Table IV. Selected Bond Angles (deg) for 2

Sb(1)–C(1)–Si(1)	118.2 (6)	C(1)–C(2)–C(3)	116 (1)
Sb(1)–C(1)–C(2)	112.3 (8)	C(1)–C(2)–C(5)	122 (1)
Sb(1)–C(4)–Si(2)	117.5 (7)	C(2)–C(3)–C(4)	118 (1)
Sb(1)–C(4)–C(3)	111.6 (8)	C(2)–C(3)–C(6)	121 (1)
Sb(2)–C(13)–Si(4)	117.9 (5)	C(3)–C(2)–C(5)	122 (1)
Sb(2)–C(13)–C(14)	111.5 (8)	C(4)–C(3)–C(6)	120 (1)
Sb(2)–C(16)–Si(13)	118.7 (6)	C(13)–Sb(2)–C(16)	81.1 (4)
Sb(2)–C(16)–C(15)	111.0 (8)	C(13)–C(14)–C(15)	117 (1)
Si(1)–C(1)–C(2)	125.8 (9)	C(13)–C(14)–C(18)	121 (1)
Si(2)–C(4)–C(3)	128 (1)	C(14)–C(15)–C(16)	118.4 (9)
Si(3)–C(16)–C(15)	127.2 (8)	C(14)–C(15)–C(17)	121 (1)
Si(4)–C(13)–C(14)	125.7 (8)	C(15)–C(14)–C(18)	122.0 (9)
C(1)–Sb(1)–C(4)	80.8 (5)	C(16)–C(15)–C(17)	120 (1)

to be the latter by structural solution and refinement. An ORTEP plot of the molecular structure of 2 that shows the numbering scheme used in the refinement is illustrated in Figure 1. Table II gives the positional values, while Tables III and IV give the more important distances and the bond angles for the non-hydrogen atoms. Table VI, a list of observed and calculated structure factors, is available in the supplementary material.

Acknowledgment. We are grateful to the Research Corp., to NATO Scientific Affairs, and to the donors of the Petroleum Research Foundation, administered by the American Chemical Society, for partial support of this work.

Registry No. 2, 139426-50-9; **3**, 139426-51-0; **5**, 137594-89-9; **6**, 137594-87-7; **7**, 139426-49-6; **8**, 139408-78-9; **9**, 139426-52-1; **10**, 137594-88-8; **11**, 139408-79-0; **12**, 139426-53-2; zirconocene dichloride, 1291-32-3; 1-trimethylsilyl-1-propyne, 6224-91-5; phenyldichlorostibine, 5035-52-9; phenyldiiodobismuthine, 39110-03-7.

Supplementary Material Available: Figure 1a, showing an ORTEP plot from a different perspective, and Table V, listing hydrogen atomic parameters for 2 (3 pages); Table VI, listing observed and calculated structure factors for 2 (22 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of Rhodium Complexes Containing a Photolabile η^2-Carbodiimide Ligand. 1,3-Dipolar Cycloaddition of Phenyl Azide to Tp′Rh(CNR)$_2$ (Tp′ = Hydrotris(3,5-dimethylpyrazolyl)borate)

Edward T. Hessell and William D. Jones*

Department of Chemistry, University of Rochester, Rochester, New York 14627

Received October 28, 1991

The 1,3-dipolar cycloaddition of phenyl azide to the metal-coordinated isocyanide ligands in Tp′Rh(CNR)$_2$ (Tp′ = hydrotris(3,5-dimethylpyrazolyl)borate, R = neopentyl, methyl, 2,6-xylyl; **1a–c**) or Cp*Rh(CN-neopentyl)$_2$ (Cp* = η^5-1,2,3,4,5-pentamethylcyclopentadienyl; **3**) in hexane produces the complexes Tp′Rh(CNR)(η^2-PhN=C=NR) (R = neopentyl, methyl, 2,6-xylyl; **2a–c**) and Cp*Rh(CNR)(η^2-PhN=C=N-neopentyl) (**4**), respectively, in high yield. The reaction is regiospecific with respect to coordination of the unsymmetrical carbodiimide ligand. Reaction of 2,4-xylyl azide with Tp′Rh(CN-2-tolyl)$_2$ (**1d**) gives Tp′Rh(CN-2-tolyl)(η^2-2,4-xylyl-N=C=N-2-tolyl) (**2d**), for which the solid-state structure has been obtained by X-ray diffraction. Complex **2d** crystallizes from toluene in the triclinic space group $P\bar{1}$ with a = 10.962 (6) Å, b = 11.238 (4) Å, c = 8.691 (14) Å, α = 96.95 (5)°, β = 104.02 (5)°, γ = 101.00 (4)°, V = 2159 (5) Å^3, and Z = 2. The structure of **2d** confirms the bidentate bonding of the carbodiimide and shows that the nitrogen of the carbodiimide arising from the azide is coordinated to rhodium. Photolysis of **2a** in benzene produces Tp′Rh(H)(Ph)(CN-neopentyl) (**5**) along with free PhN=C=N-neopentyl with a quantum yield of 1.0 ± 0.3, whereas complex **4** is photochemically unreactive in benzene solution. The conversion of **2a** to **5** can also be effected thermally, although the rate is slow at 100 °C. Photolysis of **2a** in the solid state results in an intramolecular reaction to give Tp′Rh(H)(2-(N=C=N-neopentyl)C$_6$H$_4$)(CN-neopentyl) (**7**). Addition of excess neopentyl isocyanide to **2a** gives the azametallacyclobutane complex Tp′RhC(=N-neopentyl)N(Ph)C(=N-neopentyl)(CN-neopentyl) (**8**).

Introduction

The chemistry relating to the coordination of heterocumulenes to transition metals is extensive and can be viewed as having an important relationship to the activation and reduction of carbon dioxide.[1] Many stable transition-metal complexes containing such ligands as allenes,[2] isocyanates,[3] ketenes,[4] ketenimines,[5] carbon disulfide,[6] and carbon diselenide[7] as well as carbon dioxide[1] itself have been characterized. Stable complexes of carbodiimides have also been reported.[8] Isolation of complexes in which the carbodiimide is bound in an η^2 mode are uncommon, however, and there exists only one crystallographically characterized example to date.[8a] As is typical of most cumulenes, carbodiimides only form stable

---

[1] Darensbourg, D. J.; Kodaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129.

[2] Bowden, F. L.; Giles, T. *Coord. Chem. Rev.* **1976**, *20*, 81.

[3] (a) Braunstein, P.; Nobel, D. *Chem. Rev.* **1989**, *89*, 1927. (b) Granovskii, A. D. *Koord. Khim.* **1987**, *13*, 715. (c) Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 3052.

[4] Geoffroy, G.; Bassner, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1.

[5] (a) Aumann, R. *Angew. Chem., Int. Ed. Engl.* **1988**, 1456. (b) Antinolo, A.; Fajardo, M.; Mardomingo, C. L.; Otero, A. *Organometallics* **1990**, *9*, 2919. (c) Hohn, A.; Werner, H. *Chem. Ber.* **1988**, *121*, 881.

[6] Yaneff, P. V. *Coord. Chem. Rev.* **1977**, *23*, 183.

[7] (a) Brothers, P. F.; Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1980**, *195*, C29. (b) Jensen, K. A.; Huge-Jensen, E. *Acta Chem. Scand.* **1973**, *27*, 3605. (c) Kawakami, K.; Ozaka, Y.; Tanaka, T. *J. Organomet. Chem.* **1974**, *69*, 151. (d) Clark, G. R.; Grudy, K. R.; Harris, R. O.; James, S. M.; Roper, W. R. *J. Organomet. Chem.* **1975**, *90*, C37.

[8] (a) Pasquali, M.; Gambarotta, S.; Floriani, C.; Chiesa-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 165. (b) Glueck, D. S.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2719. (c) Hoberg, H.; Korff, J. *J. Organomet. Chem.* **1978**, *150*, C20. (d) Okuda, J.; Herberich, G. E. *J. Organomet. Chem.* **1987**, *320*, C35. (e) Fehlhammer, W. P.; Mayr, A.; Ritter, M. *Angew. Chem.* **1977**, *89*, 660. (f) Anderson, R. A.; Einstein, F. W. *Acta Crystallogr.* **1978**, *B34*, 271. (g) Bycroft, B. M.; Cotton, J. D. *J. Chem. Soc., Dalton Trans.* **1973**, 1867.

0276-7333/92/2311-1496$03.00/0

complexes with the most electron-rich metal centers,[9] but metal-bound carbodiimides have also been implicated as unstable intermediates in both catalytic and stoichiometric reactions.[10]

It has long been understood that the M—C bonds in electron-rich transition-metal complexes containing isocyanide ligands possess considerable double-bond character,[11] as evidenced by the fact that they undergo reactions similar to those of C=C bonds such as [2 + 2][12] and 1,3-dipolar cycloaddition reactions.[13] We became interested in reacting the "M=C" bonds of the complexes Tp′Rh(CNR)$_2$ with a 1,3-dipole in an effort to chemically labilize an isocyanide ligand to create a vacant site at the metal center. This general method of chemical modification has been applied in several instances to transition-metal complexes containing carbon monoxide[14] and has been used for generation of the reactive [Cp*Ir(CO)] fragment via the η^2-nitrile complex.[14b,c]

It was Collman who first proposed a general class of reactions in which atom transfer between two reagents was facilitated by a transition metal and demonstrated the practical utility of the concept with the catalytic formation of isocyanates from aryl azides and carbon monoxide in the presence of MCl(CO)(PPh$_3$)$_2$ (M = Rh, Ir; eq 1).[14a,15]

$$\mathrm{ArN_3} + \mathrm{CO} \xrightarrow[\mathrm{MCl(PPh_3)_2CO}]{} \mathrm{ArNCO} + \mathrm{N_2} \quad (1)$$

M = Rh, Ir

Although Collman labeled such reactions as "metal ion promoted atom-transfer oxidation–reduction", the reaction of an azide ("oxidizing agent") with a metal-coordinated carbonyl or isocyanide ("reducing agents") can be visualized as a [2 + 3] cycloaddition of a 1,3-dipole to a "M=C" bond.

Herein we report the synthesis and characterization of stable carbodiimide complexes of rhodium, formed through the reaction of an aryl azide with a metal-bound isocyanide. These are, to the best of our knowledge, the first stable η^2-carbodiimide complexes of rhodium; however, it should be noted that Werner has recently prepared the related complexes CpCo(PhN=C=NCH$_2$Ph)(PMe$_3$) by the same method[16] and previously used a similar technique to prepare the closely related rhodium η^2-ketenimine complexes Cp*Rh(PR$_3$)(PhN=C=CHR) (R = Ph, CH$_3$).[17] We also report some of our initial results on the photochemical reactivity which is unique to our carbodiimide complexes.

