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The First Benzannulation Chemistry of Manganese Carbene Complexes: Activation by d^0 Metalation

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Summary: Fischer arylcarbene complexes of manganese bearing a Ti(IV) substituent, $(MeCp)(CO)_2MnC(Ar)(OTiCp_2Cl)$ (Ar = Ph, *p*-tolyl), undergo benzannulation reactions with 1-hexyne under mild photochemical conditions or in refluxing toluene to afford naphthoquinone products. The analogous manganese alkoxycarbene complexes are unreactive. Preliminary tests of the reaction mechanism are *not* consistent with the expected photolytic dissociation of CO ligand from manganese.

The benzannulation reaction[1] is the most widely used of the transformations of Fischer carbene complexes for the purposes of organic synthesis.[2] This chemistry has been almost entirely[3] restricted to metals of group 6, primarily complexes of the pentacarbonylchromium moiety. Two related reactions of manganese have been described, involving the insertion of alkynes into manganese–carbenoid bonds: the condensation of an alkoxycarbene complex with activated α,ω-enynes at 120 °C to afford bicyclic cyclopropanes without CO insertion and the reaction of an acylmanganate anion with 1-hexyne in refluxing THF to provide a butenolide product incorporating a CO ligand.[4] In addition, the insertion of aminoalkynes into Mn–carbene bonds to give vinylcarbene complexes has been previously observed.[5] We report here the first examples of "standard" benzannulation reactions of manganese arylcarbene complexes with alkynes to produce quinone products, under both photochemical and thermal conditions.

We have screened the reactivity of alkoxy arylcarbene complexes of manganese with alkynes to verify that these species do not engage in benzannulation reactions analogous to those of pentacarbonylchromium, as suggested by the lack of such reports in the literature. Indeed, a typical alkoxy arylcarbene complex, $(\eta^5\text{-MeCp})(CO)_2MnC(Ph)(OMe)$ (1),[6,7] failed to react with 10 equiv of 1-hexyne in refluxing THF or refluxing toluene (20 h, no disappearance of 1) or under photochemical conditions (450-W Hg lamp, Pyrex, THF or CH_2Cl_2, 8 h, decomposition of 1).

In an attempt to activate the carbene system by replacing the alkoxide moiety with an electron-withdrawing metaloxy fragment, we prepared the titanoxycarbene derivative $(\eta^5\text{-MeCp})(CO)_2MnC(Ph)(OTiCp_2Cl)$ (**2a**).[7,8]

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[7] All complexes were prepared under an inert atmosphere from the corresponding lithium acylate, synthesized in the manner of ref 6. Titanoxycarbene compounds were prepard in quantitative yield by metalation with Cp_2TiCl_2 in the manner of: Raubenheimer, H. G.; Fischer, E. O. *J. Organomet. Chem.* **1975**, *91*, C23–C26. Complex 1 was prepared by alkylation with $MeSO_2F$ or Me_3OBF_4 and purified by column chromatography under nitrogen. All manganese carbene complexes decompose in minutes in the presence of air. Complex 1: ^1H NMR ($CDCl_3$, 300 MHz, δ) 7.28 (m, 3 H), 6.92 (m, 2 H), 4.45 (s, 3 H), 4.41 (d, 4 H), 1.93 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.3 MHz, δ) 333.2, 232.6, 155.7, 127.2, 126.7, 122.4, 103.4, 88.0, 87.0, 63.2, 13.6; IR (CH_2Cl_2, cm^{-1}) 1952, 1884; UV–vis (THF, λ_{max} (nm), log ϵ) 224 (4.3), 272 (3.8), 354 (3.7).

