ORGANOMETALLICS

Synthetic Modification of Acyclic Bent Allenes (Carbodicarbenes) and Further Studies on Their Structural Implications and Reactivities

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Supporting Information

ABSTRACT: The paper describes the synthetic development of Bertrand-type acyclic carbodicarbene scaffolds derived from an unsymmetrical bis(benzimidazol-2-yl)methane bearing two sterically demanding pendant arms, isopropyl (**6a**) or cyclohexyl (**6b**). X-ray crystallographic analysis shows that the impact of these pendant arms on the overall structural parameters of carbodicarbenes is minimal. The chemical reactivity of the carbodicarbenes was evaluated with iodomethane to afford compound 7, illustrating its nucleophilic properties. Finally, experiments were also undertaken to investigate the coordination ability of carbodicarbene toward the formation of rhodium carbonyl (**10**) and palladium allyl



complexes (11). The crystal structures of the metal complexes have been determined, revealing that their metal-carbene distances are elongated only slightly, this fact was rationalized on the basis of geometrical steric considerations with regard to the ligand.

INTRODUCTION

The quest for novel bonding environments of carbon species with interesting electronic configurations has been a central theme in elemental organic chemistry for centuries. The curiosity-driven endeavors by many pioneers eventually led to the isolation of a stable free six-electron carbon species, namely phosphino-silyl carbenes^{1a,b} and N-heterocyclic carbenes (NHC).^{1c,d} More importantly, such an intensive scientific exploration of the six-electron carbon class was eventually rewarded by such advantageous features as synthetic versatility, steric and electronic tunability, and the ability to coordinate strongly to metal centers, as innovations in the field of organometallic chemistry and catalysis.²

The development in NHC toward a myriad of architectural scaffolds has flourished at a significant rate within the past decade.³ Very recently, Bertrand⁴ and Fürstner⁵ have successfully espoused a rather peculiar conceptual paradigm, coined as carbodicarbenes⁶ or bent allenes, by synthesizing the corresponding compounds **A** and **B**, respectively (Chart 1), though its family roots can be traced back to the seminal work by Ramirez on hexaphenylcarbodiphosphorane $(C(PPh_3)_2)$.⁷ As corroborated by subsequent experimental studies as well as theoretical analyses,⁸ carbodicarbenes are generally accepted as the resonance form NHC \rightarrow C \leftarrow NHC (**A**' and **B**' in Chart 1), in which each NHC donates a pair of electrons to an empty

Chart 1



orbital of the central zerovalent carbon atom possessing two orthogonal lone pairs.

Owing to its two lone pairs residing on the carbon atom, carbodicarbene has been considered to be a stronger donor than NHC with possible potential. Regrettably, interest in this captodative description of carbogenic compounds has remained a scientific curiosity due to the lack of appropriate synthetic strategies for further structural modification. We believe that an improvement in the structural diversity of carbodicarbenes might extend their utility into the realm of organometallic

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Scheme 1. Synthetic Route toward Carbodicarbene 6



chemistry and catalysis. Herein, we describe the development of a synthetic protocol for the preparation of carbodicarbenes with unsymmetrical side arms and investigate their late-transitionmetal complexes and intrinsic reactivities.

RESULTS AND DISCUSSION

Preliminary synthesis of the carbodicarbene was initiated with the commercially available 2-nitroaniline (Scheme 1), which underwent imination to 1a by treatment with acetone and hydrogenation in latter steps to furnish the diamine 2a bearing an isopropyl side arm in excellent yield (97%). Compound 2a was then refluxed with diethyl malonate to form the coupled bis(benzimidazol-2-yl)methane 3a in high yield. Bis-methylation of 3a with methyltrifluoromethanesulfonate or iodomethane in acetonitrile gave the dicationic salt 4a or 4c, respectively. Likewise, the synthesis of the cyclohexyl derivative 4b can also be attained in a similar manner, with the exception that its starting material 1b was prepared via a palladiummediated C-N coupling method. It worth noting that the successful use of alkyl iodide for an alternate preparatory route not only guarantees a cost-effective synthesis but also increases the number of potential synthetic modifications, due to the wide variety of commercially available iodide reagents.