Results and Discussion

Synthesis and Characterization of Tp′Rh(CNR)(PhN=C=NR). Addition of a hexane solution of phenyl azide to Tp′Rh(CN-neopentyl)$_2$ (**1a**; Tp′ = hydrotris(3,5-dimethylpyrazol-1-yl)borate) in hexane results in the immediate evolution of nitrogen gas and a darkening of the reaction mixture. Cooling of the resulting solution to −20 °C for 24 h produces yellow hairlike needles of a product assigned as Tp′Rh(CN-neopentyl)(η^2-PhN=C=N-neopentyl) (**2a**; eq 2). Complex **2a** is stable in air for short periods of time but is extremely light sensitive. The complex has been fully characterized by ^{1}H NMR, ^{13}C{^{1}H} NMR, and IR spectroscopy; however, proper elemental analysis could not be obtained for **2a**, a problem which has been encountered by ourselves[18] and other groups in the past.[19] Complexes **2b–d** were prepared analogously to **2a** and possess similar spectroscopic characteristics. The related complex Cp*Rh(CN-neopentyl)(η^2-PhN=C=N-

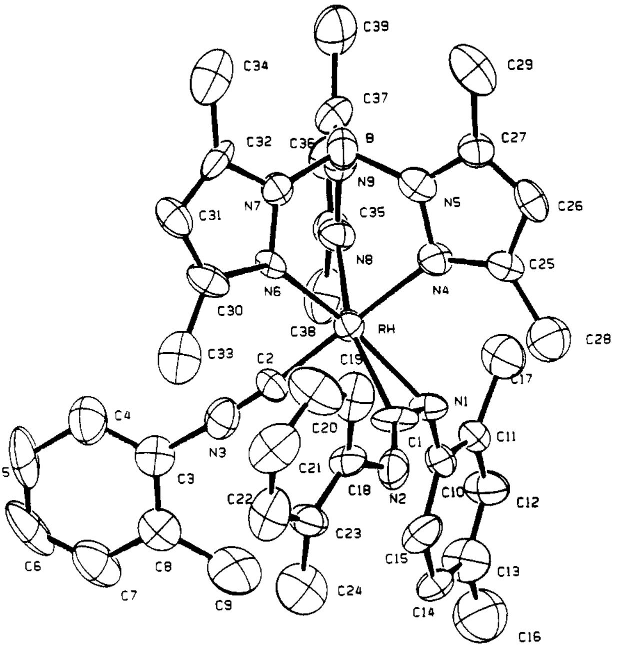
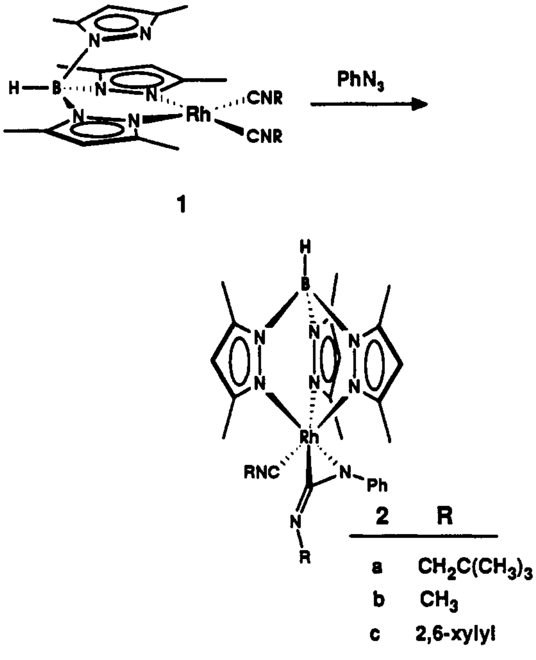


Figure 1. ORTEP drawing of Tp′Rh(CN-2-tolyl)(η^2-2,4-xylyl-N=C=N-2-tolyl)·C$_7$H$_8$ (**2d**). Ellipsoids are shown at the 50% probability level.



(2)

2	R
a	CH$_2$C(CH$_3$)$_3$
b	CH$_3$
c	2,6-xylyl

---

[9] Fehlhammer, W. P.; Mayr, A.; Ritter, M. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 641.

[10] (a) Saegusa, T.; Ito, Y.; Shimizo, T. *J. Org. Chem.* **1970**, *35*, 3995. (b) Dickson, R. S.; Nesbit, R. J.; Pateras, H.; Baimbridge, W.; Patrick, J. M.; White, A. H. *Organometallics* **1985**, *4*, 2128. (c) Otsuka, S.; Aotoni, Y.; Tatsuno, Y.; Yoshida, T. *Inorg. Chem.* **1976**, *15*, 656. (d) Hoberg, H.; Burkhart, G. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 525.

[11] Crociani, B. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1986.

[12] Werner, H.; Heiser, B.; Burschka, C. *Chem. Ber.* **1982**, *115*, 3069.

[13] (a) Strecker, B.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 275. (b) Werner, H.; Heiser, B.; Otto, H. *Chem. Ber.* **1985**, *118*, 3932.

[14] (a) Collman, J. P.; Kubota, M.; Sun, J.-Y.; Vastine, F. *J. Am. Chem. Soc.* **1967**, *89*, 169. (b) Chetcuti, P. A.; Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1988**, *7*, 641. (c) Chetcuti, P. A.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1988**, *7*, 650. (d) Werner, H.; Wolf, J.; Schubert, U. *Chem. Ber.* **1983**, *116*, 2848.

[15] Collman, J. P.; Kubota, M.; Hosking, J. W. *J. Am. Chem. Soc.* **1967**, *89*, 4809.

[16] Werner, H. Personal communication.

[17] Hohn, A.; Werner, H. *Chem. Ber.* **1988**, *121*, 881.

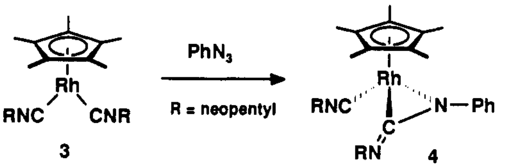
[18] Jones, W. D.; Hessell, E. T. *Inorg. Chem.* **1991**, *30*, 778.

[19] (a) May, W.; Reinsalu, P.; Powell, J. *Inorg. Chem.* **1980**, *19*, 1582. (b) Reger, D. L.; Tarquini, M. E. *Inorg. Chem.* **1982**, *21*, 840.

Table I. Positional Parameters and B_{eq} Values for Non-Hydrogen Atoms of Tp′Rh(CN-2-tolyl)(η^2-2,4-xylyl-N=C=N-2-tolyl)•C_7H_8 (2d)

atom	x	y	z	B_{eq}, Å^2
Rh	0.1216 (1)	0.0328 (1)	0.22689 (7)	2.52 (4)
N1	0.255 (1)	0.004 (1)	0.1695 (6)	2.5 (5)
N2	0.424 (1)	0.096 (1)	0.2828 (7)	3.9 (6)
N3	0.129 (1)	−0.198 (1)	0.2923 (6)	3.7 (5)
N4	0.114 (1)	0.1966 (9)	0.1841 (6)	3.0 (5)
N5	0.013 (1)	0.251 (1)	0.1917 (6)	3.0 (5)
N6	0.051 (1)	0.104 (1)	0.3137 (6)	2.4 (5)
N7	−0.048 (1)	0.1603 (9)	0.2972 (6)	2.8 (5)
N8	−0.083 (1)	−0.028 (1)	0.1637 (6)	3.2 (5)
N9	−0.159 (1)	0.056 (1)	0.1656 (6)	2.9 (5)
C1	0.308 (1)	0.056 (1)	0.237 (1)	3.6 (7)
C2	0.130 (1)	−0.111 (1)	2.666 (8)	3.3 (6)
C3	0.126 (1)	−0.301 (1)	0.3308 (8)	3.6 (7)
C4	0.040 (1)	−0.326 (1)	0.371 (1)	5.1 (8)
C5	0.036 (2)	−0.428 (2)	0.406 (1)	6.5 (9)
C6	0.114 (2)	−0.504 (2)	0.398 (1)	7 (1)
C7	0.198 (2)	−0.480 (2)	0.357 (1)	5.7 (8)
C8	0.208 (1)	−0.378 (1)	0.3244 (8)	3.8 (6)
C9	0.306 (2)	−0.351 (1)	0.280 (1)	6.0 (8)
C10	0.286 (1)	−0.099 (1)	0.1326 (8)	3.3 (7)
C11	0.212 (1)	−0.147 (1)	0.0610 (9)	3.5 (7)
C12	0.240 (1)	−0.249 (1)	0.0233 (7)	4.2 (7)
C13	0.336 (2)	−0.301 (1)	0.0551 (9)	4.8 (7)
C14	0.412 (1)	−0.250 (1)	0.126 (1)	4.1 (7)
C15	0.382 (1)	−0.150 (1)	0.1630 (8)	4.1 (7)
C16	0.110 (1)	−0.087 (1)	0.0202 (7)	4.8 (7)
C17	0.365 (2)	−0.412 (2)	0.013 (1)	7.5 (5)
C18	0.448 (1)	0.160 (1)	0.3585 (8)	3.0 (6)
C19	0.398 (1)	0.260 (1)	0.371 (1)	4.6 (7)
C20	0.428 (2)	0.328 (1)	0.441 (1)	5.8 (8)
C21	0.510 (2)	0.298 (2)	0.498 (1)	5.3 (8)
C22	0.561 (1)	0.196 (2)	0.4857 (9)	5.1 (8)
C23	0.532 (1)	0.129 (1)	0.415 (1)	3.7 (7)
C24	0.584 (1)	0.019 (1)	0.4018 (9)	6.3 (8)
C25	0.185 (1)	0.278 (1)	0.1543 (7)	3.1 (6)
C26	0.131 (1)	0.375 (1)	0.1421 (8)	3.7 (6)
C27	0.023 (1)	0.358 (1)	0.1662 (8)	3.3 (6)
C28	0.308 (1)	0.259 (1)	0.1360 (8)	5.1 (4)
C29	−0.065 (1)	0.443 (1)	0.1721 (8)	5.0 (7)
C30	0.072 (1)	0.099 (1)	0.385 (1)	3.5 (6)
C31	−0.007 (1)	0.157 (1)	0.4185 (8)	3.8 (6)
C32	−0.085 (1)	0.193 (1)	0.362 (1)	3.8 (7)
C33	0.177 (1)	0.048 (1)	0.4287 (8)	5.3 (7)
C34	−0.192 (1)	0.260 (1)	0.3592 (9)	6.0 (8)
C35	−0.162 (2)	−0.130 (1)	0.1158 (9)	3.7 (7)
C36	−0.281 (1)	−0.113 (1)	0.0911 (8)	4.0 (7)
C37	−0.280 (1)	0.004 (2)	0.1223 (9)	4.1 (7)
C38	−0.113 (1)	−0.243 (1)	0.1008 (8)	5.7 (8)
C39	−0.387 (1)	0.072 (1)	0.1129 (8)	5.5 (7)
C100	0.290 (2)	0.290 (2)	0.704 (2)	8 (1)
C101	0.302 (2)	0.321 (3)	0.629 (2)	10 (1)
C102	0.344 (3)	0.441 (3)	0.635 (1)	10 (1)
C103	0.385 (2)	0.530 (3)	0.702 (2)	11 (2)
C104	0.368 (2)	0.498 (2)	0.765 (1)	10 (1)
C105	0.314 (2)	0.377 (3)	0.763 (1)	7 (1)
C106	0.233 (2)	0.164 (2)	0.697 (1)	12 (1)
B	−0.103 (2)	0.181 (1)	0.219 (1)	3.8 (8)

neopentyl) (4) is prepared from 3 in a fashion identical with that for **2a** (eq 3) and gives proper elemental analysis.



