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A Rigid Cyclic (Alkyl)(amino)carbene Ligand Leads to Isolation of Low-Coordinate Transition-Metal Complexes**

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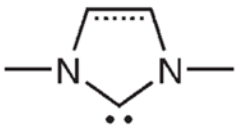
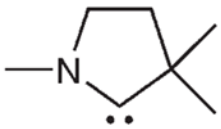
Keywords

agostic interactions; carbene ligands; low-coordinate complexes; palladium; rhodium

In the last decade the use of diamino N-heterocyclic carbenes (NHCs) **A** as ancillary ligands for transition-metal catalysts and as organic catalysts on their own has proven very fruitful.[1] The efficiency of NHCs is attributed to their strong σ-donor properties and sterically demanding structure.[1,2] Not only have NHCs yielded improved transition metal catalysts, but they have also lead to the isolation of unusual low-coordinate metal complexes,[2] which often play a key role in catalytic processes. Recently, we reported the synthesis of stable cyclic (alkyl)(amino)carbenes (CAACs) **B**[3] and demonstrated that CAACs can be even stronger σ donors than NHCs, and lead to highly efficient palladium catalysts for the α-arylation of ketones and aldehydes. Here we report that the peculiar steric and electronic properties of rigid CAAC ligands allow the preparation of low-coordinate metal complexes, hitherto not isolable with any other ligands.



A



B

To further evaluate the electronic properties of rigid CAAC **B1**, we attempted to prepare the [RhCl(CO)$_2$(**B1**)] complex, since the CO stretching frequencies of this type of rhodium complexes are recognized as an excellent measure of the σ-donor ability of the ligand L, and a large amount of data is available for comparison.[4] Reaction of carbene **B1** with half an equivalent of [{RhCl(cod)$_2$}$_2$] (cod = 1,5-cyclooctadiene) afforded complex **1**, which after purification by column chromatography on silica gel was obtained as orange crystals in 79% yield (Scheme 1). The structure of **1** was unambiguously determined by single-crystal X-ray diffraction.[5] Following the classical procedure, a solution of **1** in chloroform was treated with an excess of CO. Surprisingly, the ^{13}C NMR spectrum of the product (95% yield) showed only one CO signal, with a large coupling constant ($J_{Rh,C}$ = 134 Hz), and not two signals with smaller *J* values ($J_{Rh,C}$ = 33–82 Hz), as observed for [RhCl(CO)$_2$(L)] complexes.[4] It is known that when bulky ligands L are present [RhCl(CO)$_2$L] complexes can readily lose one CO ligand

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to give a chloro-bridged dimer.[6] However, single-crystal X-ray diffraction[5] revealed that even in the solid state complex **2** is formally a 14-electron [RhCl(CO)L] monomer (Figure 1).

Interestingly, **2** can also be synthesized in 80% yield by reaction of one equivalent of carbene **B1** with half an equivalent of $[\{RhCl(CO)_2\}_2]$. The extreme hindrance provided by the menthyl ring of CAAC **B1**, which is locked in the most sterically demanding conformation with respect to the metal center, explains in part why dimerization does not occur. Moreover, the short Rh–Ha (2.183 Å) and Rh–Hb (2.231 Å) distances suggest the existence of agostic interactions, which bring additional stabilization to the metal center. In solution, an agostic interaction is also apparent in the ^{1}H NMR spectrum, which shows a broad multiplet (1H) at 0.08 ppm. Complex **2** is indefinitely stable at room temperature in air. Related $[RhClL_2]$ complexes, exemplified by the active species of Wilkinson3s catalyst $[RhCl(PPh_3)_2]$, are known only as transient species.[7] They have only been generated in situ by ligand dissociation[8] or by hapticity changes;[9] otherwise they readily form chloro-bridged dimers, even when two very bulky ligands L are present.[6] Although other neutral T-shaped formally 14-electron Rh^I complexes have been isolated, they are still very rare, and none of them have a bridging-capable halide ligand like complex **2**.[10,11]

