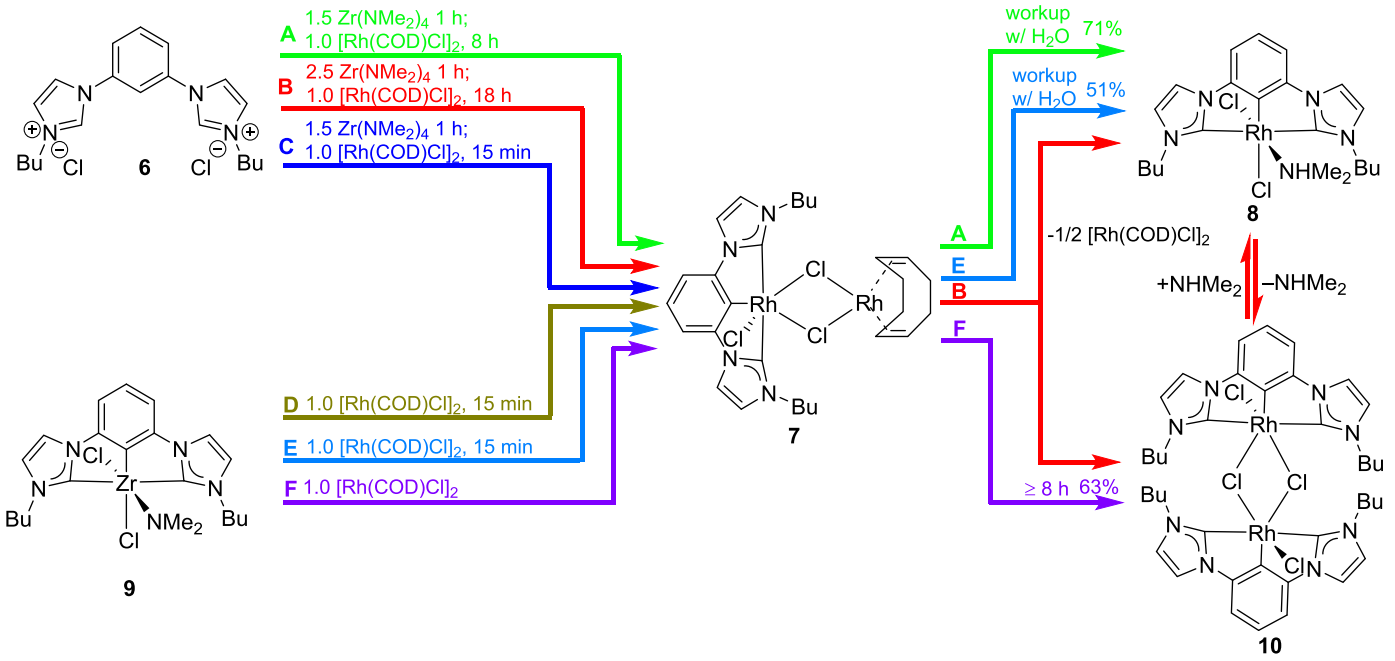
3.1.2. Identification of intermediate and characterization of **8** *and* **10**

After the metalation step was complete, $[Rh(COD)Cl]_2$ in a 1:1 mr of dimer to proligand, which results in a 2:1 ratio of Rh:proligand, was added to the reaction. After 8 h, a new multiplet signal attributed to the methylene protons alpha to the nitrogen of the butyl chain was observed at 5.04 ppm. Furthermore, new olefinic proton signals of a bound COD ligand were observed at 3.23 ppm and 4.00 ppm compared to 2.50 ppm and 4.23 ppm in the starting material, $[Rh(COD)Cl]_2$. These signals were significantly different from the olefinic proton signal of free COD (5.54 ppm) and were tentatively assigned to intermediate complex **7**, as will be confirmed (vide infra). The ^1H NMR spectrum did not contain an imidazolium proton signal 11.96 ppm indicating no decomposition occurred. Two new sets of multiplet signals were observed in the region of 4.42–5.11 ppm (see stacked spectra plot, Figure SI 25 in supporting information), and a doublet assigned to a coordinated Rh-NH$(CH_3)_2$ was observed at 1.65 ppm ($^3J_{Rh\text{-}H}$ = 6.3 Hz) consistent with formation of the monoamine complex, **8**. After addition of deionized water and completion of the workup, the monoamine Rh complex, **8** was obtained in 71% yield (Scheme 2 Path A). The NMR and mass spectroscopic data of complex **8** were consistent with the previous literature report [58].