(3)

It was possible to obtain a solid-state structure for the complex Tp′Rh(CN-2-tolyl)(η^2-2,4-xylyl-N=C=N-2-tolyl) (**2d**) by single-crystal X-ray diffraction (Figure 1). Positional parameters as well as selected bond angles and distances are listed in Table I and II. The important features of the structure are the η^2 coordination of the carbodiimide and the η^3-Tp′ ligand. The η^3-Tp′ ligand is often associated with a formally Rh(III) complex and provides some initial insight into the extent of bonding between the carbodiimide and rhodium. The geometry about rhodium is pseudo trigonal bipyramidal with the η^2-carbodiimide and two of the pyrazole rings of the Tp′ ligand in the equatorial positions.

Table II. Selected Bond Distances (Å) and Angles (deg) for Non-Hydrogen Atoms in Tp′Rh(CN-2-tolyl)(η^2-2,4-xylyl-N=C=N-2-tolyl)•C_7H_8 (2d)

Rh–N1	2.06 (1)	N1–C1	1.26 (2)
Rh–N4	2.10 (1)	N1–C10	1.41 (2)
Rh–N6	2.10 (1)	N2–C1	1.31 (2)
Rh–N8	2.20 (1)	N2–C18	1.45 (2)
Rh–C1	1.97 (1)	N3–C2	1.15 (1)
Rh–C2	1.86 (1)		
N1–Rh–N4	88.8 (4)	N8–Rh–C1	153.1 (6)
N1–Rh–N6	158.1 (4)	N8–Rh–C2	95.4 (5)
N1–Rh–N8	116.7 (4)	C1–Rh–C2	87.3 (5)
N1–Rh–C1	36.4 (5)	Rh–N1–C1	68.0 (8)
N1–Rh–C2	91.6 (5)	Rh–N1–C10	136.4 (9)
N4–Rh–N6	88.4 (4)	C1–N1–C10	125 (1)
N4–Rh–N8	85.2 (4)	C1–N2–C18	123 (1)
N4–Rh–C1	92.5 (5)	C2–N3–C3	174 (1)
N4–Rh–C2	179.0 (5)	Rh–C1–N1	75.6 (8)
N6–Rh–N8	84.7 (4)	Rh–C1–N2	145 (1)
N6–Rh–C1	122.1 (6)	N1–C1–N2	139 (1)
N6–Rh–C2	90.8 (5)	Rh–C2–N3	176 (1)

Even if a crystal structure for **2d** had not been obtained, the assignment of the structures for **2a–d** as containing a η^2-carbodiimide ligand would be possible from spectroscopic data alone. For instance, the IR spectrum of **2a** shows a strong absorption at 1724 cm^{-1} for the coordinated carbodiimide which is shifted drastically to lower energy relative to both the free carbodiimide (2137 cm^{-1}) and that expected for an N-bound complex.[8f,g] Additional evidence for the η^2-carbodiimide of **2a** comes from the $^{13}C\{^1H\}$ NMR spectrum at 100 MHz, which possesses a doublet at δ 140.3 with a coupling constant of 16.8 Hz and is assigned to the central carbon of the carbodiimide. The magnitude of the coupling constant is midway between that observed for a purely sp^3 carbon bound to rhodium in a strained metallacycle[20] and that observed for rhodium-coordinated ethylene[21] and strongly suggests that the carbon of the carbodiimide is directly bound to rhodium. Similar IR and $^{13}C\{^1H\}$ NMR spectra are also observed with complexes **2b–d**.

The structures of **2a–d** have been drawn formally as a metallaaziridine with the understanding that the bonding between any "alkene-like" ligand and a transition metal is actually a hybrid of two limiting resonance structures as shown in Figure 2. However, spectroscopic evidence seems to indicate that the dominant resonance form of **2a–d** at room temperature is the metallaaziridine. For example, the IR absorption at 2186 cm^{-1} for the isocyanide ligand in **2a** is clearly in the region for an isocyanide coordinated to a formally Rh(III) metal center.[22] Secondly, in accordance with Taube's rules for ligand substitution,[23] **2a–d** are inert toward fast exchange with added free isocyanide in solution, as would be expected for a formally Rh(III), d^6 low-spin transition-metal complex.[24] The ^{1}H NMR spectrum of **2a** in C_6D_6 to which several equivalents

---

(20) J_{RhC} = 19.1 Hz for $Cp^*RhCH_2CH_2CH_2$: Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346.

(21) J_{RhC} = 13.7 Hz for $Cp^*Rh(C_2H_4)_2$: Vasquez De Miguel, A.; Maitlis, P. M. *J. Organomet. Chem.* **1983**, *244*, C35.

(22) See IR spectrum for complex 5 in the Experimental Section.

(23) Taube, H. *Chem. Rev.* **1952**, *50*, 69.

(24) **2a** undergoes slow reaction with isocyanide over time, as will be discussed later.

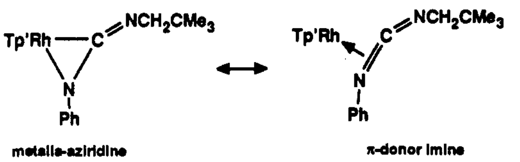


Figure 2. Limiting resonance structures for η^2-coordinated carbodiimide.

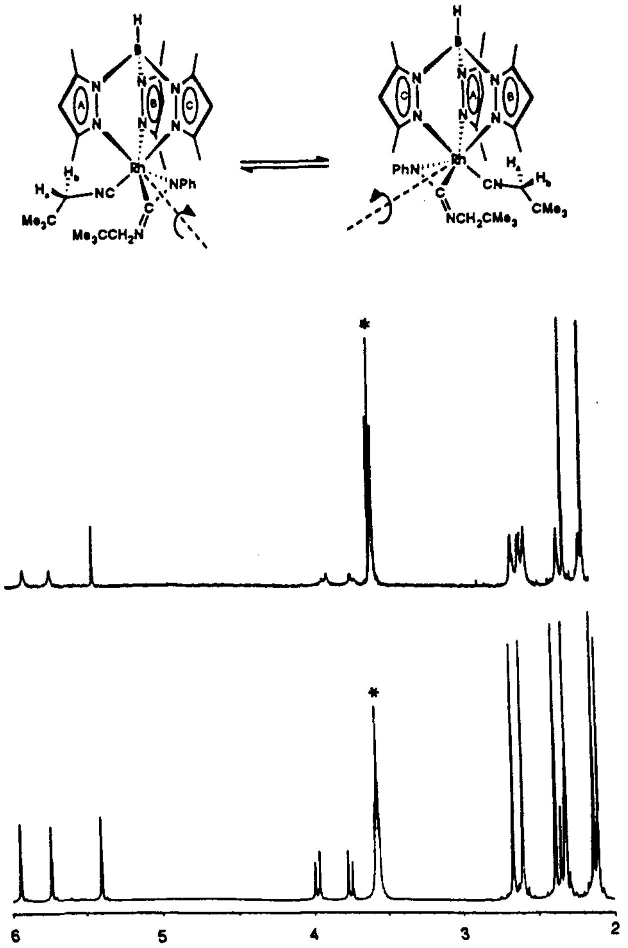


Figure 3. ^{1}H NMR spectra of **2a** in C_6D_6 at (a) 298 K and (b) 373 K. Solvent impurity resonances are marked with an asterisk (*).

of neopentyl isocyanide have been added shows separate resonances for both free and coordinated isocyanide, the inertness toward substitution consistent with observations made on other Tp'Rh(CNR)(X)(Y) complexes.[18,25] In contrast, the Rh(I) complexes **1a–d** undergo fast exchange with added isocyanide in solution.[18] The ^{1}H NMR spectrum of **1a** in the presence of added isocyanide shows broad peaks which are the averaged resonances for free and complexed isocyanide. Finally, the X-ray crystal structure of **2d** possesses a η^3-Tp' ligand which has been typically associated with rhodium complexes that are formally Rh(III) and octahedral.

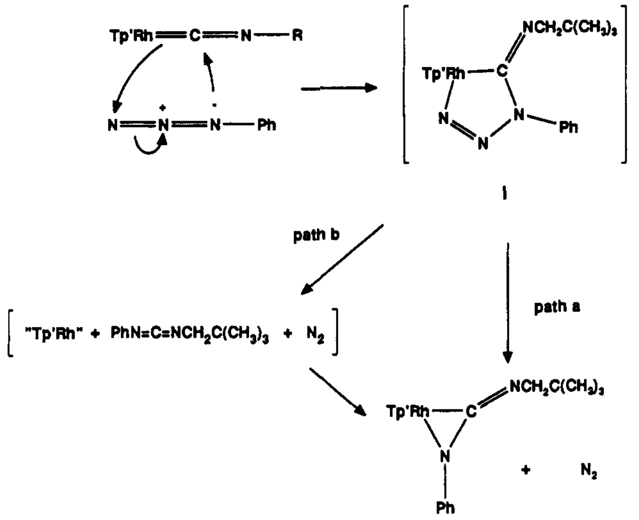
Despite the strong contribution of the metallaaziridine resonance form to **2a–d**, properties attributable to the π-donor resonance form become evident at higher temperatures in solution. The ^{1}H NMR spectrum of a benzene-d_6 solution of **2a** at 100 °C shows significant line broadening of the resonances associated with two of the three pyrazole rings of the Tp' ligand (Figure 3). Additionally, the diastereotopic methylene protons of the neopentyl isocyanide ligand at δ 3.752 and 3.976 begin to broaden. These observations are best rationalized by a propeller type rotation of the carbodiimide ligand about an axis drawn from the Rh atom through the center of the metal-bound C=N bond of the carbodiimide (Figure 3, insert). Such a rotation is well established for coordinated alkenes[26] and equilibrates enantiomers in the case of **2a**. The rapid enantiomer interconversion at 100 °C produces a ^{1}H NMR spectrum in which it appears that chirality is beginning to be lost at rhodium.

Table III. Chemical Shift and Line Width Data Used for Calculation of the Barrier to Rotation of the Carbodiimide Ligand in 2a at 373 K

chem shift, δ	line width,[b] Hz 298 K	line width,[b] Hz 373 K	ΔG^*(373 K), kcal/mol
5.395[a]	2.2	2.3	
5.732	2.2	6.0	20.2
5.940	2.0	6.5	20.0

[a] Resonance used as natural line width (W_f) at 373 K. [b] Measured at half-height.

Scheme I



The barrier to this process was determined by standard line-broadening techniques with eq 4.[27] Measurements

$$k = \pi(W - W_f) \qquad (4)$$

were made using the line widths at half height (W) at 100 °C for the two equilibrating pyrazole ring protons at δ 5.940 and 5.732 (Table III). The line width of the resonance at δ 5.395 is constant over the temperature range used for the measurement and is thus representative of the natural line width (W_f). The line widths at room temperature for all three resonances are equivalent, proving that the process is at the slow-exchange limit at this temperature. As expected, determination of the activation barrier to enantiomerization of **2a** using either of the two resonances gives a similar value of about 20 kcal/mol, which is substantially higher than the 15 kcal/mol determined for the rotation of ethylene in the closely related complex $CpRh(C_2H_4)_2$.[28]

Of the various 1,3-dipoles available,[29] phenyl azide was chosen because (1) it is easy to prepare, (2) it was thermally

---

(25) Jones, W. D.; Hessell, E. T. Submitted for publication in *J. Am. Chem. Soc.*

(26) Cramer, R.; Mrowca, J. J. *Inorg. Chim. Acta* **1971**, *5*, 528 and references within.