The isolation of this low-coordinate Rh^I complex **2** made us confident that other low-ligated transition-metal complexes could be stabilized by rigid CAAC **B1**. After close scrutiny of the literature, it came to our attention that other ligands, particularly NHCs, have consistently failed to allow the isolation of cationic 14-electron $[Pd(All)(L)]^+$ complexes (Scheme 2, All =allyl).[12] In 2003, Nolan et al.[12a] were able to abstract chloride from complex **3**, but the cationic complex generated was either unstable and decomposed upon workup or isolated and structurally characterized as an acetonitrile adduct. In 2005, Porschke et al.[12b] reported that chloride abstraction with thallium salts from NHC complexes **3** led to ionic binuclear compounds, which result from combination of the transiently formed desired cationic species with the starting neutral complex. Most recently, Glorius et al.[12c] generated cationic complex **4**, which, despite intramolecular stabilization by double-bond complexation, appeared to be rather unstable and was only characterized by ^{1}H NMR spectroscopy.

In marked contrast, chloride abstraction from [PdCl-(All)(**B1**)] (**5**)[3] with a stoichiometric amount of $AgBF_4$ produced the elusive cationic palladium complex **6** as yellow crystals (88% yield, Scheme 3). The structure of **6** was unambiguously established by single-crystal X-ray diffraction (Figure 2).[5] As expected, **6** has a T-shaped geometry with no interaction between the metal atom and tetrafluoroborate anion (shortest Pd–F distance 3.88 Å). Similar to the above-mentioned Rh^I complex **2**, at least one of the axial H atoms of the menthyl ring provides a stabilizing agostic interaction (Pd–Ha 2.048, Pd–Hb 2.509 Å). This interaction is also apparent from the ^{1}H NMR spectrum, which shows a broad multiplet (1H) at −0.17 ppm. This is the first example of a stable, formally 14-electron, Pd^{II} cation.[13]

To further demonstrate the increased stabilization of metal centers provided by the rigid menthyl moiety of carbene **B1**, we attempted to prepare complexes analogous to **2** and **6**, using the CAAC **B2**, featuring the unlocked and therefore flexible cyclohexyl ring.[3,14] Treatment of $[\{RhCl(CO)_2\}_2]$ with two equivalents of carbene **B2** afforded exclusively the classical dicarbonyl complex **7**, while treatment of **8**[3] with $AgBF_4$ led to rapid formation of palladium black (Scheme 4). Clearly, in contrast to **B1**, the cyclohexane ring of CAAC **B2** can flip to the less sterically demanding conformation, in which no H atoms are available for strong agostic interactions with the metal center.

The isolation of complexes **2** and **6** clearly demonstrates the advantages of rigid CAACs over classical ligands. By manipulating the quaternary carbon atom adjacent to the carbene center it is possible to design ligands with an electronically active wall of protection for the metal

center. We are currently exploring the possibility that CAAC ligands will stabilize even lower coordinate metal complexes.

Experimental Section

All manipulations were performed under an inert atmosphere of argon by using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^{1}H and ^{13}C NMR spectra were recorded on Varian Inova 300, 500 and Bruker Avance 300 spectrometers.