The in-situ metalation/transmetalation reaction was carried out using a 1:2.5 mr of bis(imidazolium) dichloride salt **6** and $[Zr(NMe_2)_4]$ followed by the addition of $[Rh(COD)Cl]_2$ in a 1:1 ratio of dimer to ligand. When the reaction time was extended to 18 h as illustrated in Scheme 2 Path B, a complex mixture was obtained. The exact mass ESI-TOF analysis of the reaction mixture showed peaks at *m/z* 705.0512, 504.1409, and 953.1309 corresponding to theoretical mass for $C_{28}H_{37}Cl_2N_4Rh_2$ $[M^+-Cl]^+$ = 705.0500 (**7**), $C_{22}H_{32}ClN_5Rh$ $[M^+-Cl]^+$ = 504.1396 (**8**), and $C_{40}H_{50}Cl_3N_8Rh_2$ $[M^+-Cl]^+$ = 953.1329 (**10**). Separation of the mixture using silica gel chromatography was not successful. A crystal was obtained from this mixture that was identified to be the solvate of complex **7** (Figure SI 29, p. S49, **S1**). Subsequently, the presence of dimer complex **10** was also established through selective crystallization of the mixture (Figure SI 32, p. S100, **S2**). The data were consistent with fast formation of Rh(III)/Rh(I) dimer **7**, and slow conversion of **7** to monomeric amine adduct **8**. The longer reaction time led to dimerization of amine adduct **8**, yielding **10**. From these observations it was reasoned that by carefully controlling the stoichiometry and the reaction time, the mixed valent complex **7** could be isolated and characterized by the in-situ metalation/transmetalation method.

3.1.3. Isolation and characterization of intermediate complex **7**

Thus, the in-situ reaction was completed by combining bis(imidazolium) dichloride salt, **6** and $[Zr(NMe_2)_4]$ in a 1:1.5 mr and allowed to react at room temperature for one hour. It was followed by the transmetalation step where $[Rh(COD)Cl]_2$ in a ratio 1:1 of dimer to ligand was added and allowed to react for 15 min. The mixed valent Rh(III)/Rh(I) complex **7** was obtained as a yellow microcrystalline solid in 65% yield (Scheme 2 Path C). It was readily isolated by trituration of the crude with acetone. It is worth noting that when free 1,5-cyclooctadiene (COD) was still present in the crude mixture, complex **7** did not precipitate out when the crude was triturated with acetone. However, when free COD was removed by washing the crude several times with pentane, com-



Scheme 2. Metalation/transmetalation sequence in the synthesis of CCC–NHC Rh pincer complexes at rt in THF.

plex **7** was obtained after trituration with acetone and it was collected by filtration.

