Table I. Asymmetric Nucleophilic Aromatic Substitution Providing Binaphthyls[a]

entry	X	R	**2**[b]	**1**/**2**[c]	time, h	**5**, **7**	ee, %[d]	yield, %[e]
1	MeO	c-hex	A	1.1	1.5	**7**	85 (98)[f]	90 (64)[f]
2	EtO	c-hex	A	1.1	3	**7**	62	86
3	F	c-hex	A	1.1	1.5	**7**	57	94
4	MeO	c-hex	A	0.16	6.5	**7**	78	29
5	MeO	c-hex	A	0.16	2.5 (0 °C)	**7**	34	81
6	F	c-hex	A	0.16	6	**7**	49	98
7	F	2,6-iPr$_2$Ph	A	0.16	0.5	**5**	64	>99
8	F	2,6-iPr$_2$Ph	B	0.16	2	**5**	83	>99
9	F	2,6-iPr$_2$Ph	B	1.1	1	**5**	90	>99
10	F	2,6-iPr$_2$Ph	B	0.045	3.5	**5**	82	>99
11	F	2,6-iPr$_2$Ph	B	0.025	3.5	**5**	82	97
12	F	2,6-iPr$_2$Ph	B	0	3.5	**5**	0	17

[a] The reaction procedure is described in the text. [b] 1.5–2.0 equiv of naphthyllithium **2** was used. Method A: prepared from naphthyl bromide and *tert*-BuLi; method B: prepared from naphthylpropyltellurium and BuLi.[6] [c] Equivalent of the chiral diether **1**/naphthyllithium **2**. [d] Absolute configuration was determined by optical rotation;[8] ee was determined by HPLC analysis using chiral column (Daicel ChiralPak AD hexane/isopropyl alcohol (9/1), 0.5 mL/min). [e] Yield refers to purified product by column chromatography. [f] Number in parentheses represents ee and yield after a single recrystallization from ether and hexane.

to the amount of **1** employed (entry 4). At temperatures above 0 °C, the reaction proceeded smoothly to afford **7** in 81% yield; however, the ee was only 34% (entry 5). At 0 °C, naphthyllithium **2** was able to react with **3** without the aid of the ligand **1**. It was observed that fluoro imine **3c** was a good substrate in both stoichiometric and catalytic reactions at −45 °C to provide high yields of **7** in 57 and 49% ee, respectively (entries 3 and 6). This strongly indicates that regeneration of the active species, naphthyllithium complex **9**, is possible from lithium fluoride–**1** complex **6** (X = F) through ligand exchange and is impossible or quite sluggish from lithium methoxide–**1** complex **6** (X = MeO).[9]

An improvement in the stereoselectivity was realized by using (2,6-diisopropylphenyl)imino group (**3d**),[10] with the increasing bulk probably sterically promoting effective chirality preservation in passing from central chirality to axial chirality.[11] A dramatic improvement in ee (83%) was achieved by using lithium bromide free naphthyllithium **2**, prepared from naphthylpropyltellurium and butyllithium (method B)[6] (entry 8).[12] It is highly probable that lithium bromide, produced in a lithium–halogen exchange between naphthyl bromide and *tert*-butyllithium (method A), activates **2**, allowing it to react without the aid of **1**.

Nearly constant ee (90–82%) was obtained in the range between stoichiometric amounts to 2.5 mol % of **1** (entries 8–11). The process is applicable to the reaction of 9-phenanthrenyllithium with **3d** by the addition of 4.5 mol % of **1**, providing **10**[13] in 83% ee and 83% yield.

Although further studies are required to determine the precise nature of the catalytic cycle, we believe that the results demonstrated here provide the basis for further new catalytic asymmetric reactions.[14]

Supplementary Material Available: A description of the procedure for the preparation of lithium bromide free **2** and listings of experimental details and data for **3** and **5–8** (7 pages). Ordering information is given on any current masthead page.