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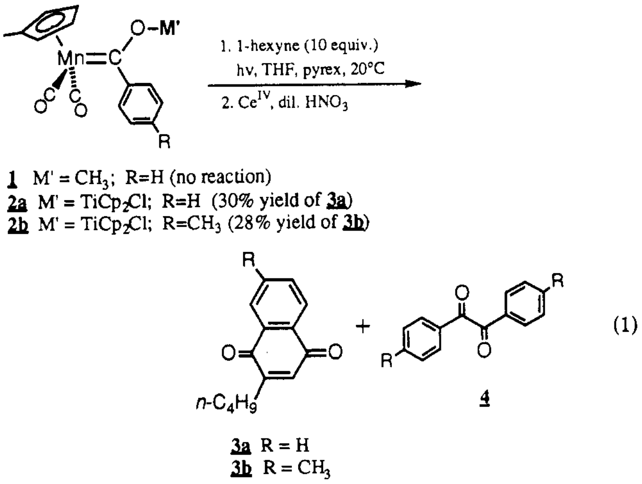
Table I. Bond Distances (Å) for $(MeCp)(CO)_2MnC(OTiCp_2Cl)(Ph)$ (2a) and $Cp(CO)_2MnC(OEt)(Ph)$ (6)[18]

bond	2a	6
Mn—C1	1.882 (8)	1.865 (14)
C1—O1	1.322 (8)	1.356 (17)
C1—C2(Ph)	1.49 (1)	1.536 (19)
Mn—CO	1.75 (1), 1.745 (9)	1.795 (14), 1.805 (15)
MnC═O	1.17 (1), 1.18 (1)	1.143 (18), 1.159 (18)

Complex **2a** was found to be an active benzannulation reagent under photochemical conditions (450-W Hg lamp, Pyrex, THF, 20 °C, 5 h), affording a 30% yield of naphthoquinone **3a**,[9] in the presence of 10 equiv of 1-hexyne followed by oxidative workup, as shown in eq 1. In addition, the diarylglyoxal (benzil) 4 derived from coupling of two arylcarbene fragments is produced in small amounts (5–10% with respect to starting carbene complex).[10] When it is refluxed in THF under room light, the titanoxycarbene complex undergoes only decomposition and no benzannulation in the presence of 10 equiv of 1-hexyne. However, heating to 110 °C in toluene for 1 h gives rise to complete disappearance of **2a** and the isolation of **3a** in 18% yield. Although the yields of quinone are low, no other products frequently isolated from reactions of Fischer carbene complexes with alkynes[2] are formed, such as indenoid or cyclobutenone compounds.[11] Thus, an electron-deficient metal center (Ti^{IV}) is apparently required to activated these systems for benzannulation.



(1)

The reaction rate is dependent upon the light intensity: a 450-W Hg lamp provides complete consumption of **2a** in 4–6 h, in contrast to 12–18 h with a 150-W Xe arc source. The reaction is also quite sensitive to solvent: photolysis with either lamp in CH_2Cl_2 affords no loss of starting material **2a**.

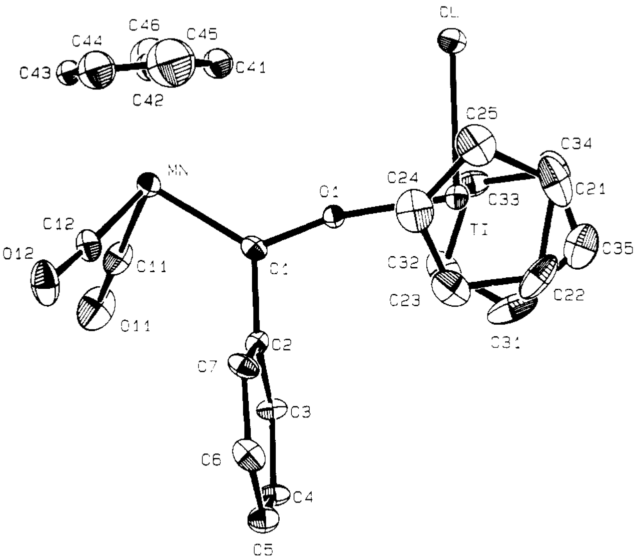


Figure 1. ORTEP structure of $(\eta^5\text{-MeCp})(CO)_2MnC(Ph)(OTiCp_2Cl)$ (**2a**) with numbering scheme.

