this is likely to be unfavorable for rings with $n = 1$–3 and favorable for larger rings, whereas a parallel approach should not be prohibitive for rings as small as $n = 2$. We thus currently favor this D_{2d}-like or pseudotetrahedral transition state in the equilibria in eq 4.

Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: Details of the experimental procedures, as well as NMR and IR spectra and elemental analysis data, for the compounds studied and listings of crystal data and refinement details, positional and thermal parameters, and bond distances and angles, as well as mono- and stereoview structural diagrams, for IIa,b (32 pages); listings of observed and calculated structure factors for IIa,b (13 pages). Ordering information is given on any current masthead page.

Cis Difunctionalization of Cyclic Olefins with Use of Organozirconium Intermediates

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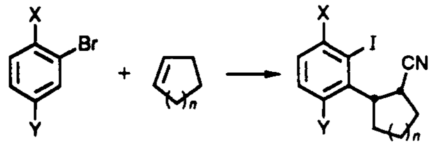
Summary: The utilization of in situ generated zirconocene–benzyne complexes as a means to effect cis carbofunctionalizations of cyclic olefins in a one-pot procedure is described. The stereospecific insertion of cyclic olefins provides the *cis*-zirconaindane metallacycles exclusively. The intermediate metallacycles were treated with a variety of electrophiles to provide diastereoselective syntheses of arylcyanoalkanes, tricyclic ketones, and 2,3-dihydrobenzo[*b*]thiophenes in moderate overall yields.

While a variety of reagents have been developed to add two heteroatoms syn to a single face of a cyclic olefin,[2] the ability to stereospecifically form two carbon–carbon bonds or a carbon–carbon bond and a carbon–heteroatom bond in a syn fashion is less common.[3] We felt that the basic approach shown in Scheme I, in which insertion of an olefin into a metal–carbon bond produces syn addition of a carbon–carbon and a carbon–metal bond, might be an attractive means to effect such cis carbofunctionalizations. We now report our initial results, in which we have used the in situ generated zirconocene–benzyne complex 1 as a means for such reactions.

Complex 1 can be generated by the addition of an aryllithium compound to zirconocene (methyl) chloride at −78 °C, followed by the thermolysis of the intermediate to effect the loss of methane (70 °C, benzene, 16 h).[4] If 1 is generated in the presence of a cyclic olefin (1.0 equiv), metallacycle 2 is the exclusive product.

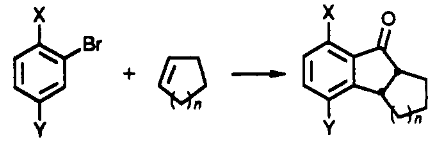
Table I

(a) Synthesis of *cis*-Cyanoarylalkanes



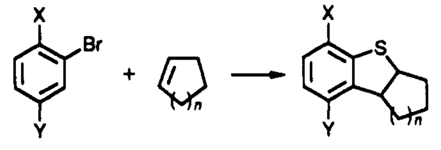
aryllithium	*n*	product (yield, %)
X = OMe, Y = H	1	**5** (41)
X = OMe, Y = H	3	**9** (41)
X = OMe, Y = OMe	1	**10** (41)

(b) Synthesis of Cis Tricyclic Ketones

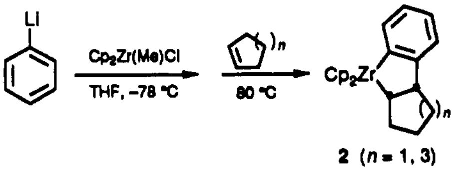


aryllithium	*n*	product (yield, %)
X = OMe, Y = H	1	**11** (47)
X = OMe, Y = OMe	1	**12** (40)
X = OMe, Y = H	3	**7** (56)
X = N(Me)$_2$, Y = H	1	**13** (25)