The identity of complex **7** was fully established by ^{1}H and ^{13}C NMR spectroscopy, ESI-TOF mass spectroscopy, and further confirmed by X-ray crystallographic determination (vide infra). In the ^{1}H NMR spectrum, the signal corresponding to the methylene protons alpha to the nitrogen in **7** was observed as a multiplet at 4.97–5.12 ppm compared to a triplet at 4.43 ppm and a multiplet at 4.40 ppm in chloride salt **6** and Zr complex **9,** respectively. Additionally, the presence of the bound COD ligand in complex **7** is also supported by the ^{1}H- and ^{13}C NMR spectra. The methylene protons of the bound COD ligand were observed to overlap with two signals of the butyl chain in the region 1.78–2.45 ppm (Figure SI 5). Those of the olefinic protons were observed at 3.75 and 4.31 ppm. In the ^{13}C NMR spectrum, the $C_{carbene}$-Rh signal was observed as a doublet at 179.52 ppm (J = 36.8 Hz) and the C_{aryl}-Rh signal was observed as a doublet at 147.91 ppm (J = 28 Hz) consistent with CCC–NHC pincer Rh complex formation. The signals due to the methylene carbons of the COD ligand were observed at 30.72 and 34.44 ppm, and those of the olefinic carbons were observed as doublets at 77.96 ppm (J_{RhC} = 13.5 Hz) and 79.23 ppm (J_{RhC} = 13.9 Hz) consistent with the structure. The high-resolution ESI-TOF mass spectrum showed peak at *m/z* 705.0505 assignable to $[M\text{-}Cl]^{+}$, corresponding to theoretical mass for $C_{28}H_{37}Cl_2N_4Rh_2$ 705.0500 (Δ = 0.7 ppm). It is noteworthy that disproportionation of complex **7** to Rh(III)/Rh(III) dimer **10** and $[Rh(COD)Cl]_2$ was observed in solution as shown in the ^{1}H NMR spectrum analysis in $CDCl_3$ (Figure SI 7).

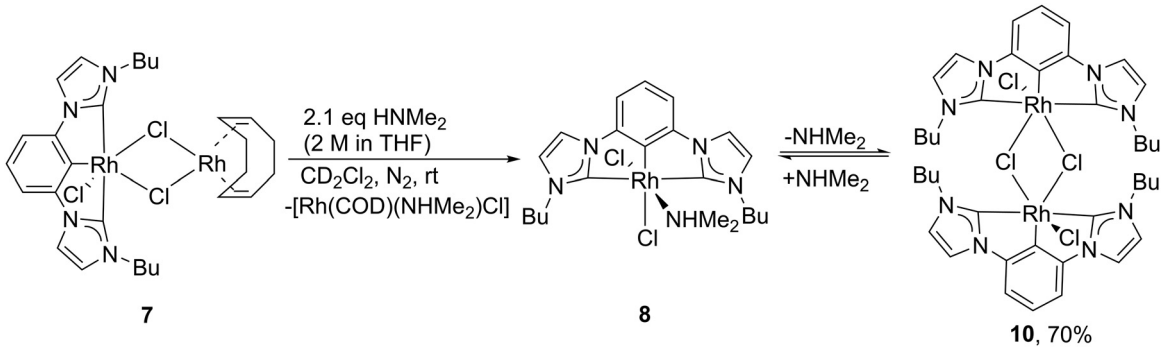
3.2. Direct transmetalation from isolated CCC-NHC Zr pincer complex, **9**

Further investigation of the intermediate complex **7** was conducted by employing direct transmetalation methodology. Direct transmetalation from isolated CCC–NHC Zr complex to late transition metals might provide an excellent route to the preparation of late transition metal pincer complexes. This method would contrast and complement existing in-situ methods, and perhaps shed more light on the mechanism of the transmetalation step. In 2016 and 2017, when the *in situ* methodology gave mixture of products or undesired products one of us employed this route to prepare series of CCC–NHC pincer complexes of Co [42,55]. Direct transmetalation from discrete CCC–NHC Zr complex to prepare CCC–NHC Rh pincer complexes was envisaged.

Initially, CCC–NHC Zr complex **9** prepared by following previous literature procedure [62], was combined with $[Rh(COD)Cl]_2$ in a 1:1 mr and the reaction was monitored by using NMR spectroscopy. The color immediately changed from pale yellow to dark greenish. Over time, a yellow precipitate formed in the reaction. The obvious change in the ^{1}H NMR spectrum was the disappearance of the diastereotopic methylene proton signal observed at 4.20–4.59 ppm of the starting CCC–NHC pincer Zr complex **9**. New distinct multiplet signals were observed at 5.09–5.19 ppm attributable to methylene protons alpha to the nitrogen in intermediate complex **7** (Figure SI 26, p. S19). Due to the formation of a precipitate during the reaction, it was difficult to get good spectroscopic handle. Therefore, the direct transmetalation reaction was conducted at synthetic scale to isolate and characterize the products.