When a *p*-tolyl substituent is employed at the carbene carbon (complex **2b**),[12] a single isomer of the quinone (**3b**) is isolated in 28% yield (eq 1; 150-W Xe arc lamp, Pyrex, 20 °C, 12–18 h).[10,13] Quinone **3b** is identical (^1H, ^{13}C NMR; capillary GLC)[14] with the naphthoquinone produced from the reaction of the chromium alkoxycarbene analogue $(CO)_5CrC(OMe)(4\text{-}C_6H_4Me)$[15] (**5**) and 1-hexyne. Thus, the selectivity "rule" for unsymmetrical alkynes[2b,16] is apparently preserved for manganese: alkyne insertion proceeds in a manner consistent with the placement of the larger alkyne substituent on the side of the carbene-bearing metal.

The X-ray crystal structure of complex **2a** is shown in Figure 1[17] and can be compared to the structure of the analogous (unreactive) alkoxycarbene complex $(Cp)(CO)_2Mn{=}C(OEt)(Ph)$ (**6**) reported by Schubert (Table I).[18] In both structures, the carbene plane bisects the

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(8) Complex **2a**: ^1H NMR ($CDCl_3$, 300 MHz, δ) 7.26–7.28 (m, 3 H), 7.09 (d, 2 H), 6.47 (s, 10 H), 4.44 (d, 4 H), 1.88 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.3 MHz, δ) 339.1 (carbene), 233.2, 153.7, 128.2, 127.0, 123.8, 118.0 ($TiCp_2$), 102.2, 86.0, 85.4, 13.9; IR (CH_2Cl_2, cm^{-1}) 1927, 1858; IR (THF, cm^{-1}) 1925, 1858; UV–vis (THF, λ_{max} (nm), log ϵ) 218 (4.5), 248 (4.4), 282 (4.2), 406 (4.0); UV–vis (hexane, λ_{max} (nm)) 212, 246, 282, 400. Anal. Calcd for $C_{25}H_{22}O_3ClMnTi$: C, 59.02; H, 4.36. Found: C, 58.48; H, 4.28.

(9) (a) **3a**: ^1H NMR ($CDCl_3$, 300 MHz, δ) 8.06 (m, 2 H), 7.77 (m, 2 H), 6.78 (s, 1 H), 2.57 (t, 2 H), 1.56 (dd, 2 H), 1.43 (dt, 2 H), 0.95 (t, 3 H); ^{13}C NMR ($CDCl_3$, 75.3 MHz, δ) 185.1, 151.9, 134.6, 133.5, 132.3, 132.0, 126.5, 125.9, 30.1, 29.2, 22.4, 13.8; IR ($CDCl_3$, cm^{-1}) 1664 (s), 1620 (m), 1597 (m). (b) For the corresponding $Cr(CO)_3$-bound hydroquinone methyl ether, see: Dötz, K. H.; Dietz, R. *Chem. Ber.* **1977**, *110*, 1555–1563.

(10) We have found diarylglyoxals to be products of the decomposition of related chromium titanoxycarbene complexes as well.

(11) Intramolecular benzannulation reactions of titanoxycarbene complexes of chromium under investigation in our laboratory do provide such products.