Consistent with the NMR analyses, the identities of 4 were confirmed by single-crystal X-ray diffraction, as illustrated in Figure 1. The short bond lengths (1.332-1.345 Å) and acute bond angle (~109°) of the N–C–N connection in 4 are in the range of those for other imidazolium salts.^{1c,d} Of more interest is that the two benzimidazolium planes in 4c are twisted by 87.22°, which appears to be necessary to avoid the steric repulsion imposed by the two isopropyl arms arranged in an anti manner with each other. Nevertheless, the magnitude of the twisting effect is smaller for 4a (72.2°), as the highly charged trifluoromethanesulfonate counteranions have overridden the steric repulsion within the molecules by having a strong electrostatic interaction (blue dotted line, Figure S11 in

the Supporting Information) with two benzimidazolium moieties.

In order to generate carbodicarbene species via a milder method, we initially turned our attention toward preparation of the silver adduct, which may serve as an effective carbodicarbene transfer agent for other metal complexes. Compound 4a was allowed to react with $1/_2$ equiv of Ag₂O in dichloromethane to afford 5a. The proton NMR study of 5a displayed the disappearance of the methylene signature peak at δ 5.51 ppm followed by the emergence of a new singlet peak at δ 4.57 ppm with one proton integration, a telltale sign of an incomplete deprotonation of the methylene carbon. The addition of excess Ag₂O to 5a did not seem to perturb its chemical nature. Crystals of 5a suitable for X-ray diffraction analysis were obtained by slow evaporation of a dichloromethane solution. The single-crystal X-ray structure determination of 5a (Figure 2) confirmed a single deprotonation of the dicationic salt 4a with no formation of a desirable silver metalcarbodicarbene complex. Similarly, reacting 1 equiv of NaOEt with 4a could also afford compound 5a. As expected, the bond lengths in the C(2)-C(12)-C(14) allenic carbon skeleton (1.396(3) and 1.393(3) Å) in **5a** are shorter than those in the precursor 4a by a difference of 0.1 Å, illustrating an increasing double-bond character with a larger bond angle $(126.41(17)^{\circ})$.

Having achieved only monodeprotonation using silver oxide, our attention shifted toward the use of a stronger and more bulky base. Double deprotonation of 4 using 2 equiv of $KN(SiMe_3)_2$ furnished a yellow solid product (6) in moderate yield (~64%). The appearance of the ¹³C NMR signal at δ 110.0 (6a) or 110.2 ppm (6b) is accompanied by the disappearance of the ¹H NMR signal at 5.51 or 5.66 ppm for the central carbon atom of 4, signaling the formation of a free carbodicarbene. Unequivocal confirmation of the structure of 6a as a carbodicarbene is provided by X-ray analysis on a single crystal grown from a saturated THF solution at -20 °C, displaying a C(1)=C(2)=C(1') moiety that is considerably



Figure 1. Molecular structures of 4a (top left), 4b (top right), and 4c (bottom) salts with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms, with the exception of the CH₂ group (4a, C(12)H₂; 4b, C(15)H₂; 4c, C(1)H₂), and solvent molecules for 4c are omitted for clarity. The representation of two symmetry unique ion pairs in 4b is depicted. Selected bond lengths (Å) and angles (deg) are as follows. 4a: C(2)–C(12) = 1.496(2), C(12)–C(14) = 1.497(2), C(2)–N(1) = 1.3346(19), C(2)–N(2) = 1.3445(19); C(2)–C(12)–C(14) = 117.97(12), C(12)–C(2)–N(1) = 124.83(13), C(12)–C(2)–N(2) = 124.89(13), N(1)–C(2)–N(2) = 109.87(13). 4b: C(15)–C(7) = 1.494(4), C(7)–N(1) = 1.342(3), C(7)–N(2) = 1.336(4); C(7)–C(15)–C(22) = 115.1(2), C(15)–C(7)–N(1) = 124.8(2), C(15)–C(7)–N(2) = 125.5(2), N(1)–C(7)–N(2) = 109.6(2). 4c: C(2)–C(1) = 1.489(3), C(2)–N(1) = 1.344(3), C(2)–N(2) = 1.337(3); C(2)–C(1)–C(13) = 115.89(18), C(1)–C(2)–N(1) = 126.0(2), C(1)–C(2)–N(2) = 124.14(19), N(1)–C(2)–N(2) = 109.88(19).