(c) Synthesis of *cis*-2,3-Dihydrobenzo[*b*]thiophenes



aryllithium	*n*	product (yield, %)
X = OMe, Y = H	1	**14** (52)
X = OMe, Y = OMe	1	**15** (47)
X = Me, Y = H	3	**16** (48)
X = OMe, Y = H	3	**8** (50)
X = N(Me)$_2$, Y = H	1	**17** (41)
X = Me, Y = H	1	**18** (28)



2 (*n* = 1, 3)

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(1) (a) National Science Foundation Predoctoral Fellow, 1989–1992. (b) Camille & Henry Dreyfus Teacher-Scholar Awardee, 1989–1994; American Cancer Society Junior Faculty Research Awardee, 1987–1989; Eli Lilly Grantee, 1988–1990; Alfred P. Sloan Research Fellow, 1988–1990; Union Carbide Innovation Recognition Program Awardee, 1989.

(2) Dihydroxylation: (a) Schröder, M. *Chem. Rev.* **1980,** *80,* 187. (b) Jacobsen, E. N.; Markö, I.; Mungall, W. S.; Schröder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988,** *110,* 1968. (c) Woodward, R. B.; Brutcher, F. V. *J. Am. Chem. Soc.* **1958,** *80,* 209. (d) Corey, E. J.; Das, J. *Tetrahedron Lett.* **1982,** *23,* 4217. Diamination: (e) Bäckvall, J. E.; Bjorkman, E. E. *J. Org. Chem.* **1980,** *45,* 2893. Hydroxyamination: (f) Sharpless, K. B.; Chong, A. O.; Shima, K. O. *J. Org. Chem.* **1976,** *41,* 177. Epoxidation: (g) Swern, D. *Org. React.* **1953,** *7,* 378. (h) Sharpless, K. B.; Verhoeven, T. R. *Aldrichim. Acta* **1979,** *12,* 63. (i) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980,** *102,* 5974.

(3) Examples of cis carbofunctionalization are as follows. (a) For a review of the Diels–Alder reaction see: Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980,** *80,* 63. (b) For a review of the Paterno–Büchi reaction see: Jones, G., II. *Org. Photochem.* **1981,** *5,* 1. (c) Trost, B. M.; Nanninga, T. N.; Satoh, T. *J. Am. Chem. Soc.* **1985,** *107,* 721. (d) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986,** *25,* 1.

(4) (a) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988,** *7,* 1044. (b) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *J. Am. Chem. Soc.* **1987,** *109,* 7137. (c) Buchwald, S. L.; Sayers, A.; Watson, B. T.; Dewan, J. C. *Tetrahedron Lett.* **1987,** *28,* 3245. (d) Erker, G. *J. Organomet. Chem.* **1977,** *134,* 189.

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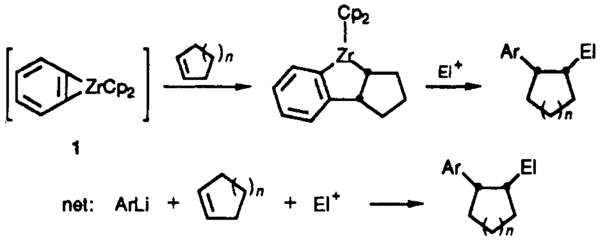
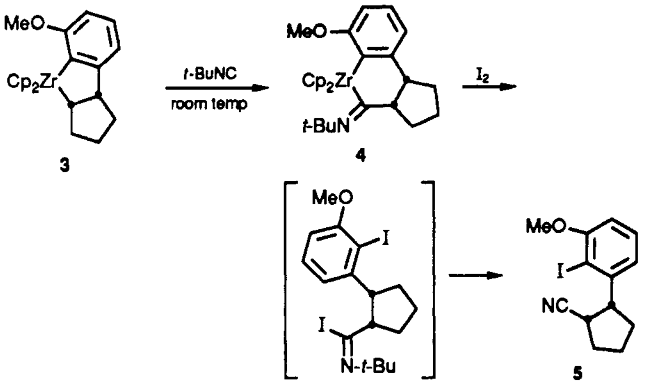
Scheme I



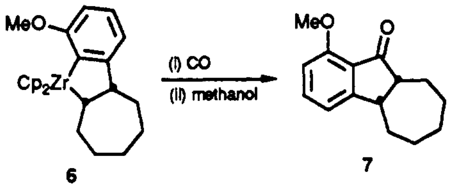
Since Erker[5] has previously demonstrated that olefin insertion into the Zr–C bond of 1 is stereospecific, it was anticipated that the insertion of cyclic olefins would proceed in a like manner, as is the case (vide infra).