(27) Brookhart, M.; Lincoln, D. M.; Bennett, M. A.; Pelling, S. *J. Am. Chem. Soc.* **1990**, *112*, 2691.

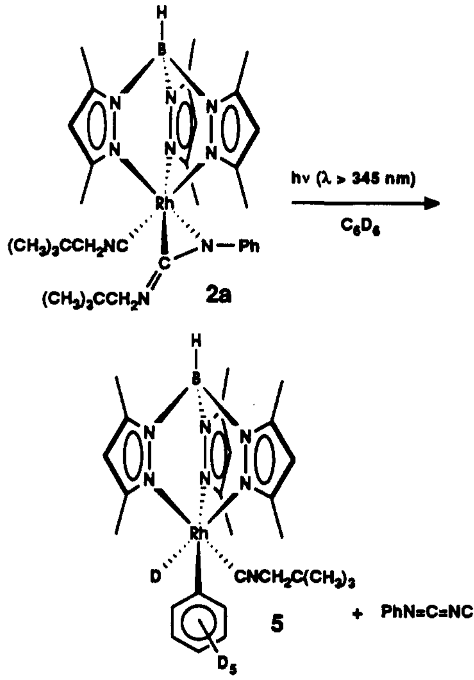
(28) (a) Cramer, R.; Kline, J. B.; Roberts, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 2519. (b) Cramer, R. *J. Am. Chem. Soc.* **1964**, *86*, 217.

(29) Padwa, A., Ed. *1,3-Dipolar Cycloaddition Chemistry*; Wiley: New York, 1984.

stable and did not have to be generated in situ,[14b] and (3) its stoichiometry could be easily controlled as opposed to gaseous 1,3-dipoles such as N_2O.[14b] The reaction of phenyl azide with complexes 1 is extremely fast and highly exothermic. A reaction conducted at -95 °C in THF-d_8 in the NMR probe showed only product within the time it took to acquire an FID. No evidence for an intermediate (see Scheme I) was observed. One rather interesting aspect to the reaction of eq 2 is that the product, 2, still bearing an additional isocyanide ligand, does not undergo further reaction with excess azide in solution. This observation further attests to the metallaaziridine structure proposed for 2 in which the electron-deficient Rh(III) can no longer undergo π-back-bonding to the remaining isocyanide ligand, a requirement for "M═C" bond character.

An important feature of the reaction of eq 2 is the regiospecificity of the carbodiimide coordination. Complexes **2a–d**, to the best of our knowledge, are the first examples of carbodiimide complexes of rhodium as well as one of only two complexes containing an *unsymmetrical* η^2-carbodiimide.[16] Only one of two possible isomers resulting from coordination of either C═N bond of the unsymmetrical carbodiimide is detected.[30] Mechanistic possibilities for this reaction are shown in Scheme I. It is predicted that the first step leading to the formation of intermediate I is a 1,3-dipolar cycloaddition reaction which in general is highly regioselective, especially when the dipolarophile is polarized, as would be expected for the "Rh═C" bonds in 1. Therefore, the regiospecific formation of the five-membered intermediate I from the azide and 1 is anticipated.[31] The observed regiospecificity of the overall reaction is most consistent with a mechanism in which the formation of the carbodiimide–nitrogen bond in 2 is concerted with the expulsion of nitrogen from the five-atom metallacycle intermediate I (Scheme I, path a). An alternative mechanism (Scheme I, path b) would involve formation of free carbodiimide and a coordinatively unsaturated metal fragment which would then rapidly recombine (a process analogous to adding free carbodiimide to a coordinatively unsaturated metal center). This latter mechanism, however, appears unlikely since the reaction of **1a** with phenyl azide in benzene shows no formation of the phenyl hydride **5**, despite the fact that (1) benzene is typically present in approximately 400:1 molar excess to free carbodiimide **6** and (2) **5** is formed quantitatively from **2a** in photolysis experiments (vide infra), where it has been assumed that light acts to dissociate the carbodiimide ligand to give a coordinatively unsaturated metal center.

Reactivity of Tp′Rh(CNR)(η^2-PhN═C═NR). The carbodiimide ligand of **2a** has been found to be extremely photolabile. Irradiation of a benzene-d_6 solution of **2a** in an NMR tube with λ > 345 nm for 10 min results in a complete bleaching of the originally bright yellow solution. ^1H NMR analysis of the solution shows clean formation of Tp′Rh(D)(C_6D_5)(CN-neopentyl) (**5a**)[32] along with an equal amount of *N*-phenyl-*N*′-neopentylcarbodiimide (**6**; eq 5). Additionally, the high solubility of **2a** in the generally nonpolar alkanes has allowed for the preparation of a vast number of C–H activated products in high yield

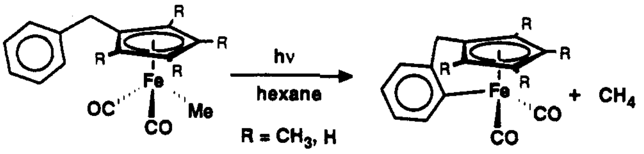


(5)

which were previously unaccessible by direct photolysis of 1,[25] which is relatively insoluble in alkanes. The only disadvantage that can be perceived thus far is that free carbodiimide is generated in conjunction with the products.

The photolysis of **2a** in benzene to give **5a** is orders of magnitude faster than the corresponding reaction with Tp′Rh(CN-neopentyl)$_2$.[33] One factor contributing to this is that the reaction solution becomes lighter as the reaction progresses (i.e., the photolysis becomes more efficient as the reaction proceeds). It is therefore easy to obtain complete conversion of **2a** to products. This is in stark contrast to photochemical reactions of Cp*Ir(H)$_2$(PMe$_3$)[34] and Cp*Rh(H)$_2$(PMe$_3$)[35] leading to C–H activated products, where the formation of trace colored impurities early on in the photolysis slows the reaction to the point where complete conversion to products is not possible. It should be noted that the favorable color change observed in the photochemical reaction of **2a** in benzene is unique among this series of complexes. The corresponding photolyses of **2b,c** in benzene result in a darkening of the reaction solutions. Although complete conversion of **2b,c** to Tp′Rh(D)(Ph-d_5)(CNMe) (**5b**) and Tp′Rh(D)(Ph-d_5)(CN-2,6-xylyl) (**5c**) can be obtained, the rate of their formation is considerably slower.

The quantum yield for the formation of **5a** from **2a** in benzene measured at 366 nm is 1.0 ± 0.3. Although the error in this measurement is significant, the value indicates that photoefficiency is high. Similar quantum yields have been determined for other types of ligand photodissociative processes. Wrighton has reported $\phi_{366nm} = 0.40$ for the intramolecular reaction shown in eq 6, where R = CH_3.[36]



(6)

---

[30] All of the previously reported complexes containing a carbodiimide ligand except for those of Bergman[8] and Werner[16] have been prepared by direct addition of a free carbodiimide to either a coordinatively unsaturated or electron-deficient metal center. Such an approach requires the use of a symmetrical carbodiimide to avoid the formation of two products.

[31] Chetcuti, P. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1987**, *109*, 942.

[32] Complex **5** was converted to the more stable aryl chloride analogue Tp′Rh(Cl)(Ph)(CN-neopentyl) (**10**), which was fully characterized (see Experimental Section).

[33] Jones, W. D.; Duttweiler, R. P.; Feher, F. J.; Hessell, E. T. *New J. Chem.* **1989**, *13*, 725.

[34] Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

[35] (a) Periana, R. A.; Bergman, R. G. *Organometallics* **1984**, *3*, 508. (b) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650.

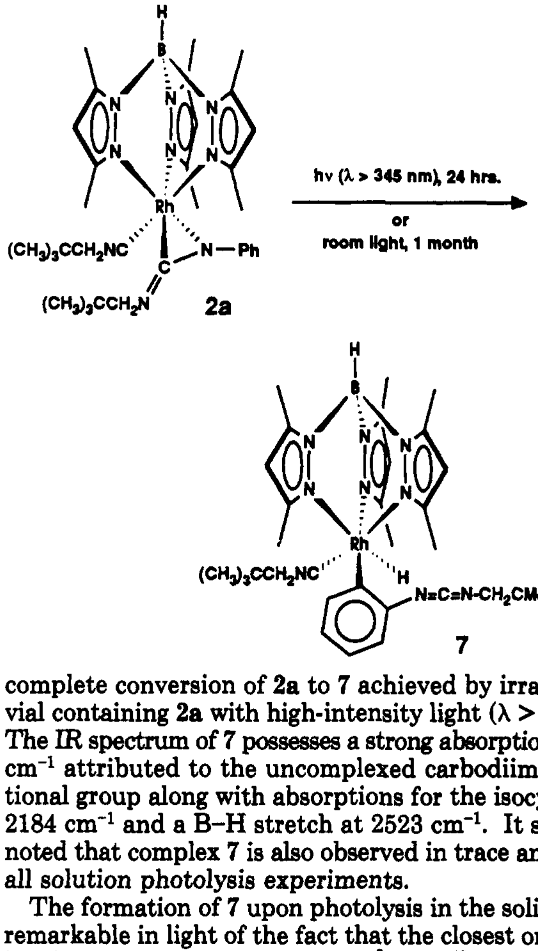
However, for the analogous reaction where R = H, the quantum yield decreases to 0.05. From reactions conducted in the presence of PPh_3 it was shown that the decrease in quantum yield was due to the efficient thermal back-reaction of CO in the case where R = H. Geoffroy has measured a quantum yield of 0.07 ± 0.02 for the loss of H_2 from $Re(diphos)_2H_3$[37] (diphos = 1,2-bis(diphenylphosphino)ethane) and $\phi_{366} = 0.1 \pm 0.02$ for loss of H_2 from Cp_2MoH_2.[38] Sutton has reported the rapid photochemical dissociation of N_2 from $Cp^*Re(CO)(PMe_3)(N_2)$ in benzene to give the C–H activation product $Cp^*Re(H)(Ph)(CO)(PMe_3)$.[39] Graham has shown that photodissociation of CO from $Tp'Rh(CO)_2$ is rapid;[40] however, in order to obtain C–H activated products efficiently, it is necessary to use a nitrogen purge to remove the free CO. The photochemical reactivity of **2a** also toward benzene is superior to that of $Cp^*Ir(CO)(\eta^2\text{-}CNC_6H_4Cl)$, which, although bound by an η^2-CN moiety, requires hours of photolysis to produce C–H addition products.[14c] Although no formal measurement of quantum yield was done by Sutton, Graham, or Hawthorne, the reported times for product formation in each instance suggests high quantum efficiency for these systems.

Assuming that loss of carbodiimide is the photochemical step in eq 5, it appears that the free carbodiimide, once generated, cannot effectively compete with the C–H bonds of solvent molecules for the vacant site on the metal. In fact, for all intents and purposes it appears that photodissociation of carbodiimide from **2** is thermally irreversible. Attempts to form **2a** independently by addition of a large excess of **6** to a solution of **5a** in cyclohexane or THF followed by heating at 100 °C only resulted in decomposition. Alkyl hydride complexes (generated by photolysis of **2a** in an alkane solvent) prefer to decompose slowly over time rather than reductively eliminate alkane and recoordinate free carbodiimide present in solution.[25] Therefore, the high observed quantum efficiency for C–H activation of solvent by **2a** arises from the absence of a pathway for thermal back-reaction of the carbodiimide with the coordinatively unsaturated intermediate (Tp′Rh(CN-neopentyl)), a favorable attribute which is not present in most photochemical ligand dissociations.