distorted from linearity with a bond angle of 136.6(5)° (Figure 3). The two N(1)–C(1)–C(2) planes in **6a** are twisted by 71° from the typical perpendicular plane for a normal allene and display slightly longer C1–C2 bond lengths of 1.335(5) Å in comparison to a normal allene (1.31 Å).⁹ Similar to the case for Bertrand's reported carbodicarbene A,⁴ the structural parameters of **6a** underline the severely disrupted π conjugation in the allenic moiety and thus reflect the bonding situation as an NHC→C donor–acceptor interaction. Sterically demanding isopropyl pendant arms seem to have no dramatic impact on the overall structure of **6a** as compared to the corresponding methyl counterpart **A**. Notably, isopropyl side arms located around termini carbon are too far away to exert any substantial steric influence on the allenic moiety.

Having isolated and characterized the free carbodicarbene 6, our attention shifted toward an examination of its intrinsic reactivity toward electrophiles. When 6a was reacted with iodomethane for 22 h, it resulted in a yellow precipitate, 7 (Scheme 2). The formation of 7 is evidenced by a new characteristic methyl signal at δ 2.41 ppm in the ¹H NMR spectrum, confirmed by the X-ray structure (Figure 4), resulting from the nucleophilic attack of the carbodicarbene at methyl iodide.

Recent efforts have been invested toward generating unconventional carbogenic species such as the ylidic adduct,

specifically 2-methyleneimidazolines $(C)^{5,10-12}$ and allenylidene (\mathbf{D}) ,¹³ which are naturally zwitterionic (Scheme 2), and have comfortably gained familiarity in coordination chemistry. Inspired by these works, we wondered whether further deprotonation of 7 could possibly afford the new zwitterion species E, which may be stabilized through the spread of π conjugation within the allenylidene moiety. Deprotonation of 7 with KHMDS afforded the yellow solid 8 in 75% yield with the appearance of two new singlet peaks in the ¹H NMR assigned to a methyl group (1.62 and 2.48 ppm) and an AB quartet peak (3.29 ppm) for methylene. To further verify the atomic connectivity, we performed a single-crystal X-ray analysis of 8, which crystallized in the monoclinic C2/c space group (Figure 5). Unexpectedly, five-membered spiro-fused heterocyclic 8 was afforded through an intramolecular cyclization via C-C bond formation, explained by deprotonation at the more acidic methyl of nitrogen, rather than the $C_{\boldsymbol{\gamma}}$ residing at the carbon (Scheme 2).

After the chemical reactivity of carbodicarbene was explored, a set of experiments was undertaken to investigate the coordination ability of **6** toward transition metals. Carbodicarbene **6a** was readily introduced to {[RhCl(CO)₂]₂} in THF to afford **9a** (Scheme 3), as shown by a large shift to lower ν_{CO} stretching frequencies in the IR spectrum (2052 and 1976 cm⁻¹). These values are in line with those for Bertrand's



Figure 2. Molecular structure of 5a with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms, with the exception of H12A, and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(2)-C(12) = 1.393(3), C(2)-N(1) = 1.371(2), C(2)-N(2) = 1.370(2), C(12)-C(14) = 1.396(3), C(14)-N(3) = 1.372(2), C(14)-N(4) = 1.368(2); C(2)-C(12)-C(14) = 126.41(17), C(12)-C(2)-N(1) = 127.43(18), C(12)-C(2)-N(2) = 124.89(17), N(1)-C(2)-N(2) = 107.51(16), C(12)-C(14)-N(3) = 126.67(18), C(12)-C(14)-N(4) = 125.56(16), N(3)-C(14)-N(4) = 107.64(16).