(12) **2b**: ^1H NMR ($CDCl_3$, 300 MHz, δ; a minor species (2–20%) is present in inverse proportion to concentration; asterisks mark the major resonances) 7.26 (br s, 4 H), 7.06* (br s, 4 H), 6.66* (s, 10 H), 6.47 (s, 10 H), 5.32 (s, CH_2Cl_2 or crystallization), 4.43* (d, 4 H), 4.22 (s, 4 H), 2.32* (s, 3 H), 2.22 (s, 3 H), 1.86* (s, 3 H), 1.83 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.3 MHz, δ; only one set of peaks visible) 339.1 (carbene), 233.0, 151.0, 138.6, 127.6, 124.8, 118.4, 102.6, 53.8 (CH_2Cl_2), 86.3, 84.1, 21.8, 14.4; IR (THF, cm^{-1}) 1924, 1856; UV–vis (THF, λ_{max} (nm), log ϵ) 218 (4.7), 244 (4.5), 282 (4.4), 398 (4.0). Anal. (when precipitated from cold CH_2Cl_2, 1 mol of solvent is retained) Calcd for $C_{26}H_{24}O_3ClMnTi{\cdot}CH_2Cl_2$: C, 53.37; H, 4.31. Found: C, 52.89; H, 4.20.

(13) When the reaction is performed with a 450-W Hg lamp, **3b** is isolated in 17% yield.

(14) **3b**: ^1H NMR ($CDCl_3$, 300 MHz, δ) 7.94 (d, 1 H), 7.88 (s, 1 H), 7.53 (d, 1 H), 6.75 (s, 1 H), 2.56 (t, 2 H), 2.49 (s, 3 H), 1.56 (dd, 2 H), 1.43 (dt, 2 H), 0.95 (t, 3 H); ^{13}C NMR ($CDCl_3$, 75.3 MHz, δ) 185.5, 185.1, 151.7, 144.6, 134.7, 134.3, 132.2, 129.9, 126.9, 126.2, 30.1, 29.2, 22.4, 21.8, 13.8; IR ($CDCl_3$, cm^{-1}) 1661 (s), 1618 (m), 1603 (m); GLC (DB1701, 30 m × 0.32 mm; temperature program 100 °C for 2 min, ramp 20 °C min^{-1} to 240 °C) 10.5 min.

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(17) Crystals obtained from 1:1 Et_2O/CH_2Cl_2 at −30 °C. Crystallographic data: $C_{25}H_{22}ClMnO_3Ti$, M_r = 508.74; monoclinic, space group $P2_1/n$ (No. 14); a = 8.482 (3) Å, b = 18.142 (7) Å, c = 14.783 (6) Å; β = 103.05 (3)°; V = 2216 (3) Å^3; Z = 4; d_{calcd} = 1.53 g cm^{-3}. The structure was solved by direct methods using TEXSAN 5.0. Full-matrix least-squares refinement gave the final $R(F)$ = 0.053 and $R_w(F)$ = 0.063 for 1999 absorption-corrected reflections with $I > 3\sigma(I)$ measured up to 2θ = 50° on a Rigaku AFC6S diffractometer (Mo Kα radiation, λ = 0.71069 Å; T = −120 °C).

OC–Mn–CO angle, consistent with molecular orbital calculations.[19] The phenyl ring is perpendicular to the carbene plane in both but is found anti to the MeCp ligand in **2a** and syn to the Cp ligand in **6**. The large C1–O1–Ti bond angle of **2a** (160.8 (5) vs 119.9° for C1–O1–C(Et) of **6**) and shortened C1–O1 distance (1.322 (8) Å for **2a** vs 1.356 (17) Å for **6**) are characteristic of titanoxycarbene structures[20] and suggest sp hybridization at O1, allowing π-donation from O1 to both C1 and the π-acidic $\mathrm{Ti^{IV}}$ center.[20] This gives rise to a red shift in the low-energy band in the electronic spectrum from 354 nm (log ϵ 3.7) in 1 to 406 nm (log ϵ 4.0) for **2a** and 398 nm (log ϵ 4.0) for **2b**, as has been noted for related complexes of chromium.[20] The low-energy band may be tentatively assigned to a metal-to-carbene charge-transfer transition by virtue of its solvent dependence (406 nm in THF vs 400 nm in hexane)[8] and a similar assignment for chromium and tungsten alkoxy Fischer carbene complexes.[21]

