Transition-Metal-Catalyzed Polymerization of Heteroatom-Functionalized Cyclohexadienes: Stereoregular Precursors to Poly(*p*-phenylene)

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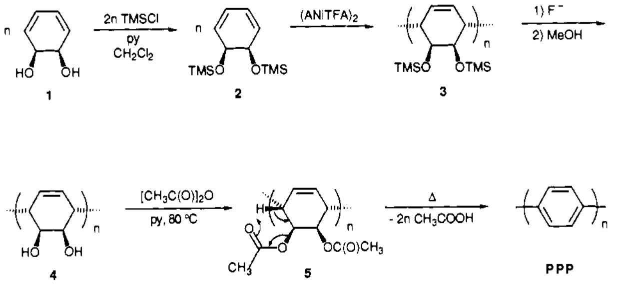
Received December 31, 1991

Poly(*p*-phenylene) (PPP) is an insoluble rigid-rod polymer that possesses remarkable thermal stability, chemical resistance, and electrical conductivity when doped.[1] The structural properties that make PPP such an attractive engineering material also make it difficult to synthesize and process. Direct synthetic approaches have given either ill-defined material with a mixture of para, meta, and ortho linkages and crosslinks[2–4] or insoluble oligomers.[5] Precursor strategies to PPP have been devised in which the synthetic and processing difficulties of the direct methods have been overcome through the use of a soluble intermediate polymer.[6–9] The most successful of the precursor strategies was developed at ICI by Ballard et al.[7] This process involves the radical polymerization of the bis(acetyl) or bis(methoxycarbonyl) derivatives of *cis*-5,6-dihydroxy-1,3-cyclohexadiene (**1**), a microbial oxidation product of benzene. The resulting polymers are subsequently aromatized to yield PPP by thermally induced acid elimination. This process, however, yields only phenylene oligomers due to fracturing of the precursors during pyrolysis.[10] Fracturing is believed to arise from the 90% 1,4-linkages, 10% 1,2-linkages, and random stereochemistry along the precursor backbones which result from the nonstereospecific nature of the radical polymerization. A route to 100% 1,4-linked PPP precursors with the correct stereochemistry for facile cis-pyrolytic elimination of the pendant groups has been developed which combines the efficiency and processability of the ICI process with the regio- and stereochemical control possible through transition-metal catalysts (Scheme I).

cis-5,6-Bis(trimethylsiloxy)-1,3-cyclohexadiene (**2**) is polymerized by bis[(allyl)trifluoroacetatonickel(II)] [$(ANiTFA)_2$][11] to give exclusively 1,4-poly(*cis*-5,6-bis(trimethylsiloxy)-1,3-cyclohexadiene) (**3**) as a white powder which is soluble in nonpolar solvents. The use of acyl derivatives of **1** resulted only in aromatization of the monomers and deactivation of the catalyst. We believe that **2** is compatible with the catalyst for two reasons: the bulky trimethylsilyl (TMS) groups sterically prevent the oxygen atoms from coordinating to the catalyst, and facile elimination/aromatization is unlikely to occur because trimethylsilanol is a poor leaving group. To our knowledge, this scheme provides the first example of the homopolymerization of a heteroatom-functionalized 1,3-diene by a transition-metal catalyst.[12]

Scheme I. Synthesis of PPP from Stereoregular Precursors Made by Transition-Metal-Catalyzed Polymerization



Polymerization of **2** with $(ANiTFA)_2$ proceeds in aromatic solvents (e.g., chlorobenzene) or with neat monomer at a temperature of 50 °C or higher. With a monomer:catalyst ratio of 80:1 and a monomer concentration of 1.5 M in chlorobenzene, polymer **3** is obtained with a number average molecular weight (M_n) of 38 000 (average degree of polymerization (DP) of 150) and a polydispersity index (PDI) of 1.64, as determined by Viscotek GPC.[13] The yield of polymer increases asymptotically (up to 93%) with increasing monomer concentration, but below a critical monomer concentration (0.14 M), polymerization does not proceed. A plot of molecular weight vs % conversion of **2** exhibits a nonlinear relationship and suggests non-"living" kinetics. However, blocking experiments, performed by adding fresh aliquots of **2** to the propagating system, resulted in predictable molecular weight increases without broadening the PDI.