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(1) Tomioka, K. *Synthesis* **1990**, 541. Bosnich, B. *Asymmetric Catalysis*; Martinus Nijhoff Publishers: Dordrecht, The Netherlands, 1986. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1983–1985; Vols. 1–5.

(2) Brunner, H. *Synthesis* **1988**, 645. Narasaka, K. *Synthesis* **1991**, 1.

(3) Difficulties in catalytic processes of organolithium nucleophiles have been described: Mazaleyrat, J.-P.; Cram, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 4585. This is in sharp contrast to the successful catalytic asymmetric reaction of the dialkylzinc–chiral amino alcohol system. See: Oguni, N.; Matsumoto, Y.; Kaneko, T. *J. Am. Chem. Soc.* **1988**, *110*, 7877. Kitamura, M.; Okada, S.; Suga, S.; Noyori, R. *J. Am. Chem. Soc.* **1989**, *111*, 4028.

(4) The stoichiometric conjugate addition reaction has been reported using ligand **1**: Tomioka, K.; Shindo, M.; Koga, K. *J. Am. Chem. Soc.* **1989**, *111*, 8266. For the diastereoselective reaction, see: Rawson, D. J.; Meyers, A. I. *J. Org. Chem.* **1991**, *56*, 2292.

(5) Only one catalytic asymmetric synthesis of biaryls has been reported by using the chiral ferrocenylphosphine–nickel complex: Hayashi, T.; Hayashizuka, K.; Kiyoi, T.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8153.

(6) The procedure is based on the following paper: Hiiro, T.; Kambe, N.; Ogawa, A.; Miyoshi, N.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1187.

(7) The new compounds described herein gave satisfactory analytical and spectroscopic data.

(8) Meyers, A. I.; Lutomski, K. *J. Am. Chem. Soc.* **1982**, *104*, 879.

(9) Since no precipitation was observed, it is apparent that lithium fluoride is soluble in the reaction solution.

(10) Other groups, 2,6-dimethylphenyl and 2,4,6-tri-*tert*-butylphenyl, did not gave satisfactory stereochemical results.

(11) Since conjugate addition of an organolithium to a naphthylimine is highly stereoselective,[4] the initial addition step is assumed to be selective. Subsequent elimination of lithium fluoride, corresponding to the transformation of central to axial chirality, determines the efficacy of the process. There are very few examples of this; see: Meyers, A. I.; Wettlaufer, D. G. *J. Am. Chem. Soc.* **1984**, *106*, 1135.

(12) Tin compounds were found to be unsatisfactory in toluene; for example, Bu$_3$NaphSn–BuLi gave 1-butylnaphthaldehyde imine.

(13) Suzuki, T.; Hotta, H.; Hattori, T.; Miyano, S. *Chem. Lett.* **1990**, 807.

(14) We are grateful to the Japan Research Foundation for Optically Active Compounds, Hoansha Foundation, and a Grant-in-Aid for Scientific Research from the Ministry of Education, Japan, for partial financial support.

Carborane Ligands in Organometallic Chemistry: A New Class of Fischer Carbene Complexes[1]

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nido-Carborane anions, especially the icosahedral fragment $R_2C_2B_9H_9{}^{2-}$ ("dicarbollide") and pentagonal-pyramidal $R_2C_2B_4H_4{}^{2-}$ species, are demonstrably versatile ligands in transition metal organometallic chemistry.[2] When η^5-coordinated to metal centers, such ligands have been shown to stabilize a remarkable variety of organometallic structures, many of which exhibit unusual geometries and/or electronic properties.[3] The metal–C_2B_4 complexes can be converted to metal–C_2B_3 building-block units

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(1) Organotransition-Metal Metallacarboranes. 26. Part 25: Stephan, M.; Davis, J. H., Jr.; Meng, X.; Chase, K. J.; Hauss, J.; Zenneck, U.; Pritzkow, H.; Siebert, W.; Grimes, R. N. *J. Am. Chem. Soc.* **1992**, *114*, 5214.