Heating of a solution of **2a** in benzene at 100 °C results in clean formation of **5a** with an observed first-order rate constant of 1.2×10^{-5} s^{-1} corresponding to an activation barrier of 30.4 kcal/mol. However, this method is only suitable for the preparation of arene C–H activated products since the products of alkane C–H activation are unstable above room temperature.[25]

Irradiation of the Cp* complex **4** for up to 24 h in C_6D_6 results in no reaction. This was surprising since the Tp′ and Cp* ligands are considered to be both sterically and electronically similar, and the two complexes have similar CNR stretching frequencies.[41] On the basis of previous studies it would at least be expected that photolysis of **4** would lead to the formation of the binuclear complex $[Cp^*Rh(\mu\text{-}CN\text{-}neopentyl)]_2$.[42] The lowest energy electronic absorption of **2a** (384 nm, ϵ = 3800 M^{-1} cm^{-1}) is, however, at higher energy than that of **4** (448 nm, ϵ = 780 M^{-1} cm^{-1}).

The high degree of photolability of the carbodiimide ligand in **2a** is further illustrated by the observation that **2a** undergoes reaction *in the solid state* when exposed to light. Exposure of a 10-mg sample of **2a** to room light for 1 month results in a bleaching of the originally yellow solid. The ^1H NMR spectrum in C_6D_6 shows a 1:1 mixture of **2a** and a new product containing a hydride resonance at δ −13.348 (J_{HRh} = 22.5 Hz) along with resonances in the aryl region at δ 6.658, 6.978, 7.216, and 7.362 in a 1:1:1:1 ratio. The observed coupling pattern of the phenyl resonances shows that the carbodiimide has undergone intramolecular activation at the ortho C–H bond of the phenyl ring to give **7** (eq 7). This solid-state reaction can be accelerated and complete conversion of **2a** to **7** achieved by irradiating a vial containing **2a** with high-intensity light (λ > 345 nm). The IR spectrum of **7** possesses a strong absorption at 2133 cm^{-1} attributed to the uncomplexed carbodiimide functional group along with absorptions for the isocyanide at 2184 cm^{-1} and a B–H stretch at 2523 cm^{-1}. It should be noted that complex **7** is also observed in trace amounts in all solution photolysis experiments.



2a

7

(7)

The formation of **7** upon photolysis in the solid state is remarkable in light of the fact that the closest ortho C–H bond of the phenyl ring is some 4 Å away[43] and is attached to a fairly rigid framework. Any conventional mechanism would require the formation of an open site at the metal prior to oxidative addition. It is possible that in the solid state the photodissociated carbodiimide cannot travel far from the metal center and in essence the reaction occurs with a "cage" as shown in Scheme II, path a. One could also speculate that the vacant site on the metal arises from photodissociation of one of the rings on the Tp′ ligand, thereby allowing for intramolecular C–H activation prior to dissociation of the carbodiimide C═N bond (Scheme II, path b). Whatever the mechanism, the process in solution competes with intramolecular activation to the extent that trace amounts of **7** can be witnessed by ^1H NMR spectroscopy in all of the photochemical reactions of **2a** in alkane and aromatic solvents.[25]

---

(36) Blaha, J. P.; Dewan, J. C.; Wrighton, M. S. *Organometallics* **1986**, *5*, 899.

(37) Bradley, M. G.; Roberts, D. A.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 379.

(38) Geoffroy, G. L.; Bradley, M. G. *Inorg. Chem.* **1978**, *17*, 2410.

(39) Klahn-Oliva, A. H.; Singer, R. D.; Sutton, D. *J. Am. Chem. Soc.* **1986**, *108*, 3107.

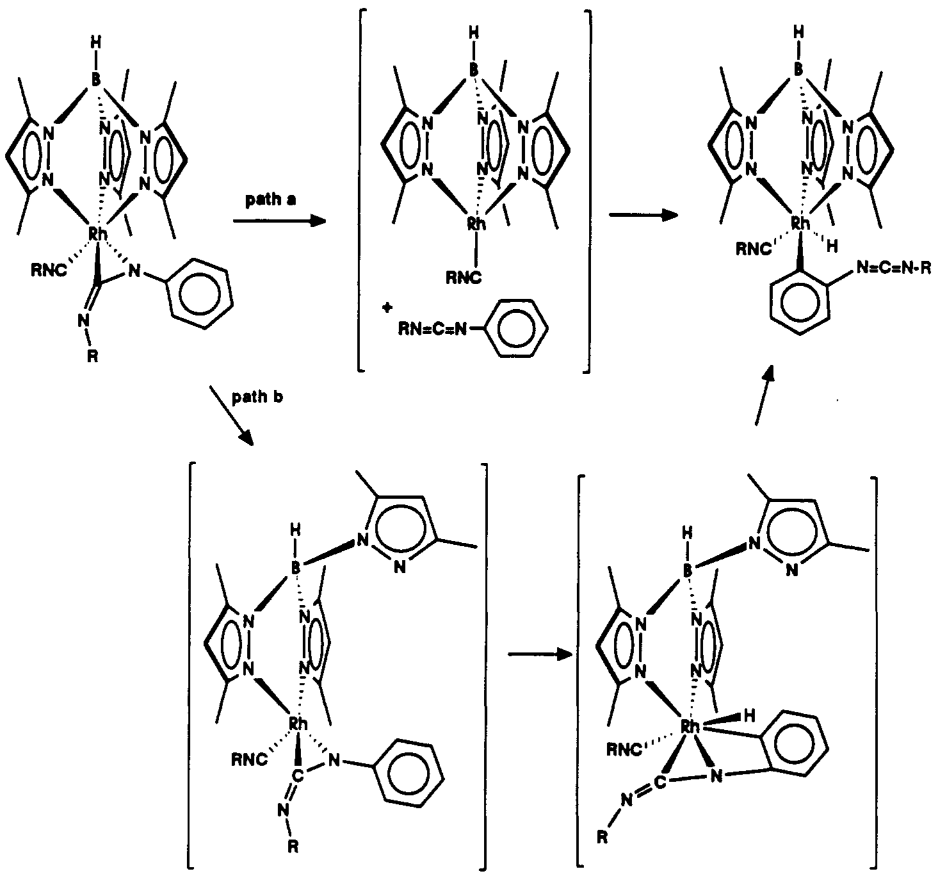
(40) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726.

(41) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3904.

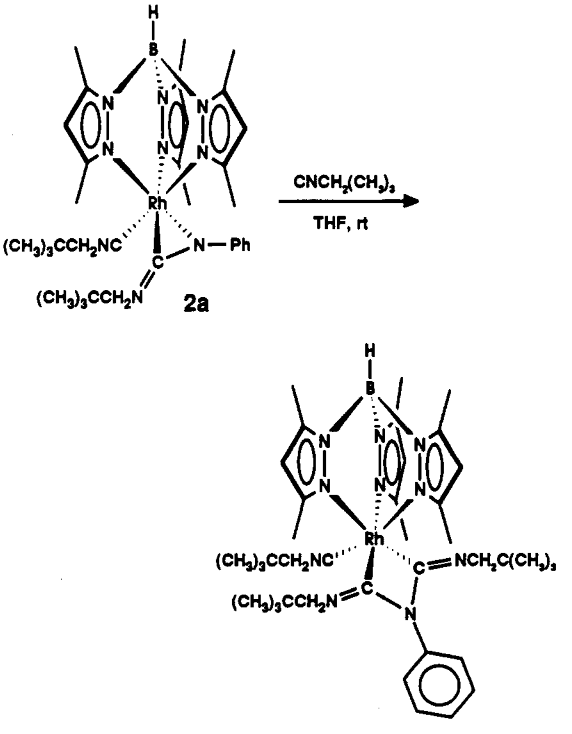
(42) (a) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 686. (b) Jones, W. D.; Duttweiler, R. P.; Feher, F. J. *Inorg. Chem.* **1990**, *29*, 1505.

(43) Estimated from the C16–Rh distance in the crystal structure of **2d**.

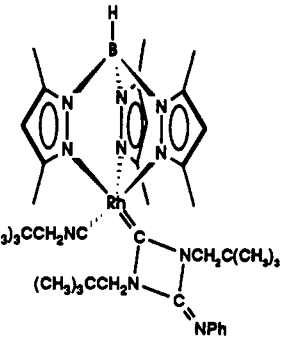
Scheme II



Reaction of **2a** with an excess of neopentyl isocyanide in tetrahydrofuran does not give back complex **1a** and free carbodiimide. Instead, isocyanide inserts into the metal–nitrogen bond of the carbodiimide ligand of **2a** to give **8** (eq 8) and indicates that an alternative reaction pathway other than carbodiimide loss is possible. The structural assignment for **8** relies heavily on the ^{1}H NMR spectrum in C_6D_6, which possesses four resonances in a 1:2:2:1 ratio between δ 2.1 and 2.6 and two resonances at δ 5.64 and 5.73 in a 2:1 ratio, indicating the existence of a plane of symmetry bisecting the Tp′Rh moiety. A singlet at δ 2.54 (2 H) is assigned to the methylene of an isocyanide ligand and is consistent with lack of chirality at rhodium. Most significant to the structural assignment are two doublet resonances (J = 13.1 Hz) at δ 2.96 and 3.57 that are integrated to a total of four protons relative to the Tp′ ligand, consistent with two equivalent methylene groups, each containing nonequivalent protons. It should be noted that the alternative structure **9** (Figure 4) would also be compatible with the observed NMR data;[44] however, we favor **8** on the basis of strong literature precedent.[45]



(8)



9

Figure 4. Alternate structure for **8**.

In order to gain some information about the mechanism of formation of **8**, the rate of reaction of **2a** with isocyanide

---

(44) Aumann, R.; Heinen, H. *Chem. Ber.* **1988**, *121*, 1085.

(45) (a) Riera, V.; Ruiz, J.; Tiripicchio, A.; Camellina, M. T. *J. Organomet. Chem.* **1987**, *327*, C5. (b) Fehlhammer, W. P.; Christian, G.; Mayr, A. *J. Organomet. Chem.* **1980**, *199*, 87. (c) Werner, H.; Heiser, B.; Linse, K.; Ziegler, M. L. *J. Organomet. Chem.* **1986**, *308*, 47.

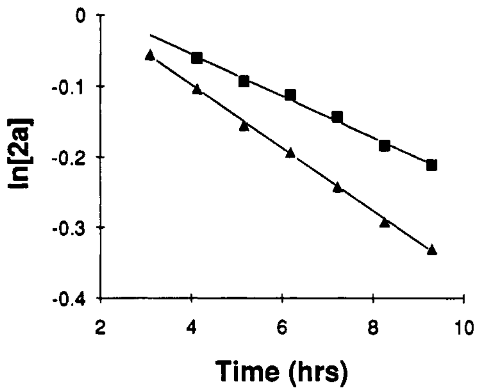


Figure 5. Plot of ln [**2a**] vs time for the formation of **8** from **2a** (11 mM) at 25 °C as a function of added isocyanide concentration: (■) [CNR] = 31 mM (k = 8.1 (3) × 10^{-6} M^{-1} s^{-1}); (▲) [CNR] = 62 mM (k = 1.20 (2) × 10^{-5} M^{-1} s^{-1}).

was measured at two different isocyanide concentrations by ^1H NMR spectroscopy (Figure 5). Although the observed dependency was not first order in isocyanide, the effect of increased isocyanide concentration on the rate of reaction suggests that an associative mechanism is operative.