Polymerization of **2** by $(ANiTFA)_2$ proceeds stereospecifically to give polymer **3** with the stereochemistry depicted in Scheme I. It appears that the cis relationship of the bulky TMS groups of **2** permit the catalyst to coordinate only to the opposite face of the diene. Subsequent syn insertion of **2** into the propagating nickel–allyl complex affords the depicted stereostructure.[14] The 1,4-stereoregular structure of **3** was confirmed by a combination of (1) ^1H NMR spectroscopy, (2) molecular modeling, (3) powder X-ray diffraction (PXRD), and (4) scanning tunneling microscopy (STM). Analysis of **3** by ^1H NMR revealed the absence of a resonance at 1.8–2.1 ppm,[15] characteristic of 1,2-linked units in model compounds;[8] it also revealed that all of the protons on the cyclohexenyl ring were nonequivalent on the NMR time scale. Computer modeling of **3** suggested that, in the lowest energy structure for the 1,4-stereostructure depicted, each cyclohexenyl ring should adopt a rigid pseudochair conformation in which all of the ring protons would be chemically nonequivalent, as observed.[16] The polymer chain itself should also adopt an ordered

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(1) Elsenbaumer, R. L.; Schacklett, L. W. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel-Dekker: New York, 1986; Vol. 1, Chapter 7.

(2) Soubiran, P.; Aeiyach, S.; Aaron, J. J.; Lacaze, P. C. *J. Electroanal. Chem.* **1988**, *251*, 89 and references therein.

(3) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357 and references therein.

(4) Tour, J. M.; Stephens, E. B. *J. Am. Chem. Soc.* **1991**, *113*, 2309.

(5) Yamamoto, T.; Hayashi, T.; Yamamoto, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2091.

(6) Frey, D. A.; Hasagewa, M.; Marvel, C. S. *J. Polym. Sci., Part A* **1963**, *1*, 2507.

(7) (a) Ballard, D. G. H.; Courtis, A.; Shirley, I. M.; Taylor, S. C. *J. Chem. Soc., Chem. Commun.* **1983**, 954. (b) Ballard, D. G. H.; Courtis, A.; Shirley, I. M.; Taylor, S. C. *Macromolecules* **1988**, *21*, 294.

(8) McKean, D. R.; Stille, J. K. *Macromolecules* **1987**, *20*, 1787.

(9) A recent alternative approach to overcoming the synthetic and processing difficulties associated with PPP has been to synthesize soluble, substituted poly(phenylene) compounds by coupling substituted aromatics: (a) Rehahn, M.; Schlüter, A.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30* (6), 1054. (b) Rehahn, M.; Schlüter, A.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30* (6), 1060. (c) Rehahn, M.; Schlüter, A.; Wegner, G. *Makromol. Chem.* **1990**, *191* (9), 1991. (d) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411.

(10) (a) Ballard, D. G. H.; Holmes, P. A.; Nevin, A.; Twose, D. L.; Shirley, I. M. Polyaromatics. Eur. Pat. Appl. 0 243 065, April 13, 1987. (b) Internal report from ICI Chemicals and Polymers Ltd., Runcorn, U.K., based on neutron scattering analysis of PPP.

(11) $(ANiTFA)_2$ is generally used for the "living" polymerization of 1,3-butadiene, demonstrating >97% 1,4-regioselectivity. See: Hadjiandreou, P.; Julêmont, M.; Teyssiê, P. *Macromolecules* **1984**, *17*, 2455.

(12) The only examples of successful polymerizations of heteroatom-functionalized 1,3-dienes by transition-metal complexes have been copolymerizations with 1,3-butadiene. Homopolymerizations were not possible: (a) Bevza, T. I.; Pokatilo, N. A.; Teterina, M. P.; Dolgoplosk, B. A. *Vysokomol. Soedin.* **1968**, *A10*, 207. (b) Borge-Visse, F.; Dawans, F. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2481.

(13) Viscotek GPC analysis of 3 in THF was performed by the Analytical and Physical Science Group at ICI Chemicals and Polymers Ltd., Runcorn, U. K.

(14) Syn-coordinative insertion is inferred as the propagation step for $(ANiTFA)_2$ from the same mechanism exhibited in similar allyl–nickel diene polymerization catalysts: Porri, L.; Aglietto, M. *Makromol. Chem.* **1976**, *177*, 1465.