Figure 3. Molecular structure of carbodicarbene 6a with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)-C(2) = 1.335(5), C(1)-N(1) = 1.397(4), C(1)-N(2) = 1.404(6; C(1)-C(2)-C(1') = 136.6(5), C(2)-C(1)-N(1) = 129.2(4), C(2)-C(1)-N(2) = 126.2(3), N(1)-C(1)-N(2) = 104.3(4).

analogous bent allene complex, 4 signifying increased σ donation in comparison to a five-membered NHC. Similarly, incorporating a cyclohexyl side arm in 9b did not severely perturb its ability to donate electron density, as the CO stretching in the IR spectrum of 9b occurs at 2051 and 1975 cm⁻¹. On the basis of linear regression using the Tonner and Frenking method for divalent carbon(0) compounds,¹⁴ the average CO stretching values of 9a and 9b could be translated into Tolman electronic parameters (TEP)¹⁵ of 2022 and 2021 cm⁻¹, respectively. These TEP values obviously indicated a very strong donor ligand. An X-ray determination of the structures of 9a and 9b (Figures 6 and 7) demonstrates that the center carbon in the allene coordinates to rhodium in an η^1 manner with a squareplanar geometry at the Rh center. In comparison to Bertrand's analogous rhodium complex consisting of four methyl pendant arms (2.089(7) Å),4 the Rh-carbodicarbene distance of 9a (2.109(2) Å) is only slightly elongated by only 0.02 Å. The slightly increased Rh-C bond distance may be attributed to no steric perturbation witnessed in the carbodicarbene skeleton, as

mentioned in an earlier section. Likewise, replacement with a more sterically demanding cyclohexyl group in **9b** has pushed incrementally the upper limit of the Rh–carbodicarbene bond distance to 2.123(2) Å (Figure 6). To gain additional information regarding the steric conditions of the carbodicarbene-ligated metal centers, the buried volume ($%V_{bur}$) of the ligand was calculated for both complexes of **9** using the SambVca software,¹⁶ given in Table 1. It is clear that the higher steric demand of ~38.6%V_{bur} for cyclohexyl has a marginal effect in lengthening the metal–carbene bond distance in comparison to the corresponding isopropyl (36.4%V_{bur}), considering that the pendant arms are too far removed from the center allenic carbon atom.

To determine if the steric effects outlined above are general for other late transition metals, the palladium complex was also considered for comparison purposes. The direct reaction of carbodicarbene 6a with [Pd(allyl)Cl]₂ resulted in the desired complex 10, consisting of a mixture of exo and endo configurational isomers (5:4 ratio) on the basis of NMR analysis. Unfortunately, the NMR data did not allow us to determine the configuration of the major isomer. Single crystals of X-ray diffraction quality were grown by slowly cooling a concentrated dichloromethane solution of 10 to afford the endo isomer, which is defined by the open face of the allyl ligand and the carbodicarbene ligand being in the same direction (Figure 8). The chloride ligand is cis to the carbodicarbene, and the allyl moiety is coordinated to the metal center in an η^3 fashion. A strong trans effect imposed by the better donor carbodicarbene has elongated the palladium-Callyl bonds, particularly the terminal carbon trans to the carbodicarbene (2.207 Å). It is interesting to note that the Pdcarbodicarbene bond distance of 10 (2.101(4) Å) is the longest in comparison to those in most typical N-aryl-substituted unsaturated imidazole NHC palladium allyl complexes (~2.04 Å). $^{17-19}$ The long Pd–carbodicarbene bond distance can perhaps be attributed to the effective steric pocket invoked by the ligand 6a.

CONCLUSIONS

In summary, we have successfully devised a synthetic roadmap for the acyclic bent allene or carbodicarbene and expanded the collection of compounds beyond the methyl pendant arms. We have shown that the free carbodicarbene structural parameters are less sensitive to the steric hindrance imposed by its pendant arms. Similarly, metal-carbodicarbene elongation and steric measurement in percent buried volume for rhodium and palladium complexes revealed the noninnocent role of the pendant arm near the termini carbon of this ligand topology, which may serve as a well-defined protective steric pocket, emulating the role of the protein scaffold in enzymatic catalysis. Our sincere hope is that our corresponding synthetic efforts toward Bertrand's acyclic bent allenic carbene will stimulate and broaden the reactivity scope and facilitate the possible application of this unique carbodicarbene beyond a laboratory curiosity.

