2352 *Organometallics* **2009,** *28,* 2352–2355

Synthesis and Characterization of NH-triazole-Bound Rhodium(I) Complexes: Substituted-Group-Controlled Regioselective Coordination

Haifeng Duan, Sujata Sengupta, Jeffrey L. Petersen, and Xiaodong Shi*

C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506

Received November 23, 2008

Summary: 4,5-Disubstituted NH-1,2,3-triazoles (TRIA) were used to coordinate with Rh(I) metal cation, forming a new class of triazole-bridged [Rh(COD)(TRIA)]$_2$ complexes in near-quantitative yields. X-ray crystallography studies revealed that the C-4-substituted groups effectively controlled the triazole binding sites, resulting in different coordination patterns. In addition, these air- and moisture-stable [Rh(COD)(TRIA)]$_2$ complexes showed effective catalytic properties in Pauson–Khand reactions, with superior stability.

Advances in transition-metal catalysis, a primary approach in modern synthesis, are strongly correlated with a fundamental understanding of the ligand–metal coordination.[1] In addition to the unique chemical properties of individual metal elements, binding ligands are crucial in determining the overall reactivity of complexes.[2] Numerous efforts have been put into the development/discovery of novel metal binding ligands in adjusting the chemical and stereo selectivity of the metal complexes.[3] Some successful examples, such as 2-(diphenylphosphino)-1-(2-(diphenylphosphino)naphthalen-1-yl)naphthalene (BINAP)[4] and salen,[5] have been extensively applied in academic research and industrial synthesis. It has been continuously demonstrated in the literature that ligands with unique functionality can significantly influence the reactivity of the transition-metal complexes/catalysts. Therefore, effective new catalytic systems are highly desirable.

Having a strong dipole moment, the 1,2,3-triazoles are considered as potential ligands in coordination with transition metals.[6] However, few studies have been reported regarding triazole–metal binding before 2000 due to the limited availability of functional triazole derivatives.[7] The discovery of Cu-catalyzed azide alkyne 1,3-dipolar cycloaddition (CuAAC; also referred to as "click chemistry") allows the formation of 1,4-substituted triazoles.[8] Since then, the importance of these compounds has been continually demonstrated in research fields as diverse as material science,[9] chemical biology[10] and medicinal chemistry.[11] Surprisingly, to date, there are still very few studies regarding the application of 1,2,3-triazole compounds in metal coordination. One recent example is the NCN-pincer Pd and Pt coordination with 1,4-disubstituted triazole complexes reported by van Koten, Gebbink, and co-workers.[12] Meanwhile, the synthesis of triazole-based P–N ligands, the clickphines, was recently reported and their Pd complexes were applied as effective catalysts for allylic alkylation.[13] Overall, among the few catalytic systems reported in the literature, the N-substituted triazoles were dominant, due to the well-developed click chemistry in the synthesis of these ligands. The NH-triazoles, which have been reported as good binding ligands even in neutral form,[14] on the other hand, have been much less studied. To the best of our knowledge, NH-triazoles have not been appliled to catalytic systems, nor has any crystal structures of a NH-triazole-bound transition-metal complex been reported so far. In this paper, we report the crystal structure of triazole-

---

* To whom correspondence should be addressed. E-mail: Xiaodong.Shi@mail.wvu.edu.

(1) (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley-Interscience: New York, 2005; (b) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*, 2nd ed.; University Science Books: Mill Valley, CA, 1999.

(2) Fu, G. C. *Acc. Chem. Res.* **2006**, *39*, 853–860.

(3) Shimizu, H.; Nagasaki, I.; Saito, T. *Tetrahedron* **2005**, *61*, 5405–5432.

(4) For recent reviews: (a) Shimizu, H.; Nagasaki, I.; Matsumura, K.; Sayo, N.; Saito, T. *Acc. Chem. Res.* **2007**, *40*, 1385–1393. (b) Berthod, M.; Mignani, G.; Woodward, G.; Lemaire, M. *Chem. Rev.* **2005**, *105*, 1801–1836.

(5) (a) Jacobsen, E. N. *Acc. Chem. Res.* **2000**, *33*, 421–431. (b) Katsuki, T. *Synlett* **2003**, *3*, 281–297.