Conclusions

This work has shown that reaction of the electron-rich rhodium complexes $LRh(CNR)_2$ (L = Tp′, Cp*) with aryl azides serves as a general method for the preparation of the complexes $LRh(CNR)(\eta^2\text{-aryl-N=C=NR})$ containing an unsymmetric carbodiimide ligand. Initial reactivity studies indicate that photolysis of the carbodiimide complexes in arene solvents affords stable products of C–H activation with high quantum efficiency. Further studies of the solution reactivity of these complexes with less activated C–H bonds are forthcoming.[25]

Experimental Section

All operations and routine manipulations were performed under a nitrogen atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corp. Dri-Lab. Tetrahydrofuran, benzene, and toluene were distilled from dark purple solutions of benzophenone ketyl. The deuterated analogues were dried similarly and stored in ampules possessing a Teflon-sealed stopcock and vacuum-line adapter. Hexane was stirred for 24 h over concentrated sulfuric acid, washed sequentially with a solution of potassium permanganate in 10% aqueous sulfuric acid, water, and saturated sodium carbonate to remove unsaturated hydrocarbon impurities. The olefin-free hydrocarbons were then predried over calcium chloride before being distilled from a purple solution of benzophenone ketyl.

Bis(μ-chloro)tetrakis(ethylene)dirhodium(I),[46] the isocyanides,[47] and azides[48] were prepared according to literature methods, checked for purity by ^1H NMR spectroscopy, and stored in a freezer at −20 °C in the Dri-Lab to prevent decomposition. The azides were periodically redistilled to maintain their purity. The syntheses of Tp′Rh(neopentyl isocyanide)$_2$,[18] Tp′Rh(methyl isocyanide)$_2$,[18] Tp′Rh(2,6-xylyl isocyanide)$_2$,[18] and Cp*Rh(neopentyl isocyanide)$_2$[42] have been previously reported.

^1H NMR (400.13 MHz) spectra were recorded on a Bruker AMX 400 spectrometer. ^{13}C NMR spectra were recorded on either a Bruker AMX 400 spectrometer at 100 MHz or a Nicolet QE-300 spectrometer at 75 MHz. The chemical shifts of all resonances are reported in δ (ppm) relative to those of tetramethylsilane using the residual resonances of the deuterated solvents as an internal reference (^1H, benzene δ 7.15, tetrahydrofuran δ 3.58, toluene δ 2.09; ^{13}C, benzene δ 128, tetrahydrofuran δ 25.3). Infrared spectra were recorded on a Mattson Instruments, Inc., Sirius 100 infrared spectrometer. Ultraviolet–visible spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Elemental analyses were performed by Desert Analytics. All photolyses were conducted with an Oriel arc source using a 200-W Hg(Xe) bulb (Oriel part No. 6291). Quantum yields were determined using a chemical actinometer[49] at 366 nm (standard band-pass filter).

***N*-Phenyl-*N*′-neopentylcarbodiimide.**[50] To a stirred solution of 3.10 g (22.9 mmol) of phenyl isothiocyanate in 40 mL of tetrahydrofuran at 0 °C was added dropwise over a 10-min period 2.0 g (22.9 mmol) of neopentylamine. The reaction was stirred overnight at room temperature and the solvent evaporated under vacuum. The residue was recrystallized from 2-propanol to give the intermediate thiourea in essentially quantitative yield.

The thiourea was dissolved in 40 mL of acetone along with 7.0 g of mercuric oxide (Merck). The reaction mixture was stirred for 24 h at room temperature and filtered to remove insolubles. To the filtrate was added a second portion of 7.0 g of mercuric oxide, and the mixture was stirred for an additional 14 h at room temperature. The reaction mixture was filtered to remove insolubles, and the filtrate was evaporated in vacuo to give a pale yellow liquid. The crude product was pure, as determined by ^1H NMR spectroscopy. All attempts to purify the crude product resulted in decomposition. The product was stored in a freezer at −10 °C and separated into two phases over time; however, a ^1H NMR spectrum of the mixture showed it to be a single product. It is well-known that carbodiimides can exist as dimers similar to ketenes. It is quite possible that the liquid monomeric carbodiimide exists in an equilibrium with the dimer, which is a solid, and that only the monomer exists in solution. ^1H NMR (C_6D_6): δ 0.769 (s, 9 H, *t*-Bu), 2.745 (s, 2 H, NCH_2), 6.871 (t, J = 7.4 Hz, 1 H, aryl H), 7.050 (t, J = 7.5 Hz, 2 H, aryl H), 7.175 (dt, J_1 = 7.5 Hz, J_2 = 0.9 Hz, 2 H, aryl H). ^{13}C NMR (C_6D_6): δ 26.9 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 58.6 (NCH_2), 123.9 (aryl C), 124.5, (aryl C), 129.6 (aryl C), 141.7 (aryl C_q); N=C=N was not observed. IR (C_6H_6): 2137 cm^{-1} (s), 1593 (m). MS (70 eV): m/z 188 (M^+).

Tp′Rh(2-tolyl isocyanide)$_2$ (1d). To a stirred suspension of 243 mg (0.625 mmol) of bis(μ-chlorotetrakis(ethylene)dirhodium(I) in 5 mL of benzene was added dropwise a solution of 285 mg (2.500 mmol) of 2-tolyl isocyanide in 3 mL of benzene. The originally orange suspension turned dark during the addition and became homogeneous. The reaction mixture was stirred for approximately 18 h and 420 mg (1.25 mmol) of potassium hydrotris(3,5-dimethylpyrazolyl)borate added, resulting in the formation of a bright red-orange solution over the next 30 min. The reaction mixture was stirred for 4 h and then filtered to remove potassium chloride. The filtrate was evaporated in vacuo to give a red glass, which was recrystallized from toluene at −20 °C; yield 306 mg (38%) of red microcrystals. ^1H NMR (C_6D_6): δ 2.095 (s, 6 H, aryl CH_3), 2.231 (s, 9 H, pz CH_3), 2.486 (s, 9 H, pz CH_3), 5.774 (s, 3 H, pz H), 6.62–6.71 (complex mult, 4 H, aryl H), 6.855 (d, J = 8.0 Hz, 2 H, aryl H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.997, 15.507, 18.546 (CH_3), 105.758 (pz CH), 125.350, 126.740, 127.262, 130.119, 130.561, 134.572, 144.428, 148.741 (C_{aryl} and/or pz C_q), 161.078 (d, J = 68 Hz, CNR). IR (KBr): 2467 cm^{-1} (B–H); 2121, 2035 cm^{-1} (CNR). Anal. Calcd (found) for $C_{31}H_{36}BN_8Rh$: C, 58.7 (58.8); H, 5.7 (5.7); N, 17.7 (17.7).

Tp′Rh(neopentyl isocyanide)(η^2-*N*-phenyl-*N*′-neopentylcarbodiimide) (2a). To a stirred suspension of 333 mg (0.560 mmol) of **1a** in 5 mL of a 3:1 hexane–THF solvent mixture was added dropwise a solution of 77 mg (0.700 mmol) of phenyl azide in 1 mL of hexane. The addition was conducted at such a rate as to allow the N_2 evolution to cease between drops of azide solution. The reaction mixture was filtered through a cotton plug to remove insolubles. The filtrate was cooled to −20 °C, during which time a flocculent precipitate formed. The beige solid was isolated by filtration and redissolved in approximately 5 mL of a 3:1 hexane–THF solvent mixture. After the solution was cooled

---

(46) Cramer, R. *Inorg. Synth.* **1974**, *15*, 14.

(47) (a) Ugi, I. *Isonitrile Chemistry*; Academic Press: New York, 1971. (b) Jones, W. D.; Kosar, W. P. *Organometallics* **1986**, *5*, 1823.

(48) Lindsay, R. O.; Allen, C. F. H. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. 3, p 710.

(49) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 341.

(50) Stevens, C. L.; Singhal, G. H.; Ash, A. B. *J. Org. Chem.* **1967**, *32*, 2895.

at −20 °C for 24 h, the pale yellow solid was isolated by filtration and dried under vacuum; yield 286 mg (74%). ^{1}H NMR (THF-d_8): δ 0.775 (s, 9 H, $C(CH_3)_3$), 1.050 (s, 9 H, $C(CH_3)_3$), 2.020 (s, 3 H, pz CH_3), 2.332 (s, 3 H, pz CH_3), 2.343 (s, 3 H, pz CH_3), 2.412 (s, 3 H, pz CH_3), 2.419 (s, 3 H, pz CH_3), 2.521 (s, 3 H, pz CH_3), 3.262 (d, *J* = 14.3 Hz, 1 H, NCH_2), 3.337 (d, *J* = 14.3 Hz, 1 H, NCH_2), 3.385 (d, *J* = 12.5 Hz, 1 H, NCH_2), 3.641 (d, *J* = 12.5 Hz, 1 H, NCH_2), 5.513 (s, 1 H, pz H), 5.783 (s, 1 H, pz H), 5.847 (s, 1 H, pz H), 6.660 (t, *J* = 7.5 Hz, 1 H, aryl H_p), 7.023 (t, *J* = 7.7 Hz, 2 H, aryl H_m), 7.426 (d, *J* = 7.6 Hz, 2 H, aryl H_o). ^{13}C NMR (THF-d_8): δ 12.269, 12.949, 13.239, 13.393, 15.214, 17.373 (pz CH_3), 26.826, 28.597 ($C(CH_3)_3$), 32.475, 33.069 ($\mathit{C}(CH_3)_3$), 35.468, 57.039 (NCH_2), 106.083, 106.643, 108.487 (pz CH), 119.197, 120.983, 129.022 (C_{aryl}), 138.550 (d, *J* = 60 Hz, *C*≡N) 140.303 (d, *J* = 16.8 Hz, carbodiimide C), 143.796, 143.865, 144.754, 148.257, 150.494, 151.366, 153.088 (pz C_q and/or aryl C_q). IR (KBr): 2525 cm^{-1} (B–H); 2186 cm^{-1} (CNR); 1724, 1589 cm^{-1} (N=C=N). UV–vis (hexane; nm (ε, cm^{-1} M^{-1})): 384 (3800). Anal. Calcd (found) for $C_{33}H_{49}BN_9Rh$: C, 57.8 (59.2); H, 7.2 (7.6); N, 18.4 (15.6).