EXPERIMENTAL SECTION

General Considerations. All air-sensitive manipulations were performed under an atmosphere of nitrogen using Schlenk techniques and/or a glovebox. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 400 (400 MHz ¹H, 100 MHz ¹³C) spectrometer using the residual proton of the deuterated solvent for reference (CDCl₃, ¹H NMR 7.24 ppm, ¹³C NMR 77.0 ppm; CD₃CN, ¹H NMR 1.94 ppm,

Scheme 2. Reactivity of 6a and Plausible Mechanism for Formation of 8



Figure 4. Molecular structure of 7 with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)-C(2) = 1.521(2), C(1)-C(3) = 1.404(2), C(1)-C(14) = 1.415(2), C(3)-N(1) = 1.3749(19), C(3)-N(2) = 1.3752(19), C(14)-N(3) = 1.3694(19), C(14)-N(4) = 1.3678(19); C(3)-C(1)-C(14) = 119.92(13), C(3)-C(1)-C(2) = 120.26(13), C(14)-C(1)-C(2) = 119.40(13), C(1)-C(3)-N(1) = 125.89(13), C(1)-C(3)-N(2) = 126.09(13), N(1)-C(3)-N(2) = 107.78(13), C(1)-C(14)-N(4) = 125.52(14), N(3)-C(14)-N(4) = 107.62(13).

¹³C NMR 118.7 ppm; C₆D₆, ¹H NMR 7.16 ppm, ¹³C NMR 128.4 ppm; CD₂Cl₂, ¹H NMR 5.32 ppm, ¹³C NMR 54.0 ppm). Chemical shifts are reported in ppm (δ); coupling constants, *J*, are reported in Hz. High-resolution mass spectra were obtained with a JEOL JMS-700 (EI or FAB+) spectrometer. Analytical TLC was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV light. Column (flash) chromatography was performed using 40–63 μm silica gel. All reagents were purchased from Acros, Aldrich, and Alfa Aesar without further purification before use. Solvents for chromatography were reagent grade. Benzene, toluene, diethyl ether, and THF were dried over sodium with benzophenone–ketyl intermediate as indicator.

Preparation of 5a from Reaction of 4a with Ag₂O. In a 20 mL vial was placed Ag₂O (0.23 g, 1.0 mmol), **4a** (0.33 g, 0.5 mmol), and molecular sieves 4A (8–12 mesh) in anhydrous CH₂Cl₂ (5 mL). The reaction mixture was stirred at ambient temperature for 6 h. The reaction mixture was subsequently filtered and concentrated in vacuo to give a white solid quantitatively. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.58–7.54 (m, 2H), 7.44–7.40 (m, 2H), 7.39–7.34 (m, 4H), 4.85–4.74 (m, 2H), 4.57 (s, 1H), 3.32 (s, 6H), 1.69 (dd, *J* = 9.4, 7.0, 12H). ¹³C NMR (100 MHz, CD₂Cl₂): δ 153.0, 134.2, 131.1, 124.6, 124.3,







Figure 6. Molecular structure of rhodium complex 9a with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)-C(2) = 1.385(3), C(1)-C(13) = 1.411(3), C(1)-Rh(1) = 2.109(2), C(2)-N(1) = 1.392(3), C(2)-N(2) = 1.390(3), C(13)-N(3) = 1.366(3), C(13)-N(4) = 1.373(3); C(2)-C(1)-C(13) = 117.4(2), C(2)-C(1)-Rh(1) = 127.50(16), C(13)-C(1)-Rh(1) = 114.43(16), C(1)-C(2)-N(1) = 127.0(2), C(1)-C(2)-N(2) = 105.35(18), C(1)-C(13)-N(3) = 125.5(2), C(1)-C(13)-N(4) = 127.6(2), N(3)-C(13)-N(4) = 106.83(18).



Figure 7. Molecular structure of rhodium complex **9b** with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)-C(8) = 1.416(3), C(1)-C(22) = 1.386(3), C(1)-Rh(1) = 2.123(2), C(8)-N(1) = 1.368(3), C(8)-N(2) = 1.367(3), C(22)-N(3) = 1.391(3), C(22)-N(4) = 1.400(3); C(22)-C(1)-C(8) = 116.8(2), C(22)-C(1)-Rh(1) = 128.60(18), C(8)-C(1)-Rh(1) = 113.18(17), C(1)-C(22)-N(3) = 128.9(2), C(1)-C(22)-N(4) = 125.8(2), N(3)-C(22)-N(4) = 105.2(2), C(1)-C(8)-N(1) = 127.9(2), C(1)-C(8)-N(2) = 125.2(2), N(1)-C(8)-N(2) = 106.8(2).