(15) A signal at 1.9 ppm was present in the 500-MHz ^1H NMR spectrum of radically polymerized oligomers of **2**. The analysis was performed at ICI, Runcorn, U. K.

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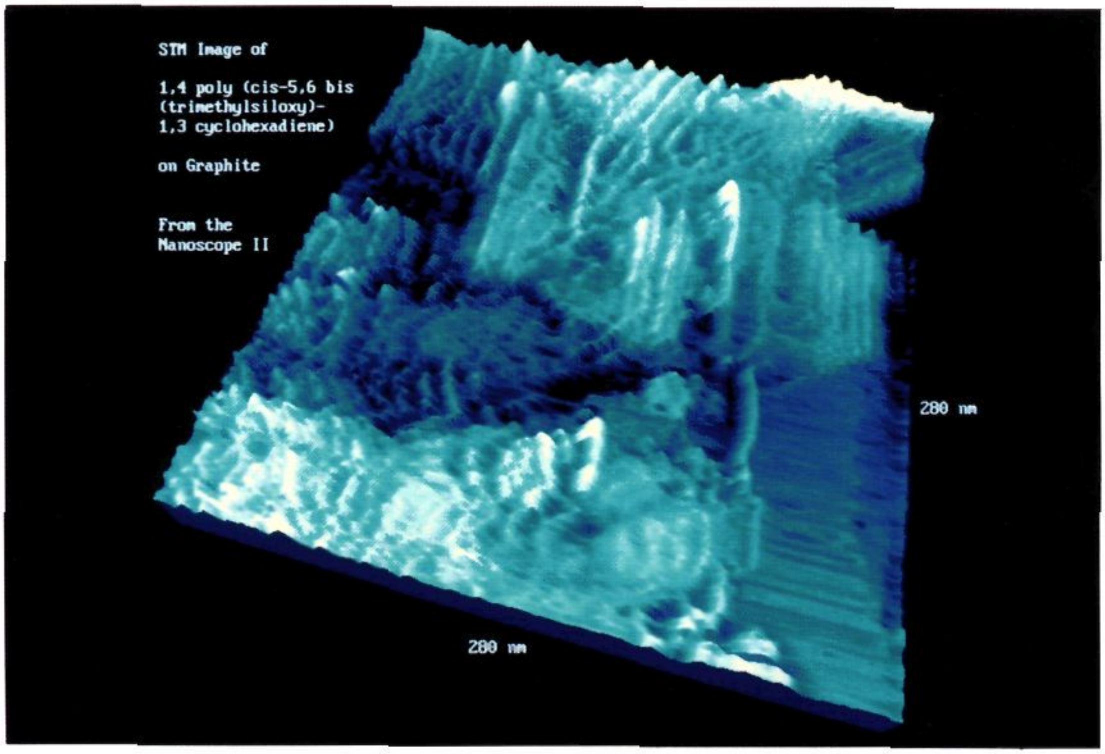

Figure 1. STM image of chains of polymer **3** (image dimensions: 280 × 280 nm). STM imaging of **3** was performed on highly oriented pyrolytic graphite (HOPG) using a Nanoscope II Scanning Tunneling microscope. Sample preparation involved dropping 10 μL of a 5 mg/L solution of **3** in HPLC grade hexane onto a freshly cleaved HOPG surface ($\sim$0.5 cm^2) and allowing the solvent to evaporate.

rodlike structure, which was confirmed by the presence of nematic order in the powder X-ray diffractogram of **3**—a property associated with rodlike molecules.[17] Further support was obtained from STM imaging of **3**, which revealed rodlike polymer chains (Figure 1). The average chain lengths inferred from Viscotek GPC analysis agree well with the qualitative data obtained by STM imaging.[18]

Direct pyrolysis of polymer **3**, however, does not yield PPP probably because the TMS ether moieties are poor leaving groups.[19] Quantitative conversion of the TMS ether groups to more facile leaving groups such as esters was accomplished by deprotection of **3** to the corresponding hydroxy polymer **4**, followed by acylation to give polymer **5**. This general procedure gives complete conversion of the TMS ether groups to ester groups without affecting the stereochemistry of the polymer backbone (>93% overall recovered yield over two steps).