The metallacycles so produced can be transformed to a number of interesting and useful organic products.[6] The addition of *tert*-butyl isocyanide (1.1 equiv) to 3 results in formation of 4. Exposure of 4 to excess iodine (3.0 equiv) produces 5 in 41% overall yield (based on 2-bromoanisole).[7] Overall this transformation represents a diastereoselective arylation–cyanation of cyclic olefins in which two carbon–carbon bonds have been formed in a syn fashion.

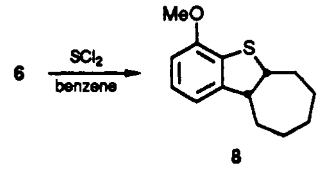


In order to establish the stereochemical course of the reaction sequence, an X-ray crystal structure of *cis*-1-cyano-2-(2-iodo-3-methoxyphenyl)cyclopentane (5) was obtained.[8] The X-ray crystal structure clearly shows the syn relationship of the substituents on the cyclopentane ring. This stereochemistry is set during the 1,2-insertion of cyclopentene into the zirconocene–benzyne bond. The subsequent insertion of *tert*–butyl isocyanide occurs with retention of configuration at carbon.[9]

Metallacycles of type 2 can be converted to tricyclic ketones via carbonylation.[10] For example, 2-bromoanisole and cycloheptene produce metallacycle 6; when a solution of 6 is stirred under CO (1 atm) for 5 h at −10 °C followed by the addition of methanol, the tricyclic ketone 7 is obtained in 56% overall yield.[11]



If 6 is treated with freshly distilled SCl_2 (1.0 equiv, benzene, room temperature, 2 h), the corresponding 2,3-dihydrobenzo[*b*]thiophene 8 is produced in 50% overall yield.[12]



In summary, we have shown that through the use of stereospecific coupling of cyclic olefins with in situ gen-

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(5) (a) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659. (b) Kropp, K.; Erker, G. *Organometallics* **1982**, *1*, 1246.