The isolated CCC–NHC Zr complex **9** suspended in THF was combined with $[Rh(COD)Cl]_2$ in a 1:1 mr and the resulting mixture was stirred at room temperature for 15 min (Scheme 2 Path D). The reaction became homogeneous. The color changed immediately to dark red, then dark greenish. The reaction was brought out of the glovebox and exposed to air. The dark green color immediately changed to bright yellow, and a precipitate formed. The solvent was removed by evaporation and the crude was extracted with DCM. The intermediate complex **7** was obtained in 78% isolated yield (Scheme 2 Path D).

The darkish green color may be due to the presence of some Zr(II) species, since in the literature, known Zr(II) complexes have been identified to appear as blackish green in color [66,67]. However, attempts to identify the nature of the reduced Zr(II) species were unsuccessful. Although, it was recently demonstrated with Ti that low valent group (IV) metal complexes could be accessed with the ligand system still intact [68]. It was speculated that Zr(IV) may have been reduced to Zr(II) while Rh(I) was oxidized to Rh(III)



Scheme 3. Reactivity of intermediate complex **7** with dimethylamine.

during the transmetalation reaction. When exposed to air the Zr(II) species may have been oxidized back to Zr(IV). The redox process, however, is beyond the scope of this report.

Similar to Scheme 2 Path D, the isolated CCC–NHC Zr complex **9** was combined with $[Rh(COD)Cl]_2$ in a 1:1 mr of Zr to dimer, in THF and stirred for 15 min, but deionized water was added. After workup, the monoamine complex **8** was obtained in 51% yield (Scheme 2 Path E). This observation may be attributed to a proton source introduced during workup with deionized water protonating metal bound NMe_2 to form $NHMe_2$.

Next, the reaction time was extended as illustrated in Scheme 2 Path F. A yellow precipitate formed in the reaction. After 8 h and without addition of deionized water during workup, the dimeric Rh(III)/Rh(III) complex **10** was obtained in 63% yield along with minor amount of mixed valent complex **7**, and $[Rh(COD)Cl]_2$ (Scheme 2 Path F). This result was consistent with slow conversion of intermediate complex **7** to complex **10**. Complex **10** was identified in solution by comparing the NMR spectrum with a known sample. In the ^{1}H NMR spectrum, the methylene protons alpha to the nitrogen were observed as doublet of doublets of doublets at 3.52 ppm and 4.84 ppm. In the ^{13}C NMR spectrum, signal due to the $C_{carbene}$-Rh was observed at 181.85 ppm (J = 37.0 Hz). The C_{aryl}-Rh signal was observed at 151.65 ppm (J = 27.7 Hz). The exact mass ESI-TOF analysis showed peak at *m/z* 953.1331 ($[M\text{-}Cl]^+$), corresponding to theoretical mass $C_{40}H_{50}Cl_3N_8Rh_2$ 953.1329 (Δ = 0.2 ppm), with isotope patterns matching perfectly. There was no evidence for the formation of a dimethylamido substituted form of complex **10** in the mass spectra data (Figure SI 17). The structure was further confirmed by X-ray crystallographic determination (vide infra).

3.3. Reaction of isolated intermediate 7

Further transformation of isolated intermediate complex **7** was conducted by reacting with stoichiometric amount of dimethyl amine ($HNMe_2$) as illustrated in Scheme 3. The ^{1}H NMR spectrum showed two sets of multiplet signals at 4.71–4.77 ppm and 5.02–5.07 ppm consistent with formation of CCC–NHC Rh amine adduct **8** when compared to authentic **8**. It was allowed to react for 8 h, during which time a yellow precipitate formed. The yellow solid was collected by filtration and characterized by spectroscopic techniques to be consistent with the dimeric Rh(III)/Rh(III) complex **10**, in 70% yield. The results are consistent with formation of complex **8** which dimerizes to complex **10** upon loss of $NHMe_2$. Due to the low solubility of **10** in dichloromethane, it precipitates out of solution. The filtrate was also analyzed by ^{1}H NMR spectroscopy and found to contain complex **8** and $[Rh(COD)(NHMe_2)Cl]$ by-product (Figure SI 22). Thus, the coordination chemistry of Rh(III)/Rh(I) dimer **7** was independently found to readily produce the Rh amine adduct **8** and less soluble Rh(III)/Rh(III) dimer **10**.