Comparison of the ^{1}H NMR spectra of the acetoxy polymer **5** with its radically polymerized counterpart[20] suggests that **5** is stereoregular. Polymer **5** has proton resonances with chemical shifts identical to its radically polymerized analogue, but the individual resonances are much narrower and more symmetric. Viscotek GPC analysis of **5** reveals that it has an M_n of approximately 27 000 with a PDI of 1.5–2.0; consequently, the observed differences in the ^{1}H NMR spectra cannot be attributed to low molecular weight material. The molecular weight of **5** has been confirmed by low angle laser light scattering (LALLS) analysis.[21] Both PXRD and computer modeling suggest that polymer **5** is an amorphous, random coil.[16,17]

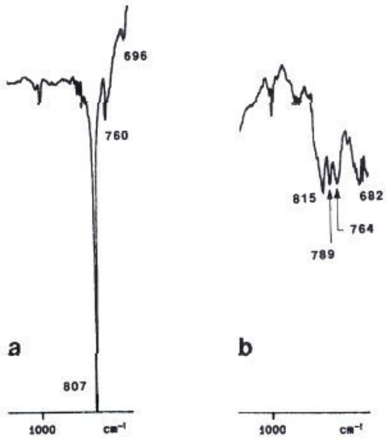

Figure 2. IR spectra of PPP made from thin films of the precursors on NaCl crystals baked at 310–340 °C under argon: (a) from polymer **5**; (b) from radically polymerized acetoxy polymer. Assignments are based on analysis by IR of biphenyl, *p*-terphenyl, *p*-quaterphenyl, *p*-sexiphenyl, and *m*-terphenyl. Also see: Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; John Wiley and Sons: New York, 1972; p 189.

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(16) Computer modeling was performed on a SiliconGraphics Iris 4D/220GTX computer using Biograf Version 2.20 to build the structures and MM2 force field minimization (1000 iterations) to equilibrate them.

(17) Powder X-ray diffraction was performed on a Scintag/USA PAD-V diffractometer using Cu Kα radiation. A more detailed description of the statistical treatment of the data is available upon request.

(18) Chain lengths of 400–700 Å were observed in the STM images of a sample of **3** made using a monomer:catalyst ratio of 80:1 and a monomer concentration of 1.5 M. M_n values of approximately 38 000 (DP $\approx$ 150) were obtained from Viscotek GPC for samples produced under the same reaction conditions, corresponding to a calculated chain length of approximately 540 Å.

(19) IR analysis of the pyrolysis product of **3** from a thermogravimetric analysis run (50 to 400 °C at 10 °C/min) reveals absorbances similar to that of the starting material, but no band at approximately 810 cm^{-1} which is characteristic of 1,4-linked phenylene units.

(20) Radically polymerized acetoxy polymer was generously provided by ICI, Runcorn, U. K.

(21) LALLS analysis was performed on THF solutions of **5** by the Analytical and Physical Science Group at ICI Chemicals and Polymers Ltd., Runcorn, U.K. (cf. weight average molecular weights (M_w): (Viscotek GPC, M_w = 41 700; LALLS, M_w = 49 400).

In contrast to polymer **3**, polymer **5** could be pyrolyzed to give high-quality PPP. Thin films of **5** on NaCl crystals were aromatized by heating under argon at 310–340 °C. The IR spectra of the resulting films (Figure 2a) are dominated by a strong band at 807 cm^{-1}, which is characteristic of the C–H out-of-plane bending of the 1,4-linked repeat units of PPP. The relative intensity of this band is much stronger than the intensities of the two bands at 760 and 696 cm^{-1}, which are characteristic of the C–H bending modes of monosubstituted aromatic end groups. This observation is a qualitative indication that the PPP films made from **5** consist of long polymer chains. In contrast, IR analysis of films similarly processed from the radically polymerized acetoxy polymer (Figure 2b) shows relative intensities of repeat unit and end group bands characteristic of oligomeric material plus an additional band at 790 cm^{-1} attributable to 1,2-linked phenylene units.

Acknowledgment. We are grateful for financial support from the Air Force Office of Scientific Research (AFOSR-88-0094). We thank D. G. H. Ballard, D. M. Haddleton, and A. Nevin at ICI, Runcorn, U. K., for providing starting materials, 500-MHz ^{1}H NMR analyses, Viscotek GPC data, and LALLS analyses. We also thank R. Blumenthal, D. R. Baselt, and Professor N. S. Lewis for assistance with the STM imaging and D. R. Wheeler and P. D. Hampton for helpful discussions. D.L.G. gratefully acknowledges the Natural Sciences and Engineering Research Council of Canada for a 1967 Science and Engineering Scholarship.