(6) Typical experimental procedures are as follows. For **3**: To a solution of 2-bromoanisole (262 μL, 0.393 g, 2.10 mmol) in 10 mL of THF at −78 °C was added *n*-butyllithium (1.43 mL of a 1.64 M solution in hexane, 2.20 mmol). After 30 min, this solution was added to a solution of $Cp_2Zr(Me)Cl$ (0.653 g, 2.40 mmol) in 20 mL of THF at −78 °C, and the resulting solution was maintained at −78 °C for 15 min before warming it to room temperature. The THF was removed in vacuo, and the residue was redissolved in 10 mL of benzene. This mixture was cannula-filtered into a sealable tube, and then cyclopentene (176 μL, 0.136 g, 2.00 mmol) was added. The reaction mixture was maintained at 70 °C for 18 h. The solution was cooled to room temperature. For *cis*-cyanoarylcycloalkane **5**: To the benzene solution of metallacycle **3** was added *tert*-butyl isocyanide (248 μL, 0.183 g, 2.20 mmol), and the resulting mixture was stirred for 2 h. The solution was cooled to 5 °C, and a solution of iodine (1.52 g in 20 mL of benzene) was added. The iodinolysis was allowed to proceed for 15 min, and then the reaction mixture was diluted with ether and washed sequentially with saturated Na_2SO_3, brine, and water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by radial plate chromatography (Chromatotron, 4-mm silica plate, hexane–ethyl acetate eluent) to give a pale yellow solid (290 mg, 41% yield): mp 102–105 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.81–1.88 (m, 1 H), 2.04–2.25 (m, 5 H), 3.49–3.58 (m, 1 H), 3.60–3.93 (m, 1 H), 3.90 (s, 3 H), 6.79 (d, J = 8.2 Hz, 1 H), 7.07 (d, J = 8.0 Hz, 1 H), 7.34 (dd, J = 7.2 Hz, 1 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 23.10, 29.62, 30.37, 34.11, 52.63, 56.47, 94.74, 110.32, 120.57, 121.09, 129.47, 143.34, 158.35; IR (KBr) 2942, 2233, 1465, 1422, 1266, 1056 cm^{-1}; mol formula $C_{13}H_{14}INO$; HRMS calcd 327.0121 amu, found 327.0121 ± 0.0008 amu. For tricyclic ketone **11**: The benzene solution of metallacycle **3** was concentrated in vacuo, and the residue was redissolved in 20 mL of THF. The solution was cooled to −10 °C and placed under 1.1 atm of CO for 5 h. Typical temperatures and times for carbonylation were −10 °C to room temperature and 5–24 h, respectively. The solution was warmed to room temperature, and then methanol (1.0 mL) was added. The reaction mixture was evaporated, and the residue was extracted several times with ether. The ether extractions were combined and washed sequentially with brine and water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by radial plate chromatography (Chromatotron, 4-mm silica plate, hexane–ethyl acetate eluent) to give a pale yellow oil (190 mg, 47% yield): ^1H NMR (300 MHz; $CDCl_3$) δ 1.04–1.16 (m, 1 H), 1.46–1.55 (m, 1 H), 1.71–2.03 (m, 4 H), 2.93–2.99 (m, 1 H), 3.59–3.68 (m, 1 H), 3.87 (s, 1 H), 6.70 (d, J = 7.8 Hz, 1 H), 6.95 (d, J = 7.8 Hz, 1 H) 7.48 (t, J = 7.8 Hz, 1 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 24.13, 30.74, 33.04, 43.18, 52.37, 55.50, 108.74, 117.74, 125.61, 136.97, 157.50, 161.79, 208.43; IR (KBr) 2949, 1711, 1595, 1479, 1275, 1206, 1067, 1041 cm^{-1}; mol formula $C_{13}H_{14}O_2$; HRMS calcd 202.0994 amu, found 202.0992 ± 0.0008 amu. For 2,3-dihydrobenzo[*b*]thiophene **14**: To the benzene solution of metallacycle **3** was added freshly distilled SCl_2 (137 μL, 2.1 mmol).[12c] The solution was maintained at room temperature for 2 h. The reaction mixture was evaporated, and the residue was extracted several times with ether. The ether extractions were combined and washed sequentially with brine and water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by radial plate chromatography (Chromatotron, 4-mm silica plate, hexane–ether eluent) to give a yellow oil (215 mg, 52% yield): ^1H NMR (300 MHz, $CDCl_3$) δ 1.61–1.89 (m, 4 H), 2.06–2.15 (m, 2 H), 3.84 (s, 3 H), 4.02–4.06 (m, 1 H), 4.18–4.25 (m, 1 H), 6.64 (d, J = 7.8 Hz, 1 H), 6.72 (d, J = 7.8 Hz, 1 H), 7.03 (t, J = 7.8 Hz, 1 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 24.92, 34.48, 36.80, 51.08, 53.95, 55.41, 108.67, 117.38, 125.68, 129.09, 145.67, 153.63; IR (neat) 2954, 1574, 1471, 1435, 1262, 1082, 1055, 760; mol formula $C_{12}H_{14}OS$; HRMS calcd 206.0765 amu, found 206.0765 ± 0.0008 amu.

(7) Buchwald, S. L.; LaMaire, S. J. *Tetrahedron Lett.* **1987**, *28*, 295.

(8) See supplementary material for details.

(9) Flood, T. C. In *Topics in Inorganic and Organometallics Stereochemistry*; Geoffroy, G. L., Ed.; Wiley: New York, 1981; Vol. 12, p 92.

(10) (a) Erker, G.; Kropp, K. *J. Organomet. Chem.* **1980**, *194*, 45. (b) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568.