Tp′Rh(methyl isocyanide)(η^2-*N*-phenyl-*N*′-methylcarbodiimide) (2b). To a stirred suspension of 163 mg (0.338 mmol) of **1b** in 3 mL of toluene was added dropwise 45 μL (0.378 mmol) of phenyl azide. The reaction mixture turned dark during the addition, and a vigorous evolution of gas ensued. The mixture was stirred for 4 h at room temperature during which time a yellow precipitate formed. The precipitate was isolated by filtration, giving 165 mg (89%) of product. ^{1}H NMR (C_6D_6): δ 1.605 (s, 3 H, NCH_3), 2.102 (s, 3 H, pz CH_3), 2.158 (s, 3 H, pz CH_3), 2.259 (s, 3 H, pz CH_3), 2.310 (s, 3 H, pz CH_3), 2.463 (s, 3 H, pz CH_3), 2.520 (s, 3 H, pz CH_3), 3.870 (s, 3 H, NCH_3), 5.343 (s, 1 H, pz H), 5.701 (s, 1 H, pz H), 5.937 (s, 1 H, pz H), 6.794 (t, *J* = 8.0 Hz, 1 H, aryl H), 7.126 (t, *J* = 7.7 Hz, 1 H, aryl H), 7.860 (d, *J* = 8.4 Hz, 1 H, aryl H). ^{13}C{^{1}H} NMR (C_6D_6): δ 12.160, 12.736, 13.106, 13.349, 14.811, 16.509 (pz CH_3), 27.799, 40.574 (NCH_3), 105.908, 106.278, 108.347 (pz CH), 119.211, 120.534, 129.245 (aryl CH), 140 (CNR), 142.809 (d, *J* = 17 Hz, carbodiimide C), 143.470, 143.586, 144.265, 147.917, 150.156 (pz C_q), 150.738 (aryl C_q), 152.879 (pz C_q). Anal. Calcd (found) for $C_{25}H_{33}BN_9Rh$: C, 52.38 (51.28); H, 5.80 (6.33); N, 21.99 (17.66).

Tp′Rh(2,6-xylyl isocyanide)(η^2-*N*-phenyl-*N*′-2,6-xylylcarbodiimide) (2c). To a stirred solution of 145 mg (0.219 mmol) of **1c** in 4 mL of a 3:1 hexane–THF solvent mixture was added dropwise 30 μL (0.252 mmol) of phenyl azide. The solution turned dark during the addition. The solvent was evaporated, and the residue was triturated with hexane. The remaining orange solid was dried in vacuo to give 127 mg (77%) of the product. ^{1}H NMR (C_6D_6): δ 1.677 (s, 6 H, aryl CH_3), 1.723 (s, 3 H, pz CH_3), 2.016 (s, 3 H, pz CH_3), 2.131 (s, 3 H, pz CH_3), 2.207 (s, 3 H, pz CH_3), 2.397 (s, 3 H, pz CH_3), 2.463 (br s, 6 H, aryl CH_3), 2.637 (s, 3 H, pz CH_3), 5.461 (s, 1 H, pz H), 5.611 (s, 1 H, pz H), 5.763 (s, 1 H, pz H), 6.404 (d, *J* = 7.5 Hz, 2 H, aryl H), 6.596 (complex mult, 2 H, aryl H), 6.937 (complex mult, 2 H, aryl H), 7.057 (d, *J* = 7.0 Hz, 1 H, aryl H), 7.296 (t, *J* = 7.5 Hz, 2 H, aryl H), 8.169 (d, *J* = 7.5 Hz, 2 H, aryl H). ^{13}C{^{1}H} NMR (C_6D_6): δ 12.261, 12.747, 13.142, 14.145, 14.650, 14.736 (pz CH_3), 17.989, 20.018 (aryl CH_3), 106.043, 106.202, 109.331 (pz CH), 120.009, 120.581, 121.955, 126.443, 130.823 (aryl CH or aryl C_q), 133.649 (d, *J* = 16.5 Hz, carbodiimide C), 134.256, 134.942, 143.454, 143.658, 144.337, 145.848, 148.156, 150.032, 151.903, 153.320 (aryl CH, aryl C_q, or pz C_q). Two resonances are presumably obscured by the solvent resonance. The isocyanide carbon was not observed. IR (KBr): 2532 cm^{-1} (B–H); 2149 cm^{-1} (CNR); 1713 cm^{-1} (N=C=N). UV–vis (hexane; nm (ε, cm^{-1} M^{-1})): 276 (19000), 390 (2000), 470 (900). Anal. Calcd (found) for $C_{39}H_{45}BN_9Rh$: C, 62.16 (62.22); H, 6.02 (5.92); N, 16.73 (16.87).

Tp′Rh(2-tolyl isocyanide)(η^2-*N*-2,4-xylyl-*N*′-2-tolylcarbodiimide) (2d). The synthesis of **2d** was identical with that of **2a** except that 120 mg (0.189 mmol) of **1d** was used with 30 mg (0.236 mmol) of 2,4-xylyl azide. The crude product was recrystallized from a 3:1 hexane–THF solvent mixture to give 92 mg (65%) of product as dark brown mushroom-shaped crystals. ^{1}H NMR (C_6D_6): δ 1.800 (s, 3 H, CH_3), 1.876 (s, 3 H, CH_3), 2.063 (s, 3 H, CH_3), 2.100 (s, 3 H, CH_3), 2.123 (s, 3 H, CH_3), 2.218 (s, 3 H, CH_3), 2.239 (s, 3 H, CH_3), 2.383 (s, 3 H, CH_3), 2.621 (s, 3 H, CH_3), 2.824 (s, 3 H, CH_3), 5.562 (s, 1 H, pz H), 5.628 (s, 1 H, pz H), 5.833 (s, 1 H, pz H), 6.48–6.65 (complex mult, 4 H, aryl H), 6.8–7.0 (complex mult, 4 H, aryl H), 7.289 (d, *J* = 7.3 Hz, 1 H, aryl H), 7.738 (d, *J* = 7.7 Hz, 1 H, aryl H), 8.439 (d, *J* = 7.7 Hz, 1 H, aryl H). ^{13}C{^{1}H} NMR (C_6D_6): δ 12.150, 12.811, 13.116, 14.087, 14.546, 14.746, (pz CH_3), 18.087, 18.576, 19.291, 21.154 (aryl CH_3), 105.887, 106.376, 109.025 (pz CH), 120.009, 121.300, 122.128, 126.398, 126.755, 127.112, 127.294, 128.762, 129.889, 130.506, 130.567, 131.510, 131.944, 133.114, 134.615, (pz C_q, aryl CH, or aryl C_q), 142.255 (d, *J* = 17 Hz, N=C=N), 142.983, 143.713, 143.863, 144.286 (pz C_q, aryl CH, or aryl C_q), 148.320 (d, *J* = 63 Hz, CN aryl), 149.486, 150.375, 151.678, 153.239 (pz C_q, aryl CH, or aryl C_q). IR (KBr): 2525 cm^{-1} (B–H); 2062 cm^{-1} (CNR); 1732 cm^{-1} (N=C=N). Anal. Calcd (found) for $C_{39}H_{45}BN_9Rh{\cdot}C_7H_8$: C, 65.33 (65.40); H, 6.32 (6.21); N, 14.91 (14.45).

Cp*Rh(neopentyl isocyanide)(η^2-*N*-phenyl-*N*′-neopentylcarbodiimide) (4). To a stirred solution of 80 mg (0.185 mmol) of **3a** in 3 mL of hexane was added dropwise a solution of 20 mg (0.185 mmol) of phenyl azide in 1 mL of hexane. The dark brown solution was cooled to −20 °C for 3 days, during which time copper-colored platelets of the product formed. The crystals were isolated by filtration and dried in vacuo; yield 45 mg (46%). ^{1}H NMR (C_6D_6): δ 0.461 (s, 9 H, $C(CH_3)_3$), 1.334 (s, 9 H, $C(CH_3)_3$), 1.876 (s, 15 H, $C_5(CH_3)_5$), 2.345 (AB q, J_1 = 15 Hz, J_2 = 25 Hz, 2 H, NCH_2), 3.574 (d, *J* = 11 Hz, 1 H, NCH_2), 3.804 (d, *J* = 11 Hz, 1 H, NCH_2), 6.700 (d, *J* = 8 Hz, 1 H, aryl H), 6.920 (t, *J* = 8 Hz, 1 H, aryl H), 7.768 (d, *J* = 8 Hz, 1 H, aryl H). ^{13}C{^{1}H} NMR (THF-d_8): δ 10.9 ($Cp(CH_3)_3$), 26.6, 28.8 ($C(CH_3)_3$), 32.3, 32.7 ($\mathit{C}(CH_3)_3$), 56.2, 68.3 (NCH_2), 119.7, 121.9, 128.7 (aryl CH), 147.8 (d, *J* = 81.4 Hz, CNR), 152.3 (aryl C_q), 156.1 (d, *J* = 16 Hz, N=C=N). IR (KBr): 2145 cm^{-1} (CNR); 1728, 1589 cm^{-1} (N=C=N). UV–vis (hexane; nm (ε, cm^{-1} M^{-1})): 246 (32000), 334 (9300), 448 (800). Anal. Calcd (found) for $C_{28}H_{42}BN_3Rh$: C, 64.2 (64.0); H, 8.1 (8.2); N, 8.0 (8.0).

Tp′Rh(H)(Ph)(CN-neopentyl) (5). Complex **5** can be prepared in a variety of ways. For preparation of quantities less than 100 mg the most straightforward method involves direct photolysis of **1a** in benzene as described below.

A stirred solution of 75 mg (0.126 mmol) of **1a** in 5 mL of benzene was irradiated with λ > 345 nm for a total of 72 h. The solvent was removed *in vacuo*, and the residue was triturated with 2 mL of hexane. Drying of the remaining solid gives 42 mg (58%) of spectroscopically pure product. ^{1}H NMR (C_6D_6): δ −13.650 (d, *J* = 24 Hz, 1 H, Rh–H), 0.604 (s, 9 H, $C(CH_3)_3$), 1.896 (s, 3 H, pz CH_3), 2.196 (s, 3 H, pz CH_3), 2.130 (s, 3 H, pz CH_3), 2.246 (s, 3 H, pz CH_3), 2.342 (s, 3 H, pz CH_3), 2.441 (s, 3 H, pz CH_3), 2.741 (s, 2 H, NCH_2), 5.540 (s, 1 H, pz H), 5.708 (s, 1 H, pz H), 5.844 (s, 1 H, pz H), 6.922 (br s, 1 H, aryl H), 7.051 (t, 1 H, aryl H), 8.073 (br s, 1 H, aryl H); other resonances for the phenyl group are not observed due to extreme broadening from a fluxional process at room temperature. ^{13}C{^{1}H} NMR (C_6D_6): δ −3.425, 7.798, 8.052, 10.004, 10.631, 10.825 (pz CH_3), 21.793 ($C(CH_3)_3$), 26.807 ($\mathit{C}(CH_3)_3$), 51.045 (NCH_2), 100.794, 101.474, 101.641 (pz CH), 138.3, 138.4, 138.7, 144.6, 145.11, 146.5, 147.95 (d, *J* = 30 Hz, aryl C_q–Rh). IR (C_6H_6): 2523 cm^{-1} (B–H); 2178 cm^{-1} (CNR).