 Table 1. Steric Measurement of Carbodicarbene Ligands on

 Rh Complexes 9 with Selected Bond Distances

entry	carbodicarbene	$%V_{\rm bur}^{\ a}$	Rh–carbene (Å)
1	6a	36.4	2.109(2)
2	6b	38.6	2.123(2)

^{*a*}Calculated using SamBVca software with a sphere radius of 3.5 Å, a metal–NHC distance of 2.10 Å, and a mesh spacing of 0.05. Hydrogen was omitted. ^{15b}

112.5, 111.2, 50.8, 49.6, 33.6, 20.7, 20.5. HR-MS (FAB): calcd for $[C_{24}H_{29}O_3N_4F_3S]^+$ 510.1912, found 510.1909.



Figure 8. Molecular structure of palladium complex **10** with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(4)-C(5) = 1.404(5), C(1)-Pd(1) = 2.207(4), C(2)-Pd(1) = 2.122(5), C(3)-Pd(1) = 2.098(4), C(4)-Pd(1) = 2.101(4), C(5)-N(1) = 1.376(5), C(5)-N(2) = 1.374(5), C(4)-C(16) = 1.377(5), C(16)-N(3) = 1.395(5), C(16)-N(4) = 1.397(5); C(5)-C(4)-C(16) = 119.7(4), C(5)-C(4)-Pd(1) = 128.4(3), C(4)-C(5)-N(1) = 126.3(3), C(4)-C(5)-N(2) = 126.7(3), N(1)-C(5)-N(2) = 126.6(4), N(3)-C(16)-N(4) = 105.8(3).

Preparation of Bis(1-isopropyl-3-methylbenzimidazol-2ylidene)methane (6a).⁴ In a 100 mL, one-necked, round-bottomed flask was placed 4a (6.60 g, 10.0 mmol) in anhydrous THF (10 mL). A solution of KHMDS (4.4 g, 22.0 mmol) in THF (40 mL) was added dropwise to the reaction flask. The reaction mixture was stirred at ambient temperature for 3 h and then filtered through Celite. The filtrate was concentrated in vacuo, and the residue was washed with diethyl ether and then dried in vacuo to afford 2.31 g of 6a (64%) as a yellow solid. ¹H NMR (400 MHz, C_6D_6): δ 6.93–6.87 (m, 4H), 6.78– 6.74 (m, 2H), 6.49–6.46 (m, 2H), 4.66–4.56 (m, 2H), 2.78 (s, 6H), 1.31 (dd, *J* = 7.0, 2.9, 12H). ¹³C NMR (100 MHz, C_6D_6): δ 142.3, 136.4, 133.8, 119.7, 119.5, 110.0, 106.9, 105.2, 46.7, 29.6, 19.9, 19.8. HR-MS (FAB): calcd for $[C_{23}H_{29}N_4 + H]^+$ 361.2392, found 361.2392.

Preparation of Bis(1-cyclohexyl-3-methylbenzimidazol-2-ylidene)methane (6b).⁴ In a 100 mL one-necked round-bottomed flask was placed **4b** (3.4 g, 4.59 mmol) in anhydrous benzene (10 mL). A solution of KHMDS (2.01 g, 10.1 mmol) in benzene (40 mL) was added dropwise to the reaction flask. The reaction mixture was stirred at ambient temperature for 3 h and then passed through Celite. The filtrate was concentrated in vacuo, and the residue was washed with diethyl ether and then dried in vacuo to afford 1.21 g of **6b** (60%) as a yellow solid. ¹H NMR (400 MHz, C_6D_6): δ 6.92–6.86 (m, 6H), 6.47–6.45 (m, 2H), 4.35 (tt, *J* = 12.0, 4.0, 2H), 2.78 (s, 6H), 2.22–2.05 (m, 4H), 1.88–1.81 (m, 4H), 1.68–1.64 (m, 4H), 1.48–1.44 (m, 2H), 1.24–0.99 (m, 6H). ¹³C NMR (100 MHz, C_6D_6): δ 142.8, 136.4, 134.3, 119.7, 119.4, 110.2, 107.2, 105.2, 55.2, 30.2, 30.1, 29.7, 26.91, 26.89, 26.3. HR-MS (FAB): calcd for $[C_{29}H_{36}N_4 + H]^+$ 441.3018, found 441.3010.