A comparison of bond distances (Table I) and carbonyl stretching frequencies in the IR spectra (1927, 1858 cm^{-1} for **2a** vs 1952, 1884 cm^{-1} for the MeCp alkoxycarbene analogue 1) shows that Mn engages in increased π-donation to the CO ligands upon $\mathrm{Ti^{IV}}$ substitution and, therefore, perhaps less π-donation to the carbene center. It is interesting to note that the C1–phenyl bond is shortened in the titanoxycarbene complex (Table I), even though π-overlap is not possible due to the perpendicular orientation of the carbene and phenyl planes. The data suggest that the enhanced reactivity of the bimetallic structure may be due to increased electrophilicity at the carbene carbon or changes in the nature of the MLCT excited state.

The first step in the benzannulation reactions of chromium alkoxycarbene complexes is generally presumed to be loss of CO.[2c,22] However, Xe arc lamp irradiation of **2b** in THF in the presence of 10 equiv of 1-hexyne gives rise to *two* new carbonyl bands of equal intensity in the IR spectrum at lower energy than those of **2b**, which disappear together as the reaction proceeds.[23] Irradiation in the absence of 1-hexyne produces a new pair of bands at higher energy than those of **2b**, which appear and disappear at a rate comparable to that of the benzannulation experiment.[23] At no point is a single CO stretching band observed, suggesting that intermediates bearing two terminal CO ligands are produced upon photolysis. In contrast, treatment of a THF solution of **2b** with $W(CO)_5$(THF) at ambient temperature induces decarbonylation of **2b** over 10 h, indicated by the formation of $W(CO)_6$ and a species with a single CO stretch at 1919 cm^{-1}. No benzannulation products are isolated when this solution is treated with 1-hexyne and allowed to stand at room temperature for 24 h, followed by heating to reflux for 2 h. These data suggest that CO loss may not be required for photochemical benzannulation reactions of manganese titanoxycarbene complexes. The possible formation of ring-slipped cyclopentadienyl intermediates is under investigation.

These results demonstrate that manganese Fischer carbene complexes, readily accessible from the relatively inexpensive $(MeCp)Mn(CO)_3$, can be activated toward photochemical and thermal benzannulation reactions by electron-deficient metal substitution.

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Registry No. 1, 34742-22-8; **2a**, 140468-47-9; **2b**, 140468-48-0; **3a**, 34491-88-8; **3b**, 140468-49-1; 4 (R = H), 134-81-6; 4 (R = Me), 3457-48-5; 1-hexyne, 693-02-7.

Supplementary Material Available: Text giving experimental details, complete tables of experimental parameters, positional parameters, bond distances and angles, and thermal parameters, and a figure showing disorder in the MeCp ring for the X-ray structural determination of **2a** (10 pages). Ordering information is given on any current masthead page.

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(23) IR resonances (ν_{CO}): **2b**, 1924 and 1856 cm^{-1}; irradiation in presence of 1-hexyne, new bands at 1896 and 1827 cm^{-1}; irradiation in the absence of 1-hexyne, new bands at 1952 and 1891 cm^{-1}.

The First Platinum η^3-Azatrimethylenemethanes and Platinapyrazolines Formed from Regioselective Addition of Amine or Hydrazine to a σ-Allenyl Complex of Platinum(II)

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Summary: Regioselective addition of an amine or hydrazine to the β-carbon of the σ-allenyl group in *trans*-$\mathrm{Pt(CH{=}C{=}CH_2)(Br)(PPh_3)_2}$ exclusively yields novel platinum η^3-azatrimethylenemethane and platinapyrazoline derivatives, respectively.

The chemistry of σ-allenyl complexes continues to develop at a rapid pace, owing to interesting structures and reactivity patterns of such complexes.[1] Particularly significant is the fact that novel metallacycles may be ac-

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