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 ¹³C 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)₂MnC(Ph)(OMe) and Cp(CO)₂ReC(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 C₂B₃ ring substituents.[21] We anticipate that these reagents will be relatively accessible, given the recent development of a facile synthesis of *nido*-R₂C₂B₄B₆ carboranes[22] that we have employed on a multigram scale.

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.

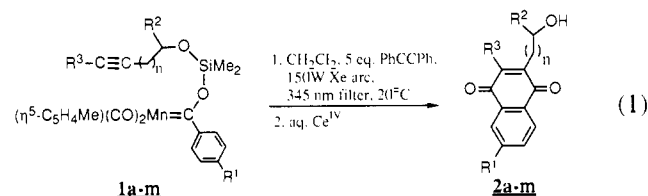## Intramolecular Benzannulation Reactions of Manganese Carbene Complexes

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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 = η⁵-C₅H₄Me) 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]

$$ (1) $$

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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(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 HNO₃ for 20 min. The organic phase was dried with MgSO₄ 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)₅CrC(Ph)(OMe) and 1-hexyne.[19]

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(5) All siloxycarbene complexes were prepared as in the following example, complex **1b**: A solution of MeCpMn(CO)₃ in dry Et₂O is treated with a slight excess of PhLi under inert atmosphere.[13] The lithium acylate, Li[MeCp(CO)₂MnCOPh], precipitates as an air-sensitive ether solvate and can be used directly or recrystallized from Et₂O. Under inert atmosphere, neat 2-butyn-1-ol is added dropwise with stirring to a 4-fold excess of neat SiMe₂Cl₂, and the volatiles are removed in vacuo to provide Me₂SiCl(OCH₂C≡CMe). Complex **1b** is then assembled in quantitative yield by the addition of the alkoxysilyl chloride to the acylate in CH₂Cl₂ or THF solution, followed by filtration through Celite to remove LiCl. All manganese siloxycarbene complexes were characterized by ¹H and ¹³C NMR, IR, and electronic spectroscopy (supplementary material).

(6) The intermolecular reaction of an analogous siloxycarbene complex, MeCp(CO)₂MnC(Ph)(OSiMe₂O-*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 ¹³C NMR, IR, and satisfactory elemental analyses (supplementary material).

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Table I. Intramolecular Benzannulation Reactions of Siloxycarbene Complexes[a]

entry	complex	R^1	R^2	R^3	n	quinone	yield (%)[b]
1	**1a**	H	H	H	0	**2a**	30
2	**1b**	H	H	Me	0	**2b**	75
3	**1c**	H	H	Et	0	**2c**	51
4	**1d**	H	H	Ph	0	**2d**	60
5	**1e**	Me	H	H	0	**2e**	20[c]
6	**1f**	Me	H	Me	0	**2f**	75
7	**1g**	Me	H	Et	0	**2g**	79
8	**1h**	OMe	H	Me	0	**2h**	48
9	**1i**	Me	H	$SiMe_3$	0	**2i**	32[d]
10	**1j**	Me	Et	Me	0	**2j**	51[e]
11	**1k**	Me	H	Me	1	**2k**	56[e]
12	**1l**	Me	H	H	1	**2l**	22
13	**1m**	Me	H	H	2	**2m**	23

[a] Substituent positions refer to numbering scheme in eq 1. [b] Isolated yields by flash chromatography. [c] Acetylation in situ affords a 45% yield of the quinone acetate. [d] Compound **2i** is unstable toward silica gel chromatography, giving diminished yields. [e] Values represent combined yields of hydroxyquinone and carbonyl product from overoxidation in workup.

carbene complexes, such as indenoid or cyclobutenone compounds,[2] are formed.

In every case in which the carbene aryl group is substituted (complexes **1e–m**), a single isomer of the corresponding quinone (**2e–k**) is produced.[9] Analogous regiocontrol in benzannulation reactions has previously been reported for tethered reactions of chromium alkoxycarbene complexes which provide tricyclic products.[8] The present method extends the intramolecular strategy by providing bicyclic products with a convenient functional group for further elaboration.

Reaction conditions were optimized for complex **1f** and include the following variables: (1) irradiation with a 150-W Xe arc lamp was found to be superior to Hg arc sources; (2) a glass filter with half-maximum absorption at 345 nm was found to protect the product from photochemical degradation[10] and to insure selective irradiation of the lowest-energy electronic band of the siloxy-carbene complexes at $\lambda_{max} \approx 360$ nm; and (3) the presence of 5 equiv of diphenylacetylene was found to roughly double the yield of naphthoquinone, without incorporation of the external alkyne. In all cases, diphenylacetylene can be recovered quantitatively. Carbon monoxide (1 atm), styrene, triphenylphosphine, dimethylacetylenedicarboxylate, and 2 equiv of diphenylacetylene were each found to be ineffective additives. Wulff and co-workers have shown the presence of an excess of alkyne to alter the course of benzannulation reactions of chromium, presumably by coordination to one or more intermediates in the multistep process.[11] Consistent with this rationale is our observation that the beneficial effect of 5 equiv of PhCCPh was eliminated in the presence of 1 atm of CO, but use of ^{13}CO resulted in *no* incorporation of label in the product quinone.

The intramolecular nature of the reaction was demonstrated by a crossover experiment in which an equimolar mixture of complexes **1b** and **1g** gave only naphthoquinones **2b** and **2g** in 78% overall yield. In contrast to all benzannulation reactions of chromium and the intermolecular reaction of a manganese titanoxy system,[4] the intramolecular reactions of **1** require irradiation and could not be effected by heating.[12]

Thus, the efficient and regioselective photochemical conversion of acetylenic alcohols to naphthoquinones has been accomplished, representing the first high-yield benzannulation chemistry of

manganese carbene compounds. Studies concerning the scope, mechanism, and applications of this process will be reported in due course.

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Supplementary Material Available: Full details of experimental procedures and characterization of all compounds (15 pages). Ordering information is given on any current masthead page.

A Sequence-Specific Molecular Light Switch: Tethering of an Oligonucleotide to a Dipyridophenazine Complex of Ruthenium(II)

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There has been considerable interest in the development of new chemical methods to distinguish and detect nucleic acids with sequence specificity.[1] One focus of our laboratory has been on the application of ruthenium complexes[2,3] as spectroscopic probes

(9) Quantitative capillary GLC analysis of the crude reaction mixtures showed a single quinone in every case. Stereochemical assignments were made for representative cases by comparison with the isomeric products produced in the reaction of $(CO)_5CrC(Ar)(OMe)$ with protected terminal alkynols, by observation of long-range ^1H-^{13}C NMR coupling, and by X-ray crystallography (supplementary material).

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