3.4. Improved metalation/transmetalation using ligand to Rh ratio of 1:1 with Cl only vs I/Cl

To understand the need for the extra equivalent of Rh during the transmetalation step, the reaction was repeated using a 1:1 ratio of proligand to Rh (i.e., 1 proligand: 0.5 mr of $[Rh(COD)Cl]_2$) in an attempt to avoid using excess Rh. The metalation/transmetalation of the diiodide salt **1** was repeated. In the ^{13}C NMR spectrum, new signal corresponding to Rh-C_{NHC} doublet appeared at 177.05 ppm (J = 53.2 Hz) and the Rh-C_{aryl} signal appeared as doublet at 154.16 ppm (J = 40.7 Hz) consistent with formation of CCC–NHC Rh pincer complex **3**. However, the CCC–NHC Zr complex **2** was still observed in the ^{13}C NMR spectrum consistent with incomplete conversion to CCC–NHC pincer Rh complex (Figure SI 2, p. S3). The results were consistent with the previous literature report [49].

Having established that using diiodide salt and proligand **1** did not give complete transmetalation to Rh with a 1:1 ratio, the counter ion was switched to chloride to remove the complications of multiple halides being present. The reaction was performed using the dichloride salt **6** in a ligand to Rh ratio of 1:1 (Scheme 4). Complete conversion to the CCC–NHC pincer Rh complex **8** was obtained. In the ^{13}C NMR spectrum, two sets of Rh-C_{NHC} doublet signals appeared at 182.43 ppm (J = 41.8 Hz) and 179.99 ppm (J = 54.3 Hz) and two different C_{aryl}-Rh signals appeared at 156.41 ppm (J = 32.2 Hz) and 151.07 ppm (42.4 Hz) consistent with equilibrium between CCC–NHC pincer Rh complex, **8** and dimeric Rh(III)/Rh(III) complex **10** (Figure SI 4, p. S5). Upon addition of deionized water and completing the workup, the monoamine Rh adduct **8** was obtained in 87% yield. The results show that an extra equivalent of Rh was not required for metalation/transmetalation reaction when starting with dichloride salt proligand **6**. The reason may be because the iodide bridged intermediate was more stable and prevented further reaction in comparison to the chloride congener. Thus, when only chloride, and no iodide, was present the reaction quickly gave full conversion with only 1:1 ratio of proligand:Rh.

Next, direct transmetalation of isolated CCC–NHC pincer Zr complexes **9** and **11** was carried out employing 0.5 mr of $[Rh(COD)Cl]_2$ which results in a 1:1 ratio of Zr:Rh as illustrated in Scheme 4. The direct transmetalation of CCC–NHC pincer Zr complex **9** with half equivalent of $[Rh(COD)Cl]_2$, then workup with deionized water, afforded a mixture of CCC–NHC pincer Rh complex **8** (33%) and **10** (67%). On the other hand, direct transmetalation of CCC–NHC pincer Zr complex **11** with half equivalent of $[Rh(COD)Cl]_2$, and workup with deionized water afforded only CCC–NHC pincer Rh complex **8** in 85% yield. It is worth mentioning that longer reaction time (above 8 h) and high vacuum can result in loss of the bound amine in complex **8**, giving rise to the equilibrium between monoamine complex **8** and the