(2) (a) Hawthorne, M. F.; Dunks, G. B. *Science* **1972**, *178*, 462. (b) Grimes, R. N. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, England, 1982; Chapter 5.5.

(3) For a recent example in $R_2C_2B_4H_4{}^{2-}$ chemistry, see: Merkert, J. M.; Geiger, W. E.; Atwood, M. D.; Grimes, R. N. *Organometallics* **1991**, *10*, 3545.

0002-7863/92/1514-8733$03.00/0

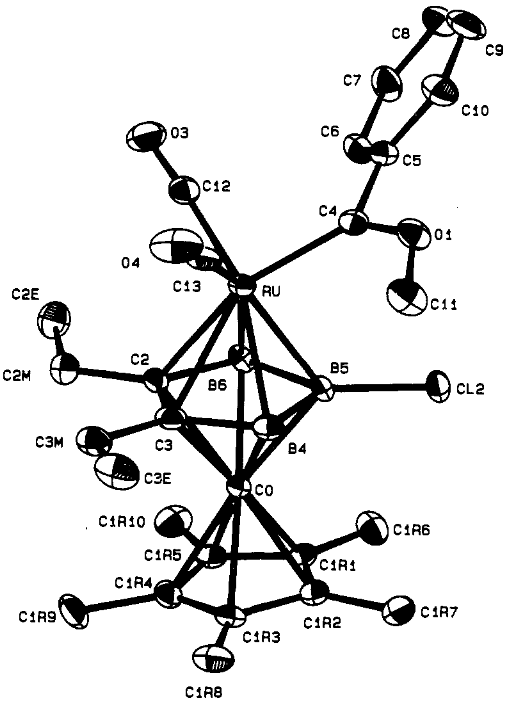
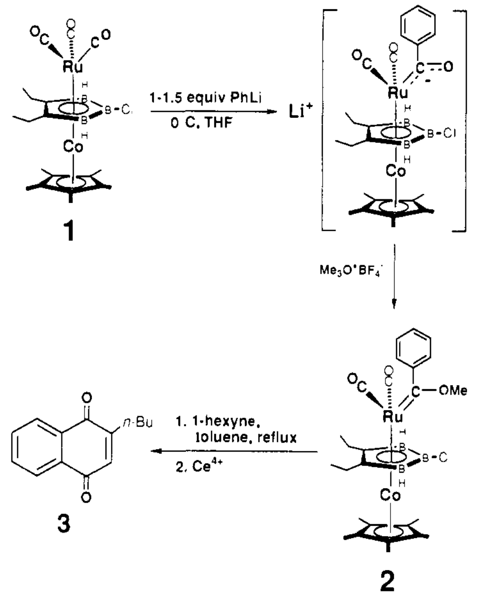


Figure 1. Molecular structure of **2** (hydrogens omitted). Selected intramolecular distances (Å): Ru–C4, 2.002 (3); Ru–C12, 1.908 (3); Ru–C13, 1.907 (3); C12–O3, 1.147 (4); C13–O4, 1.139 (4); C4–O1, 1.319 (4); O1–C11, 1.436 (4); C4–C5, 1.469 (4); Ru–C2, 2.333 (3); Ru–C3, 2.350 (3); Ru–B4, 2.312 (3); Ru–B5, 2.228 (3); Ru–B6, 2.290 (3); B5–Cl2, 1.823 (3). Selected bond angles (deg): C13–Ru–C12, 93.0 (1); C12–Ru–C4, 93.0 (1); Ru–C4–O1, 126.8 (2); Ru–C4–C5, 126.4 (2); C5–C4–O1, 106.7 (2); C4–O1–C11, 122.9 (2).

