

Available online at www.sciencedirect.com



Inorganica Chimica Acta 345 (2003) 320-326

Inorganica Chimica Acta

www.elsevier.com/locate/ica

# Formation of manganese enediyne complexes from manganese alkynylcarbene complexes

Charles P. Casey\*, Trevor L. Dzwiniel, Stefan Kraft, Michael A. Kozee, Douglas R. Powell

Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1322, USA

Received 20 June 2002; accepted 16 August 2002

Dedicated to Professor Richard Schrock on the occasion of his 60th Birthday and in recognition of his pioneering contributions to the chemistry of metal carbene complexes

### Abstract

Keywords: Manganese alkynylcarbene complexes; Enediyne; Manganese alkyne complexes

### 1. Introduction

Heteroatom substituted alkynylcarbene complexes such as  $(OC)_5M=C(OR)C\equiv CR'$  are highly reactive, easily accessible, and useful in a plethora of highyielding transformations [1]. Despite the large number of these Fischer carbene complexes [2], only recently have [1,3] metal shifts been documented, as in the case of  $Cp(OC)_2Re=C(Tol)C\equiv CPh$  (1)  $(Cp = \eta^5-C_5H_5, Tol = 4 MeC_6H_4$ ) rearranging to  $Cp(OC)_2Re=C(Ph)C\equiv CTol$  (2) upon thermolysis at 120 °C (Scheme 1) [3]. However, the major product in this reaction was the dimeric *E*enediyne complex  $[Cp(OC)_2Re]_2[\eta^2,\eta^2-TolC\equiv C(Ph)C=$  $C(Ph)C\equiv CTol]$  (3) formed by the regioselective coupling of the remote alkynyl carbons in a kinetically 2nd order process [4].

The closely related dimerization of  $Cp(OC)_2Re=C(Tol)C=CMe$  (4) at 100 °C in toluene provided

 $[Cp(OC)_2Re]_2[\eta^2,\eta^2-TolC \equiv C(Me)C = C(Me)C \equiv CTol]$ (5) as a 1.2:1 mixture of *E*- and *Z*-alkene isomers (Scheme 2), demonstrating that the coupling mechanism has no intrinsic bias toward *E*-enediyne complexes. The overall regioselectivity stands in contrast to the reported ability of Fischer carbene complexes to couple the carbene carbons and form alkenes [5]. Sierra has reported a selective 'head-to-head' coupling in the Pdcatalyzed dimerization of  $(OC)_5Cr=C(OEt)C\equiv CPh$  to (E,Z)-PhC $\equiv C(OEt)C=C(OEt)C\equiv CPh$ , with no evidence of 'tail-to-tail' or 'head-to-tail' coupling products [6].

We have recently shown that the tethered bis-(alkynylcarbene) rhenium complex,  $Cp(OC)_2Re=C(Tol)C=CCH_2CH_2CH_2C\equiv CC(Tol)=Re(CO)_2Cp$  (6) readily re-





0020-1693/02/\$ - see front matter  $\odot$  2002 Elsevier Science B.V. All rights reserved. PII: S 0 0 2 0 - 1 6 9 3 ( 0 2 ) 0 1 2 7 3 - 2

<sup>\*</sup> Corresponding author. Tel.: +1-608-262 0584; fax: +1-608-265 4534.

E-mail address: casey@chem.wisc.edu (C.P. Casey).



arranges to the cyclic enediyne complex  $[Cp(OC)_2-Re]_2[\eta^2,\eta^2-TolC=CC(CH_2CH_2CH_2)=CC=CTol]$  (7) below room temperature by the coupling of the remote alkynyl carbons (Scheme 3) [4b]. This straightforward route to enediynes under mild conditions has potential value in organic synthesis. However, this reaction is hampered by the difficulty of releasing the tightly bound alkynes from rhenium as well as by the high expense of stoichiometric rhenium reactions. Here we report the synthesis of the more economical manganese alkynylcarbene complexes and their conversion to manganese enediyne complexes and to free enediynes.