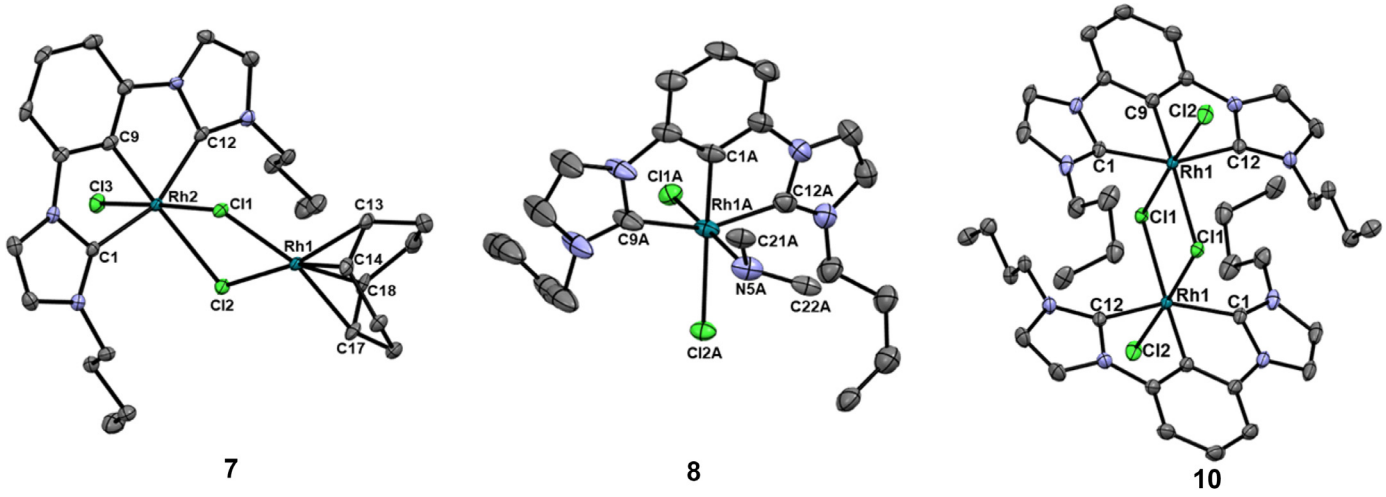
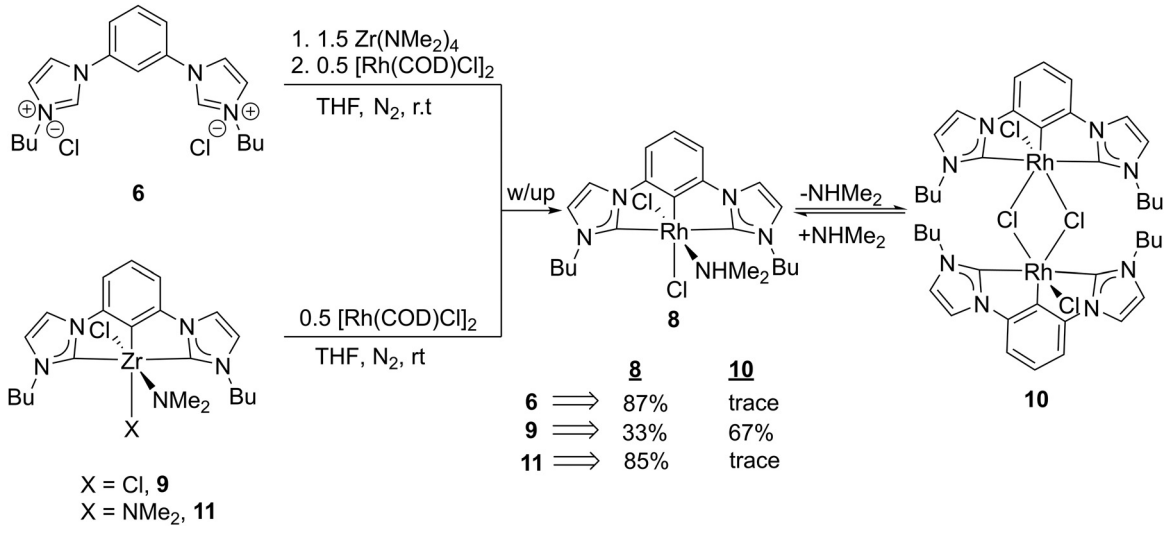


Fig. 2. Molecular structures of bimetallic Rh(III)/Rh(I) complex **7,** octahedral amine adduct **8,** and bimetallic Rh(III)/Rh(III) dimer **10**. Hydrogen atoms are omitted for clarity. Only one of the two independent molecules of **8** in the unit cell is shown.