Preparation of 7 via Reaction of 6a with Mel. In a 100 mL one-necked, round-bottomed flask was placed **6a** (0.36 g, 1.0 mmol) in anhydrous toluene (10 mL). Iodomethane (0.21 g, 1.5 mmol) was added dropwise to the reaction flask. The reaction mixture was stirred at ambient temperature for 22 h. The resulting mixture was concentrated in vacuo to afford 0.42 g of 7 (84%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.45–7.40 (m, 4H), 7.30–7.24 (m, 4H), 4.72–4.62 (m, 2H), 3.32 (s, 6H), 2.41 (s, 3H), 1.68 (d, *J* = 7.0, 6H), 1.54 (d, *J* = 6.9, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 155.8, 134.0, 130.3, 124.3, 123.9, 112.7, 111.1, 51.8, 51.5, 34.1, 21.1, 20.4, 18.2. HR-MS (EI): calcd for $[C_{24}H_{31}N_4 + H]^+$ 375.2549, found 375.2548.

Preparation of [RhCl(CO)₂(6a)] (9a).⁴ In a 20 mL vial was placed $[Rh(CO)_2CI]_2$ (0.049 g, 0.125 mmol) in anhydrous benzene (5 mL).

A 3.8 mL solution of **6a** (0.09 g, 0.25 mmol) in benzene was added dropwise to the vial. The reaction mixture was stirred at ambient temperature for 5 h. The resulting precipitate was subsequently filtered and concentrated under vacuum to give 0.074 g of **9a** (53%) as an orange solid. ¹H NMR (400 MHz, CDCl₃): δ 7.36–7.31 (m, 2H), 7.14–6.96 (m, 6H), 6.35–6.28 (m, 1H), 6.06–5.99 (m, 1H), 3.27 (s, 3H), 3.14 (s, 3H), 1.72 (t, *J* = 6.4, 6H), 1.55 (d, *J* = 7.0, 3H), 1.48 (d, *J* = 6.8, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 185.7 (d, ¹*J*_{CRh} = 56.8, RhCO), 185.4 (d, ¹*J*_{CRh} = 78.1, RhCO), 159.9, 158.5, 134.3, 133.8, 131.7, 131.2, 122.3, 122.0, 121.9, 121.7, 111.3, 111.1, 108.7, 107.9, 63.7 (d, ¹*J*_{CRh} = 26.5, CRh), 50.9, 50.0, 32.8, 32.5, 21.1, 20.5, 19.8, 19.2. HR-MS (FAB): calcd for [C₂₅H₂₈ClN₄O₂Rh + H]⁺ 555.1034. found 555.1036; IR (CH₂Cl₂): ν 2051.6, 1976.0 cm⁻¹.

Preparation of [RhCl(CO)₂(6b)] (9b).⁴ In a 20 mL vial was placed $[Rh(CO)_2Cl]_2$ (0.095g, 0.25 mmol) in anhydrous benzene (3 mL). A solution of 6b (0.22 g, 0.5 mmol) in benzene was added dropwise and was stirred at ambient temperature for 2 h. The reaction mixture was passed through Celite, and the filtrate solution was concentrated under vacuum. The crude product was washed with cold ether and then concentrated under vacuum to give 0.267 g of 9b (84%) as an orange solid. ¹H NMR (400 MHz, C_6D_6): δ 6.98–6.89 (m, 4H), 6.69 (t, J = 12.2, 1H), 6.51(d, J = 7.6 1H), 6.40 (d, J = 7.4, 1H), 6.15 (t, J = 12.4, 1H), 2.94-2.91 (m, 1H), 2.68 (s, 3H), 2.58-2.55 (m, 1H), 2.31 (s, 3H), 2.13-2.06 (m, 2H), 2.05-1.87 (m, 4H), 1.88-1.65 (m, 8H), 1.64–1.55 (m, 2H), 1.14–1.00 (m, 2H). ¹³C NMR (100 MHz, C₆D₆): δ 187.8, 187.3, 187.2, 186.5, 160.8, 158.4, 134.9, 134.1, 133.1, 132.2, 122.8, 122.31, 122.26, 121.8, 112.1, 111.7, 109.3, 108.1, 64.7, 64.4, 59.3, 58.1, 32.5, 32.1, 30.9, 30.3, 30.1, 26.9, 26.6, 26.4, 26.3, 26.2. IR (CH₂Cl₂): ν 2051.0, 1975.0 cm⁻¹