(6) (a) Busetto, L.; Marchetti, F.; Zucchini, S.; Zanotti, V. *Inorg. Chim. Acta* **2005**, 358. (b) Bronisz, R. *Inorg. Chem.* **2005**, *44*, 4463. (c) Armstrong, D. R.; Davies, R. P.; Haigh, R.; Hendy, H. M.; Raithby, P. R.; Snaith, R.; Wheatley, A. E. H. *Eur. J. Inorg. Chem.* **2003**, 3363–3366.

(7) (a) Olson, J. R.; Yamauchi, M.; Butler, W. M. *Inorg. Chim. Acta* **1985**, *99*, 121–125. (b) Purnell, L. G.; Shepard, J. C.; Hodgson, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 2376–2377.

(8) For reviews see: (a) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596–2599. (b) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004–2021. (c) Bock, V. D.; Hiemstra, H.; Van Maarseveen, J. H. *Eur. J. Org. Chem.* **2006**, 51–68. (d) Moses, J. E.; Moorhouse, A. D. *Chem. Soc. Rev.* **2007**, *36*, 1249–1262.

(9) (a) Wu, P.; Feldman, A. K.; Nugent, A. K.; Hawker, C. J.; Scheel, A.; Voit, B.; Pyun, J.; Fréchet, J. M. J.; Sharpless, K. B.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2004**, *43*, 3928–3932. (b) Aucagne, V.; Hänni, K. D.; Leigh, D. A.; Lusby, P. J.; Walker, D. B. *J. Am. Chem. Soc.* **2006**, *128*, 2186–2187. (c) Ye, C. F.; Gard, G. L.; Winter, R. W.; Syvret, R. G.; Twamley, B.; Shreeve, J. M. *Org. Lett.* **2007**, *9*, 3841–3844. (d) Liu, Q. C.; Zhao, P.; Chen, Y. M. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3330–3341.

(10) (a) Agard, N. J.; Prescher, J. A.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2004**, *126*, 15046–15047. (b) Moorhouse, A. D.; Santos, A. M.; Gunaratnam, M.; Moore, M.; Neidle, S.; Moses, J. E. *J. Am. Chem. Soc.* **2006**, *128*, 15972–15973. (c) Kumar, R.; El-Sagheer, A.; Tumpane, J.; Lincoln, P.; Wilhelmsson, L. M.; Brown, T. *J. Am. Chem. Soc.* **2007**, *129*, 6859–6864.

(11) (a) Manetsch, R.; Krasiski, A.; Radi, Z.; Raushel, J.; Taylor, P.; Sharpless, K. B.; Kolb, H. C. *J. Am. Chem. Soc.* **2004**, *126*, 12809–12818. (b) Wang, J.; Sui, G.; Mocharla, V. P.; Lin, R. J.; Phelps, M. E.; Kolb, H. C.; Tseng, H.-R. *Angew. Chem., Int. Ed.* **2006**, *45*, 5276–5281. (c) Sugawara, A.; Sunazuka, T.; Hirose, T.; Nagai, K.; Yamaguchi, Y.; Hanaki, H.; Sharpless, K. B.; Omura, S. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 6340–6344. (d) Chen, H.; Taylor, J. L.; Abrams, S. R. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 1979–1983.

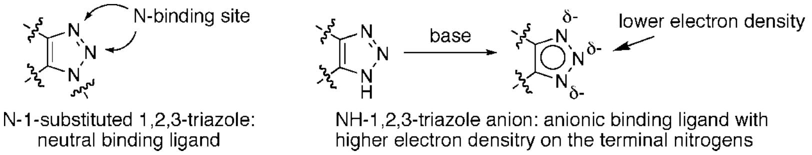
(12) Suijkerbuijk, B. M. J. M.; Aerts, B. N. H.; Dijkstra, H. P.; Lutz, M.; Spek, A. L.; van Koten, G.; Klein Gebbink, R. J. M. *Dalton Trans.* **2007**, 1273–1276.

(13) Detz, R. J.; Arevalo Heras, S.; de Gelder, R.; van Leeuwen, P. W. N. M.; Hiemstra, H.; Reek, J. N. H.; van Maarseveen, J. H. *Org. Lett.* **2006**, *8*, 3227–3231.