1

A solution of carbene **B1**[3] (0.45 g, 1.18 mmol) in THF (10 mL) was added at −78°C to a stirred solution of [{RhCl(cod)$_2$}$_2$] (0.26 g, 0.53 mmol) in THF (5 mL). The solution was warmed to room temperature and stirred for 3 h. After evaporation of the solvent under vacuum, washing with hexane (15 mL), and purification by column chromatography on silica gel with diethyl ether as eluant, complex **1** was obtained as an orange powder (0.52 g, 79%). Recrystallization from diethyl ether/pentane at −20°C afforded **1** as orange crystals (m.p. 184–186°C). $[\alpha]_D^{23} = +189^\circ$ ($CHCl_3$). ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ=7.41–7.54 (m, 2H, H_{ar}), 7.17–7.20 (m, 1H, H_{ar}), 5.44 (m, 1H, CH_{cod}), 4.65 (m, 1H, CH_{cod}), 4.21 (m, 1H, CH_{cod}), 3.06–3.23 (m, 5H), 2.68 (m, 2H), 2.51 (d, 1H, J = 12.9 Hz), 1.99–2.13 (m, 4H), 1.77 (d, 3H, CHCH_3, J = 6.0 Hz), 1.45–1.71 (m, 10H), 1.29 (d, 3H, CHCH_3, J = 6.6 Hz), 1.24 (d, 3H, CHCH_3, J = 6.6), 1.20 (s, 6H), 1.11 (d, 3H, CHCH_3, J = 6.3 Hz), 1.04 (d, 3H, CHCH_3, J =6.3 Hz), 0.97 (d, 3H, CHCH_3, J =6.6 Hz), 0.92 ppm (d, 3H, CHCH_3, J = 6.3 Hz). ^{13}C NMR ($CDCl_3$, 25 °C, 75 MHz): δ=278.26 (d, J =44.5 Hz), 148.76, 146.13, 138.42, 128.94, 127.28, 124.30, 100.03 (d, J =6.0 Hz), 99.72 (d, J =5.3 Hz), 76.62, 72.44 (d, J =16.2 Hz), 70.69, 60.43 (d, J =14.5 Hz), 54.96, 51.34, 49.81, 36.42, 35.53, 33.69, 32.93, 31.63, 29.63, 29.34, 29.13, 29.03, 28.48, 27.97, 27.70, 26.71, 25.78, 25.59, 24.90, 22.35, 22.27 ppm.

2

Carbon monoxide was bubbled (60 min) through a solution of complex **1** (0.58 g, 0.92 mmol) in chloroform (15 mL). After evaporation of the solvent under vacuum and washing with hexane (10 mL), complex **2** was obtained as an orange powder (0.48 g, 95%). Alternatively, a solution of carbene **B1** (0.40 g, 1.04 mmol) in THF (5 mL) was added at −78°C to a stirred solution of [{RhCl(CO)$_2$}$_2$] (0.18 g, 0.47 mmol) in THF (5 mL). The solution was warmed to room temperature and stirred for 2 h. After evaporation of the solvent under vacuum and washing with hexane (20 mL), a solid residue was obtained (0.41 g, 80%). Recrystallization from chloroform by slow evaporation at room temperature afforded **2** as orange crystals (m.p. 251°C decomp). $[\alpha]_D^{23} = -0.1^\circ$ ($CHCl_3$). ^{1}H NMR ($CDCl_3$, 25°C, 300 MHz): δ=7.45 (m, 1H, H_{ar}), 7.28 (m, 2H, H_{ar}), 2.83 (sept, 2H, CHCH$_3$, J = 6.6 Hz), 2.60 (m, 1H), 2.47 (d, 1H, J = 13.5 Hz), 2.27 (m, 1H), 1.89–2.12 (m, 5H), 1.61 (d, 3H, CHCH_3, J = 6.6 Hz), 1.24–1.44 (m, 20H), 1.13 (d, 3H, CHCH_3, J = 5.7), 1.06 (d, 3H, CHCH_3, J = 6.9), 0.08 ppm (m, 1H, H_{agos}). ^{13}C NMR ($CDCl_3$, 25 °C, 75 MHz): δ= 248.47 (d, J =48.8 Hz), 181.21 (d, J =134.3 Hz), 146.20, 145.72, 136.90, 130.28, 125.82, 125.70, 77.67, 71.85, 51.85, 50.39, 46.26, 40.60, 35.13, 34.78, 30.58, 30.38, 29.13, 27.11, 26.43, 26.26, 24.29, 24.16, 22.63, 20.19 ppm. IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 1989 cm^{-1}.

6

A 1:1 mixture of carbene complex **5**[3] (0.50 g, 0.9 mmol) and silver tetrafluoroborate was cooled to −40°C and 5 mL of fluorobenzene was added. The suspension was warmed to room temperature and stirred for 30 min. After filtration, evaporation of the solvent under vacuum, and washing with hexane (10 mL), a solid residue was obtained (0.48 g, 88%). Recrystallization from toluene/fluorobenzene at −20°C afforded **6** as yellow crystals (m.p. 157–159°C decomp).