Scheme 4. Improved synthetic methodology, *in situ* and direct transmetalation using 1:1 ratio of ligand to Rh.

dimeric Rh(III)/Rh(III) complex **10**. The equilibrium tends to favor the formation of the dimeric Rh(III)/Rh(III) complex **10** when less dimethyl amine is present in the system.

3.5. Molecular structures

ORTEP plots of the molecular structures of complexes **7, 8**, and **10** are presented in Fig. 2, to complement that of complex **5** in Fig. 1. Selected bond distances and angles along with those of related iodo analogs are presented in Table 1. Complexes **5** and **7** are comprised of a four-coordinate square planar Rh(I) center bridged by two halogens (I/Cl for **5** and Cl for **7**) to a six-coordinate distorted octahedron Rh(III) center. Pincer Rh complexes comprised of mixed valent Rh(III)/Rh(I) are rare with only few examples reported in the literature [69,70]. To the best of our knowledge **5** and **7** are the first reported examples of mixed valent Rh(III)/Rh(I) complexes bearing a CCC–NHC pincer ligand. The overall geometry around the square planar Rh(I) fragment is similar to related Rh(COD) complexes such as [RhCl(κ^3-C_6H_3–2,6-$(CH_2PPh_2)_2$)(μ-Cl)$_2$Rh(COD)] [71], and [RhCl(κ^3-C_6H_3–2,6-$(SPPh_2)_2$)(μ-Cl)$_2$Rh(COD)] [70]. The geometry around the Rh(III) center is distorted from an idealized octahedron due the constraints of the CCC–NHC pincer ligand [49]. The bridging halogen ligands are unsymmetrically bonded to Rh. For instance, complex **7** has Rh2-Cl1(axial) = 2.3834(7) Å and Rh2-Cl2(equatorial) = 2.5799(7) Å. The longer Rh2-Cl2 bond is caused by the strong trans influence of phenylene bridged pincer ligand. For comparison, the mixed valent pincer complexes [RhCl(κ^3-C_6H_3–2,6-$(CH_2PPh_2)_2$)(μ-Cl)$_2$Rh(COD)] [71] and [RhCl(κ^3-C_6H_3–2,6-$(SPPh_2)_2$)(μ-Cl)$_2$Rh(COD)] [70] have the Rh-Cl bonds trans to the phenylene to be 2.555(3) Å and 2.524 Å, respectively, which are consistent with strong trans influence.

The solid-state molecular structures of **8** and **10** notably bear significant structural resemblance to their iodo analogs [49,58]. The C_{NHC}-Rh-C_{NHC} angle of 156.3(2) for complex **8** and 156.89(7) for complex **10** are very similar to the iodo analogs of 156.61(14) for [($^{Bu}C^iC^iC^{Bu}$)RhI_2($NHMe_2$)] [58] and 156.98(16) for [($^{Bu}C^iC^iC^{Bu}$)RhI_2]$_2$ [49] (Table 1), and were within experimental error. Subtle changes to the average bond distances and angles were observed with changes in coordination sphere and oxidation state,

Table 1
Select metric data (distances (Å) and angles (°)) for CCC–NHC Rh complexes **5, 7, 8, 10**, and available iodo analogs [49,58] of complexes **8** and **10**.