Supplementary Material Available: ^{1}H NMR spectra, Viscotek GPC data, PXRD spectra, IR spectra, LALLS data, and photographs of computer models of the PPP precursor polymers, as well as additional STM images of polymer **3** (34 pages). Ordering information is given on any current masthead page.

Ethylene Insertion into the Rhodium–Methyl Bond in Chelated Tris(tertiary amine) Complexes. A New Class of Group 9 Organometallic Complexes

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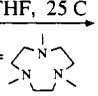
Received November 13, 1991

The organometallic chemistry of rhodium has usually been associated with strong-field, polarizable, generally π-acidic ancillary ligands. We are aware of only one previous example[1] of an alkyl complex of rhodium which bears only *saturated* amine ligands with or without additional "hard" ligands. We have begun a program directed toward the synthesis of such molecules of group 8 and 9 metals and an investigation of their organometallic chemistry. The obvious hope is that this class of compounds may reveal reactivity different from that of conventional organometallic compounds containing ancillary ligands such as phosphine, CO, cyclopentadienyl (Cp), etc., particularly with regard to the accessibility of higher oxidation states.

We report here our initial results in the investigation of Rh complexes of the facially-coordinating, tridentate ligand 1,4,7-trimethyl-1,4,7-triazacyclononane, which we dub "Cn" in analogy with the (albeit anionic) Cp. These syntheses begin with $CnRhCl_3$, originally reported by Wieghardt and co-workers.[2] Treatment with methyllithium for several days in THF gives up to 85% yields of $CnRhMe_3$, **1** (eq 1).[3] Preliminary X-ray diffraction data of

$$\mathrm{CnRhCl_3 + excess\ LiMe} \xrightarrow{\text{THF, }\overset{\circ}{2}5\text{ C}} \underset{\mathbf{1}}{\mathrm{CnRhMe_3}} \qquad (1)$$

Cn =


1 show the expected facial Cn group and octahedral coordination with average Rh–N and Rh–C bond lengths of 2.23 and 2.10 Å, respectively.[4] Complex **1** is air and water stable and is unaltered after 24 h in benzene-d_6 at 110 °C.

Stoichiometric treatment of **1** with HCl (in Et_2O/CH_2Cl_2), HBF_4, or $HOS(O)_2CF_3$ (triflic acid, HOTf) generates the species **2**–**7** (eq 2), all essentially quantitatively. Intermediates in the acid cleavages could not be detected by ^{1}H NMR even at −80 °C. The ^{1}H NMR spectrum of **6** or **7** in D_2O, presumably $[CnRh(D_2O)_2Me]X_2$, is extremely clean and unchanged after weeks at room temperature. Compounds **3** and **4** react with water, and this chemistry is under investigation.

$$\begin{array}{ccccc} \mathrm{CnRhMe_3} & \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{HX}} & \mathrm{CnRhMe_2X} & \xrightarrow{\mathrm{HX}} & \mathrm{CnRhMeX_2} \\ \mathbf{1} & & \mathbf{2}\,(\mathrm{Cl}) & & \mathbf{5}\,(\mathrm{Cl}) \\ & & \mathbf{3}\,(\mathrm{OTf}) & & \mathbf{6}\,(\mathrm{OTf}) \\ & & \mathbf{4}\,(\mathrm{BF_4}) & & \mathbf{7}\,(\mathrm{BF_4}) \end{array} \qquad (2)$$

Dimethyl triflate **3** resists reductive elimination of ethane.[5] At 80 °C in CD_2Cl_2, **3** decomposes to an as yet unidentified material with an approximate half-time of 3 h; no trace of ethane can be detected in the ^{1}H NMR spectrum, but methane is formed. Complex **3** quantitatively (by NMR) takes up CO to form $[CnRhMe_2(CO)]OTf$, **8**, which does not exchange with ^{13}CO over 9 days at 25 °C. In solution **8** is indefinitely stable at 80 °C.[6]