$[\alpha]_D^{23} = -6^\circ$ (C_6H_5F). ^{1}H NMR (C_6D_5F, 25°C, 300 MHz): δ=6.78–7.15 (m, 3H, H_{ar}), 5.00 (m, 1H, H_{allyl}), 3.34–3.48 (m, 2H, H_{allyl}), 2.90 (m, 2H), 2.59 (m, 2H), 2.36–2.41 (m, 1H), 1.91–2.17 (m, 3H), 1.65–1.82 (m, 3H), 1.13–1.22 (m, 12H), 1.06 (d, 3H, CHCH_3, J = 6.3 Hz), 1.05 (d, 3H, CHCH_3, J = 6.9 Hz), 0.99 (d, 3H, CHCH_3, J = 6.9 Hz), 0.98 (s, 3H, CH_3), 0.88 (d, 3H, CHCH_3, J = 6.9 Hz), 0.73 (d, 3H, CHCH_3, J = 6.9 Hz), –0.17 ppm (m, 1H, H_{agos}). ^{13}C NMR (C_6D_5F, 25 °C, 75 MHz): δ=251.46, 145.54, 145.33, 133.42, 130.92, 126.33, 126.17, 118.76, 81.45, 70.74, 51.49, 50.60, 45.86, 40.19, 35.20, 33.95, 29.87, 29.17, 28.93, 26.86, 26.16, 25.44, 23.88, 23.60, 22.94, 22.55, 18.58 ppm.

7

A solution of carbene **B2** (0.56 g, 1.72 mmol) in THF (10 mL) was added at −78°C to a stirred solution of [{RhCl(CO)$_2$}$_2$] (0.30 g, 0.77 mmol) in THF (10 mL). The solution was warmed to room temperature and stirred for 3 h. After evaporation of the solvent under vacuum, washing with hexane (20 mL), and extraction with chloroform (20 mL), a gray solid residue was obtained (0.67 g, 84%). ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ=7.42–7.47 (m, 1H, H_{ar}), 7.28–7.34 (m, 2H, H_{ar}), 3.02 (sept, 2H, CHCH$_3$, J = 6.6 Hz), 2.58 (m, 2H, CH_2), 2.09 (s, 2H, CH_2), 1.39–1.90 (m, 8H, CH_2), 1.34 (d, 6H, CHCH_3, J =6.6 Hz), 1.33 (d, 6H, CHCH_3, J = 6.6), 1.32 ppm (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 25 °C, 100.5 MHz): δ=259.82 (d, J =38.4 Hz), 185.95 (d, J =50.7 Hz), 184.61 (d, J =77.3 Hz), 146.41, 134.15, 129.56, 125.49, 81.81, 62.93, 45.27, 38.34, 30.47, 29.12, 28.78, 25.35, 24.94, 22.48 ppm. IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 1994, 2077 cm^{-1}.

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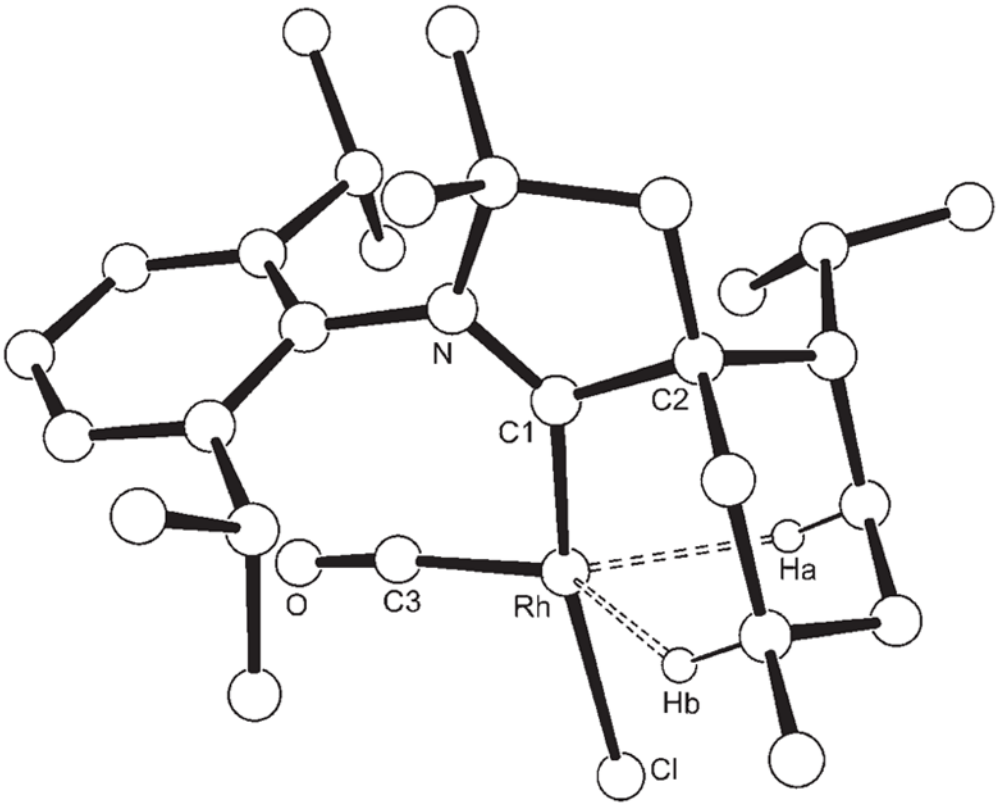