Tp′Rh(Cl)(CN-neopentyl) (10). A stirred solution of 60 mg (0.088 mmol) of **2a** in 3 mL of benzene was irradiated with λ > 345 nm for 1 h at room temperature. To the solution under inert conditions was added 2 mL of carbon tetrachloride, and the mixture was stirred at room temperature in the dark for 72 h. The solvent was removed in vacuo, and the crude product was purified by preparative thin-layer chromatography (2 mm silica gel on 20 × 20 cm^2 plate, 3:1 hexane–THF mobile phase); yield 24 mg (45%) of a white solid. ^{1}H NMR (C_6D_6): δ 0.680 (s, 9 H, $C(CH_3)_3$), 1.723, (s,.3 H, pz CH_3), 2.129 (s, 3 H, pz CH_3), 2.172 (overlapping s, 6 H, pz CH_3), 2.250 (s, 3 H, pz CH_3), 2.597 (AB q, J_1 = 14 Hz, J_2 = 12.6 Hz, 2 H, NCH_2), 2.876 (s, 3 H, pz CH_3), 5.502 (s, 1 H, pz H), 5.569 (s, 1 H, pz H), 5.756 (s, 1 H, pz H), 6.706 (d, *J* = 7.8 Hz, 1 H, aryl H), 6.873 (t, *J* = 7.9 Hz, 1 H, aryl H), 7.088 (t, *J* = 7.1 Hz, 1 H, aryl H), 7.368 (t, *J* = 7.3 Hz, 1 H, aryl H), 8.566 (d, *J* = 7.7 Hz, 1 H, aryl H). ^{13}C{^{1}H} NMR (C_6D_6): δ 12.296, 12.571, 12.859, 14.689, 14.805, 15.195, (pz CH_3), 26.554 ($C(CH_3)_3$), 31.780 ($\mathit{C}(CH_3)_3$), 56.016 (NCH_2), 106.962, 107.816, 108.264 (pz CH), 123.317, 126.434, 126.853 (aryl CH), 136.785 (C≡NR), 139.028, 141.753 (aryl CH), 142.695, 143.084, 144.327 (pz C_q), 149.832 (d, *J* = 24.7 Hz, aryl C_q), 151.215, 151.757, 153.681 (pz C_q). IR (KBr): 2527 (B–H); 2216 (CNR). Anal. Calcd (found) for $C_{27}H_{38}BClN_7Rh$: C, 53.2 (54.02); H, 6.3 (6.5); N, 16.1 (15.3).

Table IV. Summary of Crystallographic Data for Tp′Rh(CN-2-tolyl)(η^2-2,4-xylyl-N=C=N-2-tolyl)•C_7H_8 (2d)

formula	$C_{39}H_{45}BN_9Rh\cdot C_7H_8$
fw	845.70
cryst syst	triclinic
space group	$P\bar{1}$
Z	2
a, Å	10.962 (6)
b, Å	11.238 (4)
c, Å	18.691 (14)
α, deg	96.95 (5)
β, deg	104.02 (5)
γ, deg	101.00 (4)
V, Å^3	2159 (5)
d_{calc}, g/cm^3	1.30
cryst dimens, cm	0.13 × 0.15 × 0.22
temp, °C	−20
radiation; λ, Å (monochromator)	Mo; 0.710 89 (graphite)
scan type	$2\theta/\omega$
takeoff angle, deg	2.6
total bkgd time	(scan time)/2
scan rate, deg/min	2–16.5
scan range, deg	0.7 + 0.35 tan θ
2θ range, deg	2–40
no. of data collected	4292
no. of unique data $>3\sigma$	2380
no. of params varied	504
abs coeff, cm^{-1}	4.29
range of transmissn factors	0.97–1.05
agreement between equiv data (F_o)	0.100
R_1/R_2	0.0729/0.0630
goodness of fit	1.38
largest peak in final E map	0.50

Tp′Rh(H)(C_6H_4N=C=N-neopentyl)(CN-neopentyl) (7). A 10-mg (0.014-mmol) sample of **2a** was dissolved in 2 mL of benzene in a 10-mL round-bottom flask. The solvent was then evaporated, leaving the complex as a thin film on the surface of the flask. The flask was irradiated with $\lambda > 345$ nm for 24 h with periodic rotation, during which time the yellow film bleached colorless. A ^{1}H NMR spectrum of the crude product indicated clean and quantitative conversion of **2a** to **7**. ^{1}H NMR (C_6D_6): δ −13.384 (d, J = 22.5 Hz, Rh–H), 0.706 (s, 9 H, $C(CH_3)_3$), 0.980 (s, 9 H, $C(CH_3)_3$), 1.819 (s, 3 H, pz CH_3), 2.119 (s, 3 H, pz CH_3), 2.187 (s, 3 H, pz CH_3), 2.316 (s, 3 H, pz CH_3), 2.350 (s, 3 H, pz CH_3), 2.582 (s, 3 H, pz CH_3), 2.840 (AB q almost degenerate, J = 12.5 Hz, 2 H, NCH_2), 3.166 (AB q almost degenerate, J = 10.5 Hz, 2 H, NCH_2), 5.525 (s, 1 H, pz H), 5.702 (s, 1 H, pz H), 5.869 (s, 1 H, pz H), 6.658 (t, J = 7.8 Hz, 1 H, aryl H), 6.978 (t, J = 8.0 Hz, 1 H, aryl H), 7.216 (d, J = 7.7 Hz, 1 H, aryl H), 7.362 (d, J = 7.9 Hz, 1 H, aryl H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.560 (overlapping pz CH_3), 12.791, 14.823, 15.260, 15.630 (pz CH_3), 26.670, 27.283 ($C(\mathit{C}H_3)_3$), 31.499, 32.458 ($\mathit{C}(CH_3)_3$), 56.043, 59.313 (NCH_2), 105.526, 106.248, 106.321 (pz CH), 122.384, 123.100, 123.361, 128.499 (aryl CH), 136.051 (N=C=N), 141.895, 143.179, 143.246, 143.513, 147.128, 149.676, 149.761, 150.983 (pz C_q or aryl C_q). IR (KBr): 2523 cm^{-1} (B–H); 2184 cm^{-1} (CNR); 2133 cm^{-1} (N=C=N); 2077 cm^{-1} (Rh–H).

Tp′Rh[C(*N*-neopentyl)N(Ph)C(*N*-neopentyl)](CN-neopentyl) (8). To a stirred solution of 40 mg (0.058 mmol) of **2a** in 2 mL of tetrahydrofuran was added 12 μL (0.100 mmol) of neopentyl isocyanide. The reaction mixture was stirred for 72 h and the solvent reduced in volume to 0.5 mL. The solution was cooled to −20 °C for 1 month, during which time crystals of the product formed; yield 33 mg (66%) of amber crystals. ^{1}H NMR (THF-d_8): δ 0.959 (s, 18 H, $C(CH_3)_3$), 0.996 (s, 18 H, $C(CH_3)_3$), 2.225 (s, 3 H, pz CH_3), 2.345 (s, 6 H, pz CH_3), 2.418 (overlapping s, 9 H, pz CH_3), 2.656 (d, J = 13 Hz, 2 H, NCH_2), 3.200 (d, J = 13 Hz, 2 H, NCH_2), 3.539 (s, 2 H, NCH_2), 5.685 (s, 1 H, pz H), 5.721 (s, 2 H, pz H), 6.841 (t, J = 7.7 Hz, 1 H, aryl H), 7.135 (t, J = 7.5 Hz, 2 H, aryl H), 8.778 (d, J = 8.4 Hz, 2 H, aryl H). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 12.586, 13.358, 14.865, 16.575 (pz CH_3), 26.945, 28.440 ($C(\mathit{C}H_3)_3$), 32.634, 32.851 ($\mathit{C}(CH_3)_3$), 56.891, 64.315 (NCH_2), 106.085, 108.407 (pz CH), 121.902, 123.553, 127.473 (aryl CH), 141.419 (pz C_q), 142.040 (d, J = 63 Hz, CNR), 144.141 (pz C_q), 144.207 (aryl C_q), 150.290 (pz C_q), 150.602 (d, J = 26 Hz, Rh—C=NR(NPh)), 153.502 (pz C_q). IR (KBr): 2526 cm^{-1} (B–H); 2197 cm^{-1} (CNR); 1732 cm^{-1} (C=NR). Anal. Calcd (found) for $C_{39}H_{60}BN_9Rh$: C, 60.9 (59.6); H, 7.9 (7.6); N, 16.4 (17.6).

Solution and Refinement of Crystal Structure for Tp′Rh(CN-2-tolyl)(η^2-2,4-xylylN=C=N-2-tolyl) (2d). A well-formed crystal of approximate dimensions 0.13 × 0.15 × 0.22 cm^3 was mounted on a glass fiber and placed on a Enraf-Nonius CAD4 diffractometer under a cold stream of nitrogen at −20 °C. The lattice constants were obtained from 25 centered reflections with values of χ between 0 and 70°. Cell reduction revealed a primitive triclinic crystal system. Data were collected in accord with the parameters in Table IV. The intensities of two representative reflections which were measured after every 60 min of X-ray exposure time remained constant throughout the data collection, indicating crystal and electronic stability (no decay correction was applied). The space group was uniquely assigned as $P\bar{1}$ on the basis of the calculated density for a Z value of 2, and the correctness of the fit was confirmed by successful placement of the rhodium atom in the unit cell with use of the Patterson map. The structure was expanded using the DIRDIF program supplied by the Molecular Structure Corp., whose programs were used for further refinement of the structure.[51] The expansion allowed for the location of all non-hydrogen atoms along with the seven carbon atoms of a toluene solvate molecule. An empirical absorption correction was applied using the program DIFABS after full isotropic refinement of all non-hydrogen atoms. Subsequent anisotropic refinement resulted in atoms C17 and C28 possessing negative thermal parameters. Attempts to eliminate the negative values by decreasing the number of variables through rigid-group refinement of the toluene and aryl rings failed. The structure was therefore refined anisotropically, except for carbons C17 and C28, which were kept isotropic. Final refinement of all non-hydrogen atoms allowed for use of a difference Fourier map for the location of at least one hydrogen atom on each methyl group. The remainder of the hydrogen atoms were generated in idealized positions and were refined with their thermal and positional parameters "riding" on the atom to which they were attached.

Acknowledgment is made to the U.S. Department of Energy (Grant DE-FG02-86ER13569) for their support of this work.

Registry No. **1a**, 132079-33-5; **1b**, 132079-36-8; **1c**, 132079-34-6; **1d**, 139167-86-5; **2a**, 139167-87-6; **2b**, 139167-88-7; **2c**, 139167-89-8; **2d**, 139167-90-1; **2d**·C_7H_8, 139167-95-6; **3a**, 85028-81-5; **4**, 139167-91-2; **5a**, 139198-74-6; **5a**-*d*, 139167-96-7; **5b**-d_6, 139167-97-8; **5c**-d_6, 139167-98-9; **6**, 139167-85-4; **7**, 139167-93-4; **8**, 139167-94-5; **10**, 139167-92-3; phenyl isothiocyanate, 103-72-0; neopentylamine, 5813-64-9; *N*-phenyl-*N*′-neopentylthiourea, 15093-39-7; bis(μ-chloro)tetrakis(ethylene)dirhodium(I), 12081-16-2; 2-tolyl isocyanide, 10468-64-1; potassium hydrotris(3,5-dimethylpyrazolyl)borate, 17567-17-8; phenyl azide, 622-37-7; neopentyl isocyanide, 72443-18-6; 2,4-xylyl azide, 35523-91-2; benzene, 71-43-2.

Supplementary Material Available: Tables S-I–S-IV, giving intramolecular bond angles and distances and anisotropic thermal parameters for all non-hydrogen atoms along with positional parameters and B_{eq} values for the hydrogen atoms of **2d** (10 pages); a listing of calculated and observed structure factors for **2d** (19 pages). Ordering information is given on any current masthead page.

---

(51) $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$, $R_2 = [\sum w(|F_o| - |F_c|)^2]^{1/2}/\sum wF_o^2$, where $w = [\sigma^2(F_0) + (\rho F_o^2)^2]^{1/2}$ for non-Poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of scattering factors f_0, f', f'': Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.