Scheme I



which have been used to construct multi-decker sandwich arrays.[4]

In addition to their role as synthons, metallacarboranes are potentially valuable as reagents in organic synthesis; however, this aspect has been relatively unexplored, aside from the definitive work of Hawthorne and his co-workers on homogeneous catalysis utilizing dicarbollide complexes of rhodium, ruthenium, and iridium[5a,b] and a report by Jordan et al. on group 4 dicarbollide alkyl compounds.[5c] An area of considerable interest would be carborane-stabilized carbene complexes, but no such species have been described (polymetallic carborane clusters having bridging carbene or carbyne ligands have been extensively investigated by Stone[6]). We report here the preparation and properties of the first example of a new class of Fischer carbene complexes in which an active $(CO)_2Ru{=}C(Ph)(OMe)$ group is bound to the readily generated[7] $Cp^*Co(Et_2C_2B_3H_3)^{2-}$ sandwich unit.

Treatment of $Cp^*Co(Et_2C_2B_3H_2Cl)Ru(CO)_3$ (**1**)[8] with 1.1–1.5 equiv of phenyllithium at 0 °C followed by alkylation with Me_3OBF_4 in the manner of Fischer[9] afforded a 73% isolated yield of the methoxycarbene complex **2** (Scheme I) as an air-stable dark brown-black solid.[10] The molecular structure of **2**, established from X-ray diffraction data[11] (Figure 1), incorporates a diamagnetic 30-electron triple-decker sandwich that is isoelectronic with previously described dicobalt and ruthenium–cobalt carborane–bridged triple-decker compounds.[7,12] Equivalently, the ruthenium carbene unit in **2** can be regarded as an 18-electron fragment containing a formal Ru(II) center coordinated to a 6-electron-donor cobaltacarborane dinegative ligand.[13] Thus, **2** extends to group 8 the family of neutral dicarbonyl carbene complexes of π-donor ligands [$(\eta^6\text{-arene})(CO)_2M$ (M = Cr, Mo, W) and $Cp(CO)_2M$ (M = Mn, Re)].

The central 7-vertex RuC_2B_3Co cluster exhibits normal distances and angles.[7,12] The methoxy group is aligned in an s-cis

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[4] (a) Grimes, R. N. In *Electron-Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; John Wiley and Sons: New York, 1991; Chapter 11, pp 261–285. (b) Grimes, R. N. *Chem. Rev.* **1992**, *92*, 251.

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[6] Pilotti, M. U.; Stone, F. G. A.; Topaloglu, I. *J. Chem. Soc., Dalton Trans.* **1991**, 1621 and references therein.

[7] Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 4776.

[8] Complex **1**, a chloroboron derivative of the previously reported[7] $Cp^*Co(Et_2C_2B_3H_3)Ru(CO)_3$ (**1a**), was prepared from $Cp^*Co(Et_2C_2B_3H_2Cl)^{2-}$ and $[(CO)_3RuCl_2]_2$ as described[7] for the synthesis of **1a**.

[9] Fischer, E. O.; Maasbol, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580.