Figure 1.

Molecular structure of **2** in the solid state. Selected bond lengths [Å] and angles [°]: N–C1 1.3174(14), C1–C2 1.5368(15), C1–Rh 1.9399(10) Rh–Cl 2.3740 (3), Rh–C3 1.7955(11), C3–O 1.1433(14), Rh–Ha 2.183(17), Rh–Hb 2.231(17); N-C1-C2 108.70(9), C1-Rh-C3 97.99(5), C3-Rh-Cl 94.55(4), C1-Rh-Cl 167.35(3), Rh-C3-O 173.46(10).

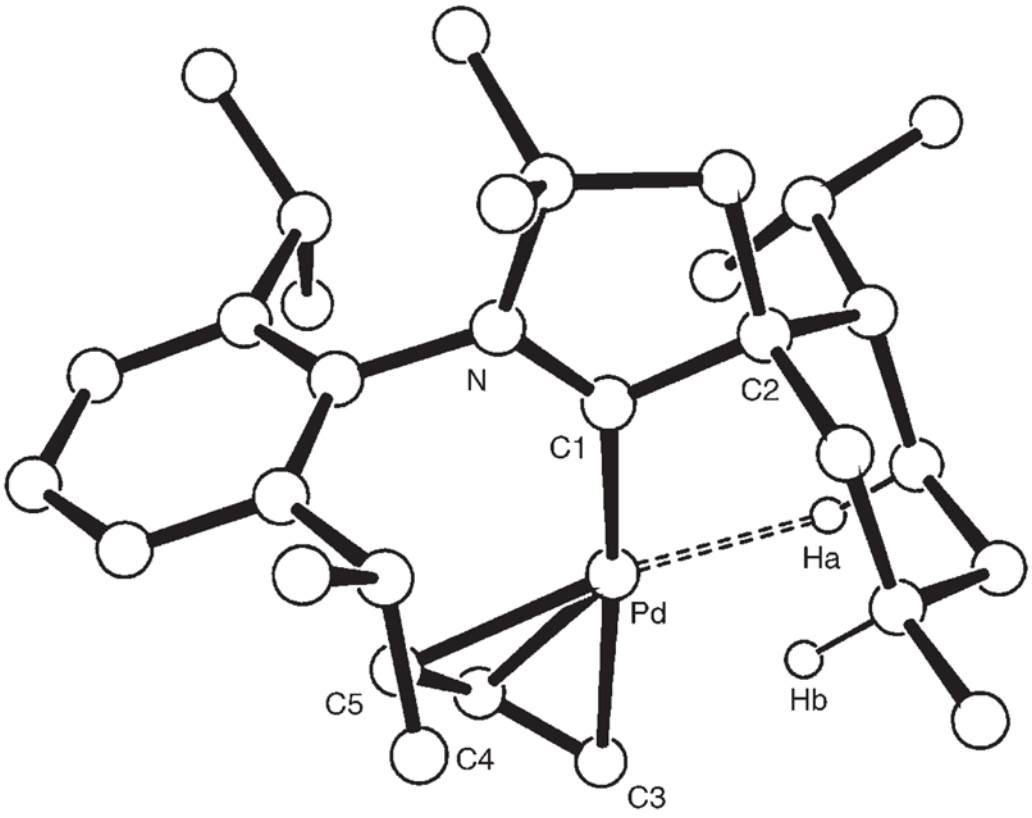
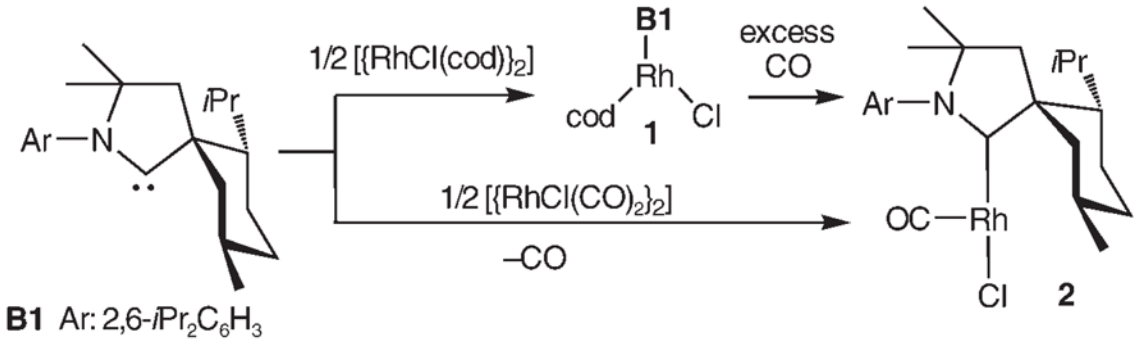
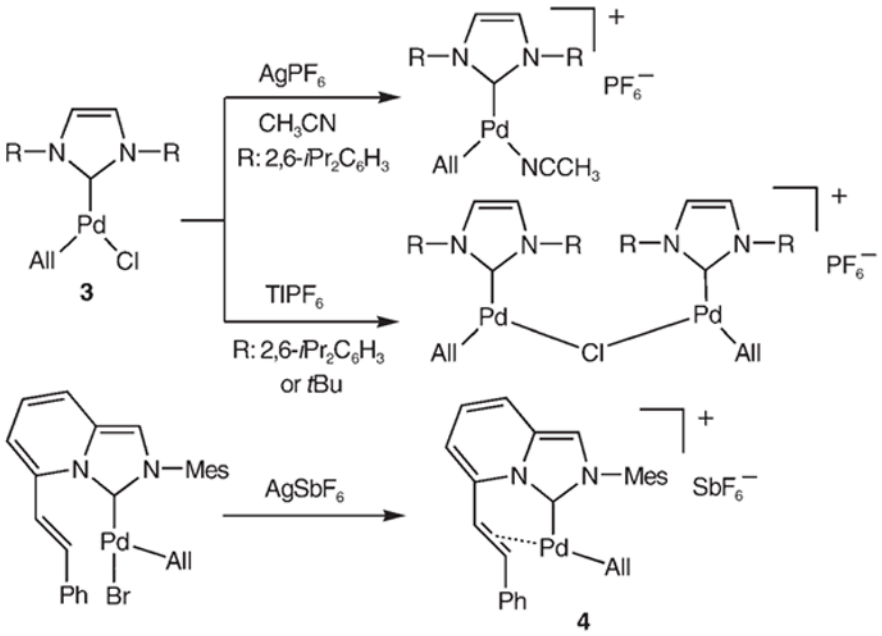


Figure 2.