(11) In certain instances, direct carbonylations of zirconacycles by CO have been complicated by side reactions. A strategy to circumvent this problem has been to employ an oxidative workup; cf.: Rousset, C. J.; Swanson, D. R.; Lamaty, F.; Negishi, E. *Tetrahedron Lett.* **1989**, *30*, 5105. However, for metallacycles such as **6** we found that direct methanolysis was superior to iodinolysis for obtaining the desired tricyclic ketones.

(12) (a) Buchwald, S. L.; Fang, Q. *J. Org. Chem.* **1989**, *54*, 2793. (b) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (c) We have found the yields of the desired dihydrobenzo[*b*]thiophenes to be improved by utilizing freshly distilled SCl_2 in place of S_2Cl_2. *Caution*! Sulfur dichloride has been reported to be unstable to heat, exposure to moisture, and contact with alkalies or organic solvents; cf.: *Chem. Eng. News*, 1988, *66* (Aug 8), 2.

erated zirconocene–benzyne species, followed by treatment of the intermediate metallacycles with an appropriate electrophile, the net syn 1,2-difunctionalization of the cyclic olefin can be effected. The work described represents some of the first examples of such cis carbofunctionalizations. We are currently probing the generality of this reaction strategy in order to extend this methodology to the synthesis of other carbocyclic and heterocyclic systems.

Acknowledgment. We thank the National Institutes of Health for financial support, the ICFES-BID-UIS for a 3-month fellowship (A.G.), and Drs. William Davis and Richard Fisher for the X-ray crystal structure.

Supplementary Material Available: Experimental details concerning the preparations and spectroscopic and analytical characterizations of the compounds, experimental details for the crystallographic analysis of 5, an ORTEP diagram, and lists of atom positions, thermal parameters, and bond lengths and angles (16 pages). Ordering information is given on any current masthead page.

Application of Phosphine and Arsine–Phosphoranimine Backbones to the Formation of Early–Late-Transition-Metal Bimetallics. Synthesis and Characterization of New Titanium–Palladium Frameworks: $(\eta^5\text{-}C_5H_5)Cl_2TiN{=}PPh_2(CH_2)_xEPh_2PdCl_2$ (x = 1, E = P; x = 2, E = As)

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Received July 2, 1990

Summary: Titanium–palladium bimetallics of the form $CpCl_2Ti{-}N{=}PPh_2(CH_2)_xPPh_2PdCl_2$ can be prepared from the phosphine (or arsine) phosphoranimines $Ph_2P(CH_2)_xEPh_2{=}NSiMe_3$ (E = P, x = 1; E = As, x = 2) by either of two routes: (a) metathetical replacement of $SiMe_3$ by $CpTiCl_2$ followed by complexation of $PdCl_2$ or (b) complexation of the phosphoranimine ligand with $PdCl_2$ followed by reaction of the complex with $CpTiCl_3$ to form the bimetallic and Me_3SiCl.

There are many reasons for seeking means of constructing transition-metal heterobimetallic complexes connecting the "early" and "late" metals. These systems may provide models for the complex phenomena of "strong metal–support interactions", which are apparent in heterogeneous catalysts.[1] In addition, bimetallics may yield useful new homogeneous catalysts providing directed synthesis of specific organics.[2]

Although there has been considerable interest and significant achievements[3] in constructing such systems in recent years, a major barrier to success is presented by the general difficulty of developing compounds that can simultaneously and effectively bind both the early and the late transition metals, a combination which necessarily presents widely differing chemical reaction character.