(14) According to ref 12, the K_a value for NH-triazole to NCN-pincer Pd complex is 4.16, while the value for pyridine is 19.5 and for aniline is 0.30.

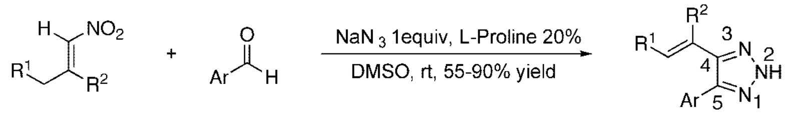
10.1021/om8011163 CCC: $40.75

Scheme 1. Coordination Sites on 1,2,3-Triazoles

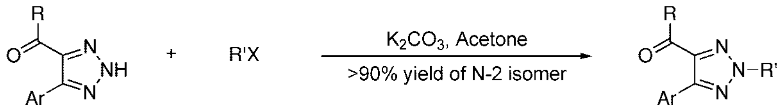


Scheme 2. Synthesis of 1,2,3-Triazoles and Selective N-2 Derivatization

A) A facile, catalytic cascade synthesis of NH-triazoles



B) Regioselective synthesis of N-2 substituted triazoles through conformation control



bridged Rh(I) complexes along with their catalytic activity toward the Pauson−Khand reaction.

In comparison to N-substituted triazoles, the NH-triazole possesses acidic N−H protons (pK_a < 10)[15] and can therefore be applied as an anionic ligand with multiple binding sites. So far, all reported efforts regarding triazole anion binding have focused on benzotriazoles,[16] which decreased the overall interest in this class of complexes (limited functionality and difficulty in derivatization), especially their unlikely potential in the discovery of new chiral ligands. Moreover, the presence of multiple nitrogen binding sites in the triazole anion can result in complicated coordination systems, where two terminal nitrogens possess higher electron density while the internal N-2 nitrogen is more exposed for coordination. Therefore, systems with regioselective coordination of the triazole anion are highly desirable.

Recently, our group reported a catalytic cascade three-component condensation of nitroalkene, aryl aldehyde, and NaN_3, giving 4,5-disubstituted-NH-1,2,3-triazoles in one step with good yields (Scheme 2A).[17] Furthermore, with the application of substrate conformational control, the N-2-substituted triazoles were successfully prepared by a simple alkylation reaction, as shown in Scheme 2B.[18] This new synthetic methodology and the success in regioselective triazole functionalization spurred our interest in investigating the use of NH-triazole as a new bridging ligand in the preparation of metal complexes with good regioselectivity.

With the 4,5-disubstituted NH-triazoles in hand, we examined the binding ability of the triazole anion with Rh(I) complexes by treating the NH-triazoles with $[(COD)RhCl]_2$ under basic conditions. As expected, the triazole anion effectively substituted the Cl^- anion and the triazole−Rh(I) complexes $[Rh(COD)(TRIA)]_2$, were produced in nearly quantitative yields. These new complexes showed great stability toward air and moisture and can even be purified by column chromatography.[19] Single crystals of triazole−Rh(I) complexes **1a**,**b** were successfully prepared, and their structures were determined by X-ray diffraction (Scheme 3).

As revealed by the crystal structures, in both complexes, two triazole anions coordinate with the Rh(I) cation as bridging ligands to link two metal cations, forming bis-metallic complexes. The two Rh cations, with two COD ligands and two nitrogen coordinations, adopt a 16-electron square-planar geometry. In these two complexes, both the N-2 and N-3 nitrogens were bound to the metal, while the N-1 nitrogen was left open with no coordination. The electron-withdrawing *p*-NO_2 group on the aromatic ring does not change the fundamental binding pattern (complex **1b**). The complexes pack in a chiral lattice, where the two triazoles adopt a pseudo-C_2 symmetry, omitting the dynamic COD coordination.

To evaluate the chiral selectivity of these complexes, the chiral triazole **1c** was prepared to coordinate with Rh(I), and the crystal structure is shown in Scheme 4.