[10] A 204-mg (0.384 mmol) sample of dark green **1** in dry THF at 0 °C was treated with 1.5 equiv of phenyllithium in 1:1 cyclohexane/diethyl ether, which produced a color change to brown. Me_3OBF_4 (169 mg, 1.15 mmol, 3.0 equiv) was added under inert gas, after which the solution was stirred at 0 °C for 15 min, at which point IR spectroscopy indicated that the reaction was complete. The solution was opened to air and the solvent removed in vacuo. The dark brown residue was extracted with CH_2Cl_2, filtered through Celite, and chromatographed on preparative silica gel TLC plates, which were developed in 5:1 hexane/dichloromethane. A minor green band (**1**, <2%) and a brown band (**2**, 177 mg, 0.284 mmol, 73%) were collected, the latter compound as dark brown air-stable crystals: mp 149–151 °C dec; ^1H NMR (δ, ppm, $CDCl_3$) 7.83 (d, CH), 7.45 (t, CH), 7.36 (t, CH), 4.78 (s, OMe), 2.75 (m, CH_2), 2.53 (m, CH_2), 1.71 (s, C_5Me_5), 1.50 (t, CH_3); ^{13}C NMR (δ, ppm, $CDCl_3$, proton decoupled) 304.7 (carbene), 197.5 (CO), 151.1 (ipso C6), 133.0 (CH, phenyl), 129.8 (CH, phenyl), 129.0 (CH, phenyl), 99.8 (C_2B_3 ring), 90.4 (C_5 ring), 69.8 (OMe), 25.1 (ethyl CH_2), 16.9 (Cp* CH_3), 9.5 (ethyl CH_3); ^{11}B NMR (δ, ppm relative to $BF_3{\cdot}OEt_3$, CH_2Cl_2, B–H coupling not resolved) 57.9 (1 B), 1.8 (2 B); IR (neat, cm^{-1}) 2963 m, 2927 m, 2478 m, 2000 vs, 1949 vs, 1451 m, 1259 s, 1080 m, 1023 m, 1001 m, 802 m; UV–vis (nm) 204, 252, 314; MS (CI) (CH_4) cutoff at *m/z* 629 corresponding to parent ion envelope, base peak *m/z* 624, intensity pattern consistent with calculated spectrum based on natural isotope abundances for $RuCoClO_3C_{26}B_3H_{36}^+$, fragments at *m/z* 596 (–CO), 568 (–2CO), and 532; cyclic voltammetry [$E_{1/2}$ ($|E_p^c - E_p^a|$, i_p^c/i_p^a) V vs $FeCp_2$, 0.2 M Bu_4NPF_6 in CH_2Cl_2, 23 °C, 1 V s^{-1}, referenced to internal $CoCp^*_2$ at +1.34 V vs SCE]: +0.105 (140 mV, 0.93), +0.84 (irreversible), –1.84 (130 mV, 0.69). Anal. Calcd for $RuCoClO_3C_{26}B_3H_{25}$: C, 50.09; H, 5.46. Found: C, 49.94; H, 5.46.

[11] Crystal data: space group $P2_1/n$; a = 8.977 (3) Å, b = 10.007 (3) Å, c = 30.214 Å, β = 91.00 (2)°, V = 2714 (2) $Å^3$; crystal size 0.47 × 0.42 × 0.36 mm; μ(Mo Kα) = 12.81 cm^{-1}. Data collection parameters: T = –140 °C; 2θ max 55.0°; R = 0.032 for 5562 reflections having $F_o^2 > 3.0\sigma(F_o^2)$.

[12] Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 4784.

[13] For examples of other unchanged, mononuclear Ru(II) carbene complexes, see: (a) Adams, H.; Bailey, N. A.; Ridgway, C.; Taylor, B. F.; Walters, S. J.; Winter, M. J. *J. Organomet. Chem.* **1990**, *394*, 349. (b) Boyd, L. M.; Clark, G. R.; Roper, W. R. *J. Organomet. Chem.* **1990**, *397*, 209. (c) Hoskins, S. V.; Pauptit, R. A.; Roper, W. R.; Waters, J. M. *J. Organomet. Chem.* **1984**, *269*, C55. (d) Casey, C. P.; Palermo, R. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 549. (e) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L.; Thomas, S. *J. Chem. Soc., Dalton Trans.* **1979**, 1929.

planar conformation (Ru—C4—O1—C11 dihedral angle 0.7°), consistent with π-donation from O1 to the carbene moiety and giving rise to a C4—O1 distance similar to those of other alkoxycarbenes.[14] The short Ru—C4 distance of 2.002 (3) Å implies substantial π-donation from Ru to the carbene ligand, as found in $Cp(CO)_2Mn$ and -Re systems.[14] In common with arene dicarbonyl group 6 complexes,[15] the carbene group in **2** is approximately perpendicular to the plane bisecting the CO—Ru—CO fragment; this is in contrast to $Cp(CO)_2Mn$–carbene complexes in which the M═C—O plane usually bisects the CO—M—CO angle,[16] in agreement with theory.[15a,17] This orientation may be sterically favored, although the appearance of a single CO resonance in the ^{13}C NMR spectrum suggests rapid rotation about the Ru—C4 bond.