Preparation of [PdCl(C₃H₅)(6a)] (10). In a 20 mL vial was placed $[PdCl(C_3H_5)]_2$ (0.09 g, 0.25 mmol) in anhydrous THF (5 mL). A solution of 6a (0.18 g, 0.50 mmol) in THF (7.5 mL) was added dropwise, and the reaction mixture was stirred at ambient temperature for 3 h. The resulting precipitate was subsequently filtered and concentrated in vacuo to give 0.160 g of 10 (51%) as an orange solid. ¹H NMR (400 MHz, CDCl₃): major product, δ 7.27–6.85 (m, 8H), 6.28-6.22 (m, 1H), 5.99-5.93 (m, 1H), 5.25-5.12 (m, 1H), 4.09-4.06 (m, 1H), 3.36-3.03 (m, 8H), 2.16 (d, J = 11.5, 1H), 1.75-1.45 (m, 12H); minor product, δ 7.27–6.85 (m, 8H), 6.55–6.49 (m, 1H), 5.64-5.58 (m, 1H), 5.25-5.12 (m, 1H), 4.09-4.06 (m, 1H), 3.36-3.03 (m, 8H), 2.24 (d, J = 11.6, 1H), 1.75–1.45 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 157.9, 157.1, 156.5, 155.5, 134.4, 134.1, 132.0, 131.3, 121.8, 121.5, 121.2, 120.9, 110.9, 110.4, 110.3, 110.1, 108.2, 107.9, 107.4, 107.0, 69.8, 69.7, 62.6, 62.2, 49.2, 48.8, 48.5, 47.4, 47.0, 32.4, 32.1, 20.8, 20.4, 20.2, 19.6, 19.2.

X-ray Crystallography Studies. In the crystallographic studies for 4a-c, 5a, 6a, 7, 9a,b, and 10, crystals were mounted using viscous oil onto glass fibers and cooled to the data collection temperatures. Data were collected on a Bruker-AXS APEX CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Unit cell parameters were obtained from 60 data frames, $0.3^{\circ} \omega$, from three different sections of the Ewald sphere. The systematic absences are uniquely consistent for the reported spacegroups for 4a, 5a, 7, 9a,b, and 10. No symmetry higher than triclinic was observed for 4b,c, and solution in the centrosymmetric option yielded chemically reasonable and computationally stable results. The unit-cell parameters and systematic absences are consistent for Aba2 (space group No. 39) and Abmm [Cmmb] (Sspace group No. 67) for 6a. The presence of a molecular 2-fold and Z = 4 was consistent with Aba2 for 6a; however, the absence of heavy atoms did not allow for significant Flack parameter refinements. The data sets were treated with SADABS absorption corrections on the basis of redundant multiscan data.²⁰ The structures were solved using direct methods and refined with fullmatrix least-squares procedures on F^2 . Two symmetry unique but chemically equivalent molecules were found in the asymmetric unit for 4b. Solvent molecules were located cocrystallized in 4c (CH₃CN), 5a (CHCl₃), 9a (THF), 9b (toluene), and 10 (CH₂Cl₂). The molecule is located at a 2-fold in 6a with the isopropyl group disordered by pyramidal inversion at the adjacent amine N atom such that the tertiary C atom is in two positions with a refined site occupancy ratio

of 54/46. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion coefficients are contained in various versions of the SHELXTL program library (G. M. Sheldrick) or the Olex2 program.²¹

ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving additional detailed experimental procedures, characterization data for new compounds, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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