A similar triazole-bridged bis-Rh(I) complex was formed. However, rather than the N-2 and N-3 binding as revealed in complexes **1a**,**b**, a different binding pattern was obtained in **1c**, in which the N-1 and N-2 nitrogens bind to the metal and the N-3 is left uncoordinated. In both cases, the triazole anions bind to two Rh cations. The N-2 nitrogen, although with a relatively lower electron density than the N-1 and N-3 nitrogens, is a favored σ-donor due to less steric hindrance. Meanwhile, since the C-4- and C-5-substituted groups are bearing significant steric repulsion, the conformations of these two groups influence each other. As revealed in our previous N-2 alkylation report, the C-5 aryl group is preferred to adopt a coplanar conformation with the triazole ring to achieve the best π conjugation. This is observed again in complexes **1a**,**b**, where the C-4 styrenyl group is perpendicular to the triazole ring. As a result, the C-5 group blocks the N-1 binding site and leaves the N-3 nitrogen as the preferred σ donor. In contrast, with the more bulky group on the C-4 position (complex **1c**), the C-5 aryl possesses a smaller dihedral angle with the triazole ring (less planar). Therefore, an increase of steric hindrance on the N-3 position in combination with less protection on the N-1 position leads to a different coordination pattern, as observed in **1c**.

---

(15) Poznanski, J.; Najda, A.; Bretner, M.; Shugar, D. *J. Phys. Chem. A* **2007**, *111*, 6501–6509. According to the paper, the pK_a of benzyl triazole is 8.3.

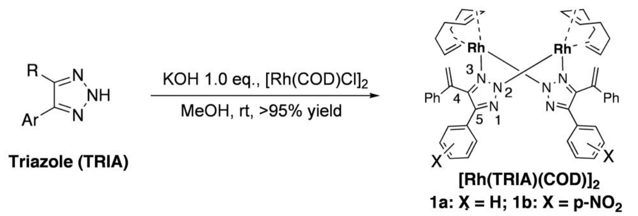
(16) (a) Katritzky, A. R.; Lan, X.; Yang, J. Z.; Denisko, O. V. *Chem. Rev.* **1998**, *98*, 409. (b) Verma, A. K.; Singh, J.; Sankar, V. K.; Chaudhary, R.; Chandra, R. *Tetrahedron Lett.* **2007**, *48*, 4207–4210.

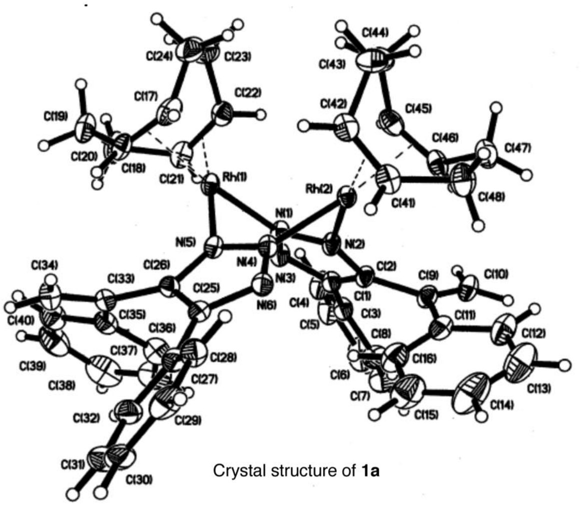
(17) Sengupta, S.; Duan, H.; Lu, W.; Petersen, J. L.; Shi, X. *Org. Lett.* **2008**, *10*, 1493–1496.

(18) Chen, Y.; Liu, Y.; Petersen, J. L.; Shi, X. *Chem. Commun.* **2008**, 3254–3256.

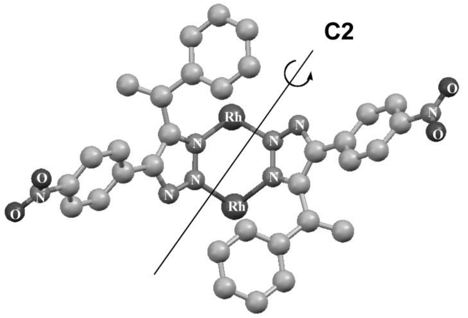
(19) The complex is stable enough to be dissolved in methylene chloride and purified by flash column chromatography (R_f = 0.5, hexane−ethyl acetate, 6/1 v/v).