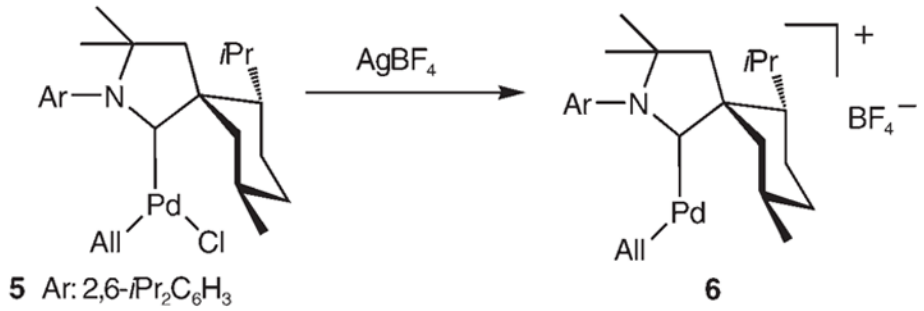
Structure of the cation of **6** in the solid state. Selected bond lengths [Å] and angles [°]: N–C1 1.293(3), C1–C2 1.519(3), C1–Pd 2.038(3), Pd–Ha 2.048, Pd–Hb 2.509, Pd–C3 2.272(13), Pd–C4 2.148(4), Pd–C5 2.126(9); N-C1-C2 109.4(2), N-C1-Pd 133.96(18), C2-C1-Pd 116.64 (15).



Scheme 1.
Synthesis of [RhCl(CO)(**B1**)] complex **2**.

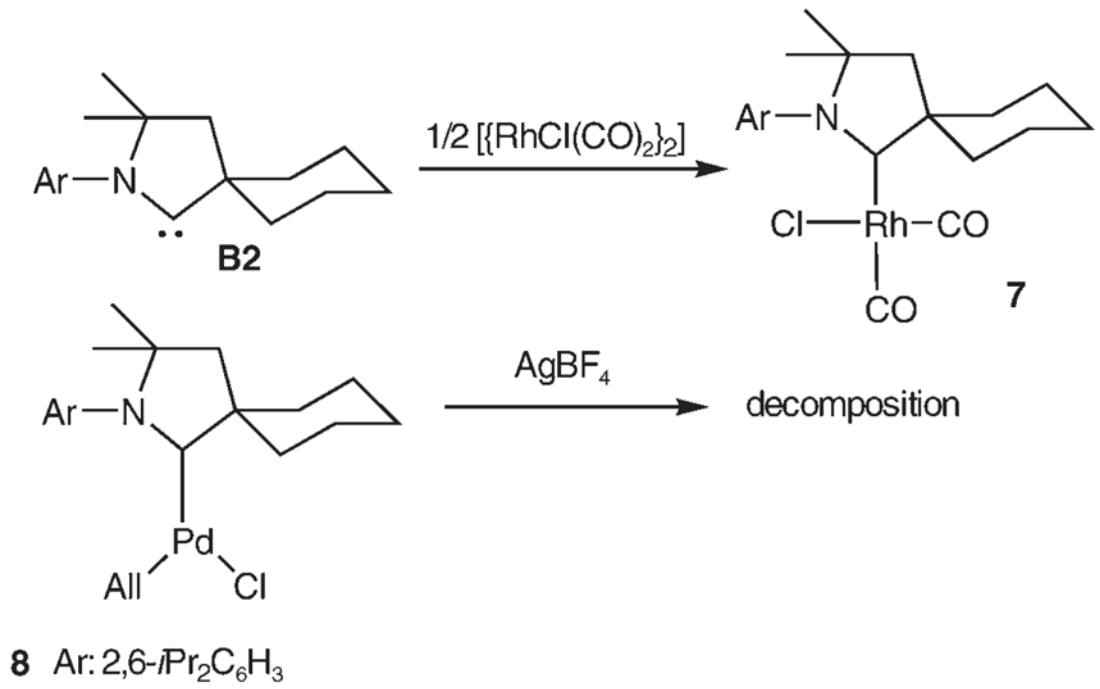


Scheme 2.
Previous attempts to prepare cationic 14-electron $[Pd(All)(L)]^+$ complexes.



5 Ar: 2,6-*i*Pr$_2$C$_6$H$_3$ 6

Scheme 3.
Synthesis of [Pd(All)(**B1**)]$^+$ complex **6**.



Scheme 4.

Synthesis of [RhCl(CO)$_2$(**B2**)] complex **7**, and attempted chloride abstraction from [PdCl(All)(**B2**)] complex **8**.