Complex **2** is relatively stable toward thermolysis, decomposing at 80 °C in THF with a half-life of 1.5 h in a sealed cell and forming the tricarbonyl precursor **1** as the only carbonyl-containing product. Reaction of **2** with an excess of 1-hexyne in refluxing toluene followed by oxidation of the reaction mixture generated the naphthoquinone **3** (Scheme I).[18] This is the first observation of the benzannulation reaction[19] for a group 8 metal–carbene complex,[20] occurring under conditions in which (MeCp)$(CO)_2$MnC(Ph)(OMe) and $Cp(CO)_2$ReC(Ph)(OMe) are unreactive.[16b]

The isolation of **2** presages the synthesis of a new family of ruthenium (and perhaps other metal) carborane-stabilized carbenes with unusual properties, which can be tailored by varying the C_2B_3 ring substituents.[21] We anticipate that these reagents will be relatively accessible, given the recent development of a facile synthesis of *nido*-$R_2C_2B_4B_6$ carboranes[22] that we have employed on a multigram scale.

Acknowledgment. This work was supported by the National Science Foundation (Grant Nos. CHE 90-22713 to R.N.G. and 91-09000 to M.G.F.). We thank Dr. Kent Piepgrass for a sample of complex **1**.

Supplementary Material Available: Listing of complete experimental details and tables of crystal structure data, thermal parameters, bond distances and angles, and mean planes (13 pages). Ordering information is given on any current masthead page.

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(14) Schubert, U. In Transition Metal Carbene Complexes; Dötz, K. H., Fischer, H., Hofmann, P., Kreissl, F. R., Schubert, U., Weiss, K., Eds.; Verlag Chemie: Weinheim, Germany, 1983; Chapter 3.

(15) (a) Kostic, N. M.; Fenske, R. F. *J. Am. Chem. Soc.* **1982**, *104*, 3879. (b) Schubert, U. *J. Organomet. Chem.* **1980**, *185*, 373.

(16) (a) Schubert, U. *Organometallics* **1982**, *1*, 1085. (b) Balzer, B. L.; Cazanoue, M.; Sabat, M.; Finn, M. G. *Organometallics* **1992**, *11*, 1759.

(17) Schilling, B. E. R.; Hoffman, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

(18) A solution of 178 mg (0.286 mmol) of **2** in 8 mL of toluene was refluxed with 117 mg (1.43 mmol) of 1-hexyne for 3 h, and the reaction was judged complete by IR analysis. The flask was opened to air, the solvent was removed by evaporation, and the dark brown residue was taken up in ether and oxidized with 5.70 mL of 0.5 M ceric ammonium nitrate containing 0.1 M HNO_3 for 20 min. The organic phase was dried with $MgSO_4$ and the solvent was removed, affording an orange residue that was column-chromatographed in 10% ethyl acetate/petroleum ether to give 11 mg (0.051 mmol, 18%) of the naphthoquinone **3**, which was identified by ^1H NMR and comparison (NMR, capillary GLC) with an authentic sample prepared from $(CO)_5$CrC(Ph)(OMe) and 1-hexyne.[19]

(19) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644. (b) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Libeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol 1. (c) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5. (d) Bos, M. E.; Wulff, W. D.; Miller, R. A.; Chamberlin, S.; Brandvold, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 9293.

(20) Reaction of tetracarbonyliron–carbene complexes with alkynes gives pyrone products without annulation: Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Springer, J. *J. Am. Chem. Soc.* **1984**, *106*, 5363.

(21) (a) Davis, J. H., Jr.; Attwood, M. D.; Grimes, R. N. *Organometallics* **1990**, *9*, 1171. (b) Piepgrass, K. W.; Grimes, R. N. *Organometallics* **1992**, *11*, 2397. (c) Piepgrass, K. W.; Stockman, K. E.; Sabat, M.; Grimes, R. N. *Organometallics* **1992**, *11*, 2404.