Scheme 3. Synthesis and Crystal Structures of Triazole−Rh(I) Complexes



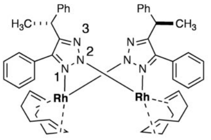


Crystal structure of **1a**



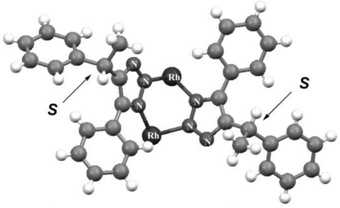
pseudo C2 symmetry of **1b**. Hs and COD are omitted for clarity

Scheme 4. Switching the N-Binding Site with a Different C-4 Group



1c

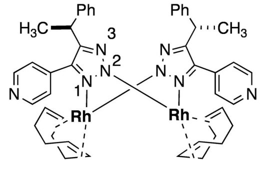
Chiral self-sorting of ligands:
homo chiral complexes, *S*,*S* or *R*,*R*



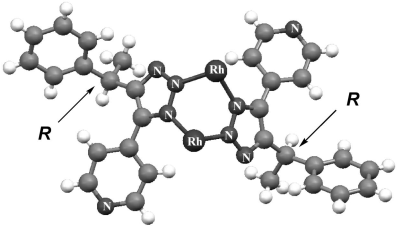
Crystal structure of **1c**. CODs are omitted for clarity

Another factor that may be contributing to the triazole binding site is electronic effects, which may provide different electron densities on the N-1 and N-3 nitrogens. To investigate this effect, the pyridine−triazole−Rh(I) complex **1d** was synthesized and the crystal structure is shown in Scheme 5.

Scheme 5. Crystal Structure of 1d: Anionic Triazoles as Better Coordination Ligands than Pyridine



1d



Crystal structure of **1d**. CODs are omitted for clarity

Table 1. N−Rh Bond Distances (Å) and Dihedral Angles (deg) of Triazole−Rh Complexes

				dihedral angle with triazole	
	N1−Rh	N2−Rh	N3−Rh	C-4 Ph	C-5 Ar
1a		2.06 ± 0.01	2.12 ± 0.01	129 ± 6	33 ± 1
1b		2.06 ± 0.01	2.12 ± 0.01	131 ± 1	34 ± 1
1c	2.10 ± 0.01	2.08 ± 0.01		100 ± 4	49 ± 1
1d	2.12 ± 0.01	2.06 ± 0.01		99 ± 1	44 ± 1

As indicated in the crystal structure, a similar N-1 binding was observed in **1d**, which strongly suggested that steric effects, as discussed above, are dominant in triazole−metal coordination. Notably, even with the presence of the strong σ donor pyridine, the triazole anion is still the preferred binding site and the complex is stable enough for column chromatography. A direct comparison of all four complexes is given in Table 1.

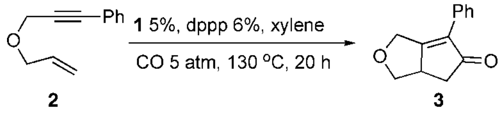
Interestingly, enantiomeric self-sorting is observed in complexes **1c**,**d**. Similar to the case for **1a**,**b**, complexes **1c**,**d** are chiral with pseudo-C_2 symmetry between the two triazoles. With a stereogenic center on the C-4 position, homochiral coordination (only *R*,*R* or *S*,*S*) was observed for $[Rh(COD)(TRIA)]_2$ in the solid state. This result is crucial, because it allows this new class of bis-metal complexes to be potential chiral catalysts for stereoselective functional group transformation. Solution NMR studies gave complex spectra even at low temperature (−50 °C), due to the dynamic exchange of the COD ligands (see spectra in the Supporting Information). However, considering the superior stability of these complexes, it is likely that the bimetal coordination should also exist in solution to maintain the 16-electron configuration on the rhodium. With the least steric hindrance, the N-2 nitrogen should be the preferred binding site. It is possible that the N-1 and N-3 metal binding is dynamic in solution. The dissociation of the bis-metal skeleton is highly unlikely.

Finally, to evaluate the catalytic reactivity of this new class of Rh(I) complexes, catalytic Pauson−Khand reactions of enyne **2** were carried out to compare with those of the air- and moisture-sensitive $[Rh(COD)Cl]_2$. The results are shown in Scheme 6.

Even with their greater stability toward air and moisture, all four complexes showed effective catalytic reactivity. Development of new chiral catalysts based on this new class of catalysts toward asymmetric Pauson−Khand reactions is currently under investigation and will be reported in due course.