Complex **3** reacts with ethylene in CD_2Cl_2 as shown in Scheme I (monitored by ^{1}H and $^{13}C\{^1H\}$ NMR): above −50 °C, ethylene complex **9** gradually builds up; above −40 °C, **9** converts to allyl hydride **10** with the concurrent formation of methane; above 0 °C, **10** is chlorinated by the CD_2Cl_2 solvent to allyl chloride **11**, which exists as a mixture of two rotational isomers. These reactions are all clean, and **11** is formed quantitatively (by NMR). Structures of **9** and **10** were assigned from their spectra, particularly with use of $(^{13}C)_2H_4$ and $CnRh(^{13}CH_3)_2OTf$, **3**-$(^{13}C)_2$.[7] The structure of **11** was confirmed by X-ray crystallography.[8] We interpret the **9** → **10** transformation as a rare example of the direct

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(1) $[Rh(R)(NH_3)_5]^{2+}$ (R = Et, Pr, Bu) has been reported: Thomas, K.; Osborn, J. A.; Powell, A. R.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 1801–1806.

(2) Wieghardt, K.; Chaudhuri, P.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1982**, *21*, 3086–3090. Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329–436.

(3) Spectral data for **1**: ^{1}H NMR (360 MHz, DMSO-d_6) δ −0.58 (d, J_{RhH} = 2.5 Hz, $Rh(CH_3)_3$), 2.35 (s, $3[NCH_3]$), 2.40–2.70 (m, NCH_2); $^{13}C\{^1H\}$ NMR (90 MHz, DMSO-d_6) δ −0.21 (d, J_{RhC} = 35.3 Hz, $Rh(CH_3)_3$), 47.73 (NCH_3), 56.71 (NCH_2).

(4) R. Bau, R. Gellert, and D. Zhao, unpublished results. The average N–Rh–N angle of 80° shows that the ligand is slightly displaced up along the 3-fold axis.

(5) $[(Me_2PhP)_3RhMe_2](BF_4)$ is reported to lose ethane at room temperature in solution in the presence of ethylene. No ethylene insertion into the Rh–Me bond is reported. Lundquist, E. G.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1990**, *9*, 2254–2261.

(6) This behavior is in strong contrast to that of $[(triphos)RhMe_2](BF_4)$, which instantly reacts with CO to form acetone and $[(triphos)Rh(CO)_2](BF_4)$. Rauscher, D. J.; Thaler, E. G.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1991**, *10*, 2209–2216.

(7) ^{1}H NMR of **9** (360 MHz, CD_2Cl_2, −32 °C): δ 0.28 (d, J_{RhH} = 1.8 Hz, $Rh(CH_3)_2$), 2.56 (s, $2[NCH_3]$), 2.64 (d, J_{RhH} = 0.8 Hz, NCH_3), 2.3–3.2 (m, NCH_2), 3.27 (d, J_{HRh} = 1.5 Hz, $CH_2{=}CH_2$). $^{13}C\{^1H\}$ NMR of **9** (90 MHz, CD_2Cl_2, −32 °C): δ 8.20 (d, J_{CRh} = 22.5 Hz, $Rh(CH_3)_2$), 49.50, 49.66, 57.55, 58.52, 60.32 (NCH_2 and NCH_3), 78.94 (d, J_{CRh} = 8.2 Hz, $Rh[CH_2{=}CH_2]$). ^{1}H NMR of **10** (360 MHz, CD_2Cl_2, −15 °C): δ −22.40 (d, J_{RhH} = 16.5 Hz, RhH), 2.17 (ddd, 2 H, J_{trans} = 11.8 Hz, $^3J_{HC\text{-}RhH} \cong {}^2J_{HC\text{-}Rh} \cong 2$ Hz, anti terminal allyl), 2.54 (d, J_{RhH} = 1.0 Hz, NCH_3), 2.58 (br d, 2 H, J_{cis} = 7.3 Hz, syn terminal allyl), 2.6–2.7 + 2.9–3.3 (m, NCH_2), 3.37 (s, $2[NCH_3]$), 4.32 (tt, J = 11.8, 7.3 Hz, central allyl). $^{13}C\{^1H\}$ NMR of **10**-$(^{13}C)_3$ (90 MHz, CD_2Cl_2, −15 °C): δ 36.40 (dd, J_{CC} = 43.4 Hz, J_{CRh} = 10.9 Hz, terminal allyl), 58.08 ($2[NCH_3]$), 50.58, 58.13, 59.89, 60.40 (NCH_2 and NCH_3), 104.09 (td, J_{CC} = 43.4 Hz, J_{CRh} = 6.2 Hz, central allyl).

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