	5	**7**	**8**	**10**	[(^{Bu}C^{i}C^{i}C^{Bu})RhI$_2$(NHMe$_2$)][58]	[(^{Bu}C^{i}C^{i}C^{Bu})RhI$_2$]$_2$[49]
Rh-C_{aryl}	1.938(9)	1.938(3)	1.949(5)	1.9335(17)	1.948(4)	1.943(4)
Rh-C_{NHC}	2.070(7)	2.075(3)	2.070(5)	2.0655(16)	2.083(4)	2.063(4)
Rh-C_{NHC}	2.070(8)	2.068(3)	2.053(6)	2.0497(17)	2.074(4)	2.061(4)
Rh-X_{ax}	2.648(1)	2.3834(7)[b]	2.3648(12)	2.3716(4)	2.6610(4)	2.6694(5)[b]
Rh-X_{ax}	2.633(1)	2.3369(7)	2.185(13)[a]	2.3286(4)	2.136(3)[a]	2.6567(5)
Rh-X_{eq}	2.706(2)	2.5799(7)	2.5185(11)	2.5681(4)	2.8555(4)	2.8366(5)
C_{NHC}-Rh-C_{NHC}	157.3(3)	157.56(12)	156.3(2)	156.89(7)	156.61(14)	156.98(16)
C_{aryl}-Rh-X_{ax}	92.5(2)	94.2(1)[b]	92.9(2)	90.41(5)	88.20(10)	88.3(1)[b]
C_{aryl}-Rh-X_{ax}	89.6(2)	89.5(1)	93.1(4)[a]	92.36(5)	92.55(13)[a]	91.6(1)
C_{aryl}-Rh-X_{eq}	179.6(2)	176.5(1)	172.5(2)	175.08(5)	176.12(10)	174.8(1)
C_{aryl}-Rh-C_{NHC}	78.9(3)	78.9(1)	78.1(2)	78.78(7)	78.48(14)	78.56(18)
C_{aryl}-Rh-C_{NHC}	78.4(3)	78.6(1)	78.7(2)	78.70(7)	78.41(15)	78.54(17)
C_{NHC}-Rh-X_{ax}	89.1(2)[b]	90.77(1)[b]	89.3(2)	93.94(5)	88.86(10)	89.7(1)[b]
C_{NHC}-Rh-X_{ax}	90.9(2)	89.44(9)	97.0(4)	87.61(5)	94.56(13)[a]	88.7(1)
C_{NHC}-Rh-X_{eq}	101.4(2)	100.77(9)	100.4(2)	102.17(5)	100.46(10)	101.8(1)

[a] X_{ax} = $NHMe_2$.
[b] X_{ax} = bridging Cl, or I.

but the rigid CCC–NHC ligand dictates the basic structure of these complexes.

4. Conclusion

An intermediate for the CCC–NHC metalation/transmetalation sequence has been isolated and characterized by X-ray crystallography, NMR spectroscopy, elemental analysis, and time-of-flight high resolution mass spectrometry. The new mixed valent Rh(III)/Rh(I) complex **7** was obtained by employing the in-situ metalation/transmetalation methodology and direct transmetalation from isolated CCC–NHC Zr pincer complex **9**. The investigation of this novel intermediate led to an improved stoichiometric synthesis of series of CCC–NHC pincer Rh complexes. It was found that switching the proligand salt from diiodide to dichloride as counterion obviated the need for extra equivalent of Rh. When the dichloride salt proligand was employed in a ligand to Rh ratio of 1:1 for the in-situ metalation/transmetalation sequence, the CCC–NHC pincer Rh complex **8** was obtained in 87% yield. This improvement cuts the amount of Rh required by half in comparison to the previously reported procedure in which two atom equivalents of Rh per ligand was employed. Also, direct transmetalation from isolated CCC–NHC pincer Zr complexes **9** and **11** employed in a 1:1 ratio of Zr to Rh efficiently afforded desired CCC–NHC pincer Rh complexes **8** and **10** in good yields (85 and 67%). The improved stoichiometric synthetic methodology offers a facile and cost-effective way to scale up the synthesis of CCC–NHC pincer Rh complexes for future applications.

Declaration of Competing Interest

The authors declare that they do not have known competing interests in the work reported in this paper.

Data availability

The data are included in the supporting information.

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Supplementary materials

CCDC numbers 2101948 (**5**), 2101949 (**7**), 2101950 (**8**), 2101951 (**10**), 2101952 (**S1**), 2101953 (**S2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223–336,033.

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2022.122499.

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