In conclusion, we have reported the synthesis and structural characterization of 4,5-disubstituted triazoles as organo-anionic

Scheme 6. Triazole−Rh(I) Complex Catalyzed Pauson−Khand Reactions



catalyst	yield
$[Rh(COD)Cl]_2$	82%
1a	80
1b	88
1c	82
1d	60

ligands in coordination with Rh(I) complexes. The first examples of X-ray structures of NH-triazole-bound transition-metal complexes were reported. With the application of chiral triazoles, enantiomeric self-sorting of the ligands was achieved, where only homochiral complexes were observed. As a new class of air- and moisture-stable compounds, these complexes showed effective catalytic reactivity in Pauson−Khand reactions, further illustrating the great potential of these complexes as new catalysts in stereoselective reactions. Application of these complexes to other metal-catalyzed reactions and further development of triazole analogues for the formation of different chiral derivatives are currently under investigation in our group.

Experimental Section. General Procedures. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. $[RhCl(COD)]_2$ (crystalline solid) and DPPP were purchased and stored under nitrogen. ^1H NMR and ^{13}C NMR spectra were recorded on 270 and 600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) for ^1H and $CDCl_3$ (δ 77.0 ppm) for ^{13}C. Flash column chromatography was performed on 230−430 mesh silica gel. Analytical thin-layer chromatography was performed with precoated glass baked plates (250 μm) and visualized by fluorescence. Melting points were determined on a MelTemp apparatus and are uncorrected. Elemental analyses were performed in the Department of Chemical Engineering, College of Engineering and Mineral Resources, West Virginia University.

Synthesis of Rh−Triazole Complexes. A typical procedure for the synthesis of Rh−triazole complexes is as follows. To a suspension of $[RhCl(COD)]_2$ (100 mg, 0.2 mmol) and triazole (0.4 mmol) in 30 mL of methanol was added 10 mL of 0.04 M KOH (22.4 mg, 0.4 mmol) solution in methanol, dropwise at room temperature with constant stirring. After 8 h of stirring at room temperature, a yellow powder of Rh−triazole was produced and filtered using a folded filter paper (Whatman No. 2). The yellow powder was then washed with methanol and dried by vacuum pump: yield ∼95%. (For further purification, the yellow solids were stable enough to be dissolved in dichloromethane and purified by flash column chromatography (R_f = 0.5, hexane−EtOAc, 6/1 v/v).)

Rh−Triazole-Catalyzed Pauson−Khand Reaction. A typical procedure for the Rh−triazole-catalyzed Pauson−Khand reaction is as follows. In a 20 mL dry sealable flask were added the rhodium−triazole complex (0.025 mmol Rh), dppp (12.4 mg, 0.03 mmol), and xylene (3 mL). Then the mixture was stirred for 10 min, after which the enyne (0.5 mmol) was added. The flask was then charged with 5 atm of CO and heated to 130 °C for 20 h, after which the flask was cooled and the CO was cautiously released in the hood. The crude product was purified using flash column chromatography (hexane−EtOAc, 3/1 v/v) to afford **3** as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$): δ 7.52 (d, J = 7.2 Hz, 2H), 7.41−7.38 (m, 2H), 7.35−7.32 (m, 1H), 4.92 (d, J = 16.2 Hz, 1H), 4.57 (d, J = 16.2 Hz, 1H), 4.36 (t, J = 8.4 Hz, 1H), 3.31−3.30 (m, 1H), 3.22 (dd, J = 10.8 Hz, J = 7.8 Hz, 1H), 2.83 (dd, J = 18.0 Hz, J = 6.6 Hz, 1H), 2.32 (dd, J = 18.0 Hz, J = 3.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.7, 177.3, 134.6, 130.5, 128.6, 128.5, 127.9, 71.3, 66.2, 43.2, 40.2.

Acknowledgment. We deeply appreciate the C. Eugene Bennett Department of Chemistry and the Eberly College of Arts and Science, WVNano Initiative, PsCoR program at West Virginia University, Senate research award of West Virginia State, and the donors of the Petroleum Researcb Foundation (PRF-G), administered by the American Chemical Society, for financial support.

Supporting Information Available: Text, figures, tables, and CIF files giving general experimental methods for the preparation of the complexes and crystallization, NMR spectra, and crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM8011163