(22) Cendrowski-Guillaume, S. M.; Spencer, J. T. *Organometallics* **1992**, *11*, 969.

Intramolecular Benzannulation Reactions of Manganese Carbene Complexes

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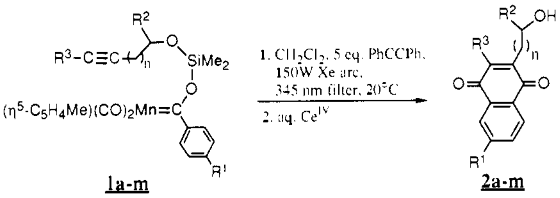
The benzannulation reaction[1,2] of α,β-unsaturated Fischer carbene complexes with alkynes is largely restricted[3] to complexes bearing the pentacarbonylchromium moiety. We have recently found that manganese carbene complexes activated with a titanoxy substituent undergo benzannulation with 1-hexyne in modest yields.[4] Here we report that *intramolecular* benzannulation reactions of siloxycarbene compounds of manganese bearing tethered alkynes produce functionalized naphthoquinones in efficient fashion with complete regioselectivity under photochemical conditions.

Facile connection of the $MeCp(CO)_2Mn$ carbene (MeCp = η^5-C_5H_4Me) and acetylenic alcohol fragments can be accomplished with the dimethylsilyl group, as shown in the general structure **1**.[5] The intramolecular benzannulation reaction of **1** is shown in eq 1.[6]



1a-m   2a-m   (1)

Preliminary results concerning the scope of the intramolecular benzannulation process under a standard set of conditions are summarized in Table I.[7] As in intramolecular benzannulation reactions of chromium alkoxycarbene complexes,[8] yields are low for terminal alkynes (entries 1, 5, 12, and 13) and a trimethylsilyl-substituted substrate (entry 9). In contrast, a variety of substituted propargylic and homopropargylic alcohols afford fair to good yields of naphthoquinones. No other products that can be obtained from alkyne insertion reactions of group 6 Fischer

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(1) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644–646.

(2) (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (b) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813–5832. (c) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Libeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol. 1. (d) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5. (e) Semmelhack, M. F.; Bozell, J. J.; Keller, L.; Sato, T.; Spiess, E. J.; Wulff, W.; Zask, A. *Tetrahedron* **1985**, *41*, 5803–5812.

(3) Wulff, W. D.; Gilbertson, S. R.; Springer, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 520–522.

(4) Balzer, B. L.; Cazanoue, M.; Sabat, M.; Finn, M. G. *Organometallics* **1992**, *11*, 1759–1761.

(5) All siloxycarbene complexes were prepared as in the following example, complex **1b**: A solution of $MeCpMn(CO)_3$ in dry Et_2O is treated with a slight excess of PhLi under inert atmosphere.[13] The lithium acylate, Li[MeCp$(CO)_2$MnCOPh], precipitates as an air-sensitive ether solvate and can be used directly or recrystallized from Et_2O. Under inert atmosphere, neat 2-butyn-1-ol is added dropwise with stirring to a 4-fold excess of neat $SiMe_2Cl_2$, and the volatiles are removed in vacuo to provide $Me_2SiCl(OCH_2C{\equiv}CMe)$. Complex **1b** is then assembled in quantitative yield by the addition of the alkoxysilyl chloride to the acylate in CH_2Cl_2 or THF solution, followed by filtration through Celite to remove LiCl. All manganese siloxycarbene complexes were characterized by ^1H and ^{13}C NMR, IR, and electronic spectroscopy (supplementary material).

(6) The intermolecular reaction of an analogous siloxycarbene complex, $MeCp(CO)_2$MnC(Ph)$(OSiMe_2O$-*n*-Bu), with 1-hexyne provides a 15% yield of the corresponding quinone. See ref 4 for similar reactions.

(7) All quinone products were characterized by ^1H and ^{13}C NMR, IR, and satisfactory elemental analyses (supplementary material).

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