Table I. Phosphorus-31 NMR[a] Spectroscopic Data for the Phosphoranimine–Phosphine and –Arsine Ligands and Their Mono- and Bimetallic Complexes

compd	$\delta_{P^{III}}$	$\delta_{P^{V}}$	$^2J_{PP}$, Hz
$Me_3SiN{=}PPh_2CH_2PPh_2$ (**1**)[b]	−28.2	−1.4	57.7
$(\eta^5\text{-}C_5H_5)Cl_2TiN{=}PPh_2CH_2PPh_2$ (**3**)[b]	−29.0	38.6	59.7
$Me_3SiN{=}PPh_2CH_2PPh_2PdCl_2$ (**5**)[c]	16.6	34.8	26.2
$(\eta^5\text{-}C_5H_5)Cl_2TiN{=}PPh_2CH_2PPh_2PdCl_2$ (**7**)	16.2	33.4	8.0
$HN{=}PPh_2CH_2PPh_2PdCl_2$ (**9**)[c]	25.2	53.8	29.9
$Me_3SiN{=}PPh_2CH_2CH_2AsPh_2$ (**2**)[d]		1.8	
$(\eta^5\text{-}C_5H_5)Cl_2TiN{=}PPh_2CH_2CH_2AsPh_2$ (**4**)		40.1	
$Me_3SiN{=}PPh_2CH_2CH_2AsPh_2PdCl_2$ (**6**)[c]		32.8	
$(\eta^5\text{-}C_5H_5)Cl_2TiN{=}PPh_2(CH_2)_2AsPh_2PdCl_2$ (**8**)		43.0	

[a] All spectra in $CDCl_3$; in ppm vs 85% H_3PO_4. [b] Data from ref 7. [c] Data from ref 8. [d] Data from ref 9.

There are, of course, many conventional heterodifunctional (and polyfunctional) ligand systems available, but it seemed desirable to us to also attempt to form one metal–element σ bond for enhanced stability. Typical examples of such systems are the functionalized phosphine derivatives Ph_2PCH_2O–[4] and $Ph_2PCH_2CH_2S$–[5] of the early metals Ti and Zr containing oxygen or sulfur to metal σ bonds. The free phosphine center in these compounds can then be used to coordinate late metals such as Pd and Rh to form early–late bimetallics. Extensive examples are given in ref 3.

We have synthesized a variety of new bifunctional silylimino–phosphorus and –arsenic ligands[6-9] (**1**, **2**), which also show considerable promise as versatile backbones for heterobimetallics of the transition metals and in addition

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(1) (a) Imelik, B., Naccache, C., Coudurier, G., Praliaud, H., Meriaudeau, P., Galizot, P., Martin, G. A., Verdin, J. C., Eds. *Metal-Support and Metal-Additive Effects in Catalysis*; Elsevier: New York, 1982. (b) Baker, R. T. K., Tanster, S. J., Dumesic, J. A., Eds. *Strong Metal-Support Interactions*; American Chemical Society: Washington, DC, 1986. (c) Stevenson, S.; Baker, R. T. K.; Dumesic, J. A. *Metal Support Interactions*; Van Nostrand: New York, 1988.

(2) See for example: (a) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 6, pp 763–877. (b) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665. (c) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *Organometallics* **1984**, *3*, 504. (d) Casey, C. P.; Nief, F. *Organometallics* **1985**, *4*, 1218. (e) Casey, C. P.; Palermo, R. E.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 4597. (f) Tso, C. T.; Cutler, A. R. *J. Am. Chem. Soc.* **1985**, *108*, 6069. (g) Wark, T. A.; Stephan, D. W. *Inorg. Chem.* **1984**, *26*, 363 and references therein. (h) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167 and references therein. (i) Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4853. (j) Jacobsen, E. N.; Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3706. (k) White, G. S.; Stephan, D. W. *Organometallics* **1988**, *7*, 903. (l) Gelmini, L.; Stephan, D. W. *Organometallics* **1988**, *7*, 849. (m) Ozawa, F.; Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Henling, L. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 1319. (n) Mackenzie, P. B.; Coots, R. J.; Grubbs, R. H. *Organometallics* **1989**, *8*, 8.

(3) Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 4107.

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(5) White, G. S.; Stephan, D. W. *Inorg. Chem.* **1985**, *24*, 1499.

(6) Katti, K. V.; Cavell, R. G. *Organometallics* **1988**, *7*, 2236.

(7) Katti, K. V.; Cavell, R. G. *Inorg. Chem.* **1989**, *28*, 413.

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