### 2. Results and discussion

### 2.1. Synthesis of manganese alkynylcarbene complexes

Simple manganese alkynylcarbene complexes have been prepared by us [7] and by Lugan [8]. Addition of acetylide anions to manganese carbyne complexes leads to good yields of manganese alkynylcarbene complexes as dark brown to black materials (Scheme 4). The Cp compounds are generally highly crystalline while the C<sub>5</sub>H<sub>4</sub>Me complexes are often oily. In a representative procedure, the deep yellow thermally sensitive manganese carbyne complex  $[Cp(OC)_2Mn \equiv CTol]^+BCl_4^-$  (8) [9] was dissolved in methylene chloride at -35 °C. When an equivalent amount of PhC=CZnBr in THF, prepared from PhC=CLi and ZnBr2, was added to carbyne complex 8, the solution turned deep redbrown. After slow warming to room temperature,  $Cp(OC)_2Mn=C(Tol)C\equiv CPh$  (9) was isolated in 44% yield after preparative thin layer chromatography as a red-brown solid. The reaction yield depends strongly on the purity of carbyne complex 8; higher yields were obtained using freshly prepared 8. The related manganese alkynylcarbene complexes  $(\eta^5 - C_5 H_4 Me)(CO)_2 Mn =$  $C(Tol)C \equiv CTol (10), (\eta^{5}-C_{5}H_{4}Me)(CO)_{2}Mn = C(Ph)C \equiv$ CTol (11), and  $(\eta^5-C_5H_4Me)(CO)_2Mn=C(Tol)C=CPh$ (12) were prepared by similar procedures.

The spectroscopic properties of the manganese alkynylcarbene complexes are similar to those of their rhenium analogues. The <sup>13</sup>C NMR spectrum of **9** contains two characteristic peaks, one at  $\delta$  234.3 assigned to the CO ligands and the other at  $\delta$  301.1 assigned to the carbene carbon. Infrared spectroscopy



Fig. 1. X-Ray crystal structure of  $Cp(OC)_2Mn=C(Tol)C=CPh$  (9). Selected bond lengths (Å) and angles (°): Mn=C(1), 1.892(2); C(1)-C(2), 1.423(2); C(2)=C(3), 1.201(3); C(1)-C(11), 1.487 (2); Mn-C(4), 1.792(2); Mn-C(1)-C(2), 117.6 (1); Mn-C(1)-C(11), 129.9(1); C(2)-C(1)-C(11), 112.4(2); C(1)-C(2)-C(3), 178.1(2); C(2)-C(3)-C(18), 175.1(2); C(1)-Mn-C(4), 95.4(1); C(1)-Mn-C(5), 90.8(1); C(4)-Mn-C(5), 87.9(1).

2 C17

shows two metal carbonyl peaks at 1975 and 1915  $\text{cm}^{-1}$ . X-ray quality crystals were obtained by slow evaporation of a methylene chloride/pentane solution. X-ray crystallography confirmed the structure of **9** (Fig. 1) [10].

# 2.2. Dimerization of manganese alkynylcarbene complexes to enediyne complexes

We have found that mild heating converts the manganese alkynylcarbene complexes to a mixture of E- and Z-enediyne manganese complexes. Thermolysis

of a 0.8 M solution of  $(\eta^5-C_5H_4Me)(CO)_2Mn = C(Tol)C \equiv CTol (10)$  in toluene at 65 °C for 8 h provided the bright red enediyne complex  $[(\eta^5-C_5H_4Me)-(OC)_2Mn]_2[\eta^2,\eta^2-TolC \equiv C(Tol)C = C(Tol)C \equiv CTol]$  (13-*E* and 13-*Z*) in 30% yield after column chromatography (Scheme 5). Infrared spectroscopy showed only two peaks for 13 at 1978 and 1915 cm<sup>-1</sup>. However, the <sup>1</sup>H NMR spectrum exhibited at least six separate methyl resonances, consistent with the presence of *E*- and *Z*enediyne isomers with three methyl resonances each. Note that, unlike the dimerization of rhenium alkynylcarbene complex 2 which gave only *E*-enediyne complex 3, similar amounts of manganese *E*- and *Z*-enediyne complexes13-*E* and 13-*Z* were obtained.

Some dimerization of  $(\eta^5-C_5H_4Me)(CO)_2Mn = C(Ph)C=CTol (11)$  occurred when it was stored as an oil over 7 days at room temperature. The high concentration of 11 in the oil speeds up the kinetically 2nd order dimerization and allows dimerization to occur at room temperature. In contrast, dilute solutions of 11 require heating in toluene for dimerization. The mixture of dimers was difficult to separate from alkynylcarbene complex 11 due to their similar polarity; however, a small amount of the mixture of dimers was isolated by preparative TLC.

The <sup>1</sup>H NMR spectrum of this mixture of dimers showed at least eight overlapping methyl resonances, suggesting a mixture of several isomeric manganese enediyne complexes. Two methyl resonances each would be expected for the E- and Z-enediyne isomers from 'tail-to-tail' and from 'head-to-head' coupling; and four methyl resonances each would be expected for the Eand Z-enediyne isomers from 'head-to-tail' coupling.

# 2.3. Thermal release of enediynes from manganese enediyne complexes

Manganese enediyne complexes are much more thermally labile than their rhenium counterparts. Thermolysis of  $(\eta^5-C_5H_4Me)(CO)_2Mn=C(Tol)C=CTol$  (10) in toluene at 100 °C generated a 1:1 mixture of the metal-free *E*- and *Z*-enediynes TolC=CC(Tol)= C(Tol)C=CTol (14-*E* and 14-*Z*) and small amounts of  $(\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)Mn(CO)<sub>3</sub> (Scheme 5). The presence of a peak at *m*/*z* 816.2 in the mass spectrum of 14 clearly indicated the formation of dimers. Thermolysis of the isolated manganese enediyne complex 13 at 100 °C for several hours resulted in decomplexation and formation of free *E*- and *Z*-enediynes 14-*E* and 14-*Z* [11]. In contrast, rhenium enediyne complexes 3 and 5 are stable at 120 °C.

Thermolysis of the regioisomeric manganese alkynylcarbene complexes **11** and **12** at 100 °C for 8–12 h produced free enediynes directly, as determined by mass spectrometry (Scheme 6). There are six possible enediyne isomers: *E*- and *Z*-PhC=C(Tol)C=C(Tol)C= CPh (**15**-*E* and **15**-*Z*) from 'tail-to-tail' dimerization of **11**, *E*- and *Z*-PhC=C(Tol)C=C(Ph)C=CTol (**16**-*E* and **16**-*Z*) from 'tail-to-tail' cross-dimerization of **11** and **12**, and *E*- and *Z*-TolC=C(Ph)C=C(Ph)C=CTol (**17**-*E* and **17**-*Z*) from 'tail-to-tail' dimerization of **12**. The symmetric dimers **15** and **17** have one kind of methyl group each, while the cross dimers **16** have two different methyl groups each, giving a total of eight different methyl groups.

The <sup>1</sup>H NMR spectra of the mixtures of enediyne dimers from thermolysis of both 11 and 12 showed the same eight methyl resonances between  $\delta$  2.5 and 2.25 but in different ratios, suggesting some regioselectivity in the dimerization. If no isomerization of the starting alkynylcarbene complex 11 occurred, regioselective 'tail-to-tail' dimerization would produce only 15-*E* and 15-*Z* and only two methyl resonances should have been seen. If isomerization of alkynylcarbene complexs 11 and 12 were much faster than dimerization, the same ratio of eight methyl resonances would be expected from either complex. Our observations require competitive rates of isomerization and dimerization and regioselectivity in the dimerization process.

Tentative but self-consistent assignments of the methyl resonances of the enediyne dimers to specific isomers were made by assuming that: (1) the major product in each reaction was an *E*-enediyne resulting from 'tail-totail' coupling of the starting alkynylcarbene complex, as



Scheme 5.



seen for the related dimerization of rhenium complex 2; and (2) cross-dimerization products 16-*E* and 16-*Z* give rise to two equal-intensity peaks in the products from either 11 or 12. The chemical shift assignments for the complexes were: 15-*E* ( $\delta$  2.429), 15-*Z* (2.314), 16-*E* (2.423 and 2.304), 16-*Z* (2.360 and 2.337), 17-*E* (2.330), and 17-*Z* (2.366). Using these assignments, the ratio of 15:16:17 from the thermolysis of 0.75 M 11 was 0.54:0.36:0.10. Thermolysis of a more dilute solution (0.3 M) of the regioisomeric alkynylcarbene complex 12 gave a 0.20:0.35:0.45 ratio of 15:16:17. The lower initial concentration in 12 allows the 1st order isomerization to more effectively compete with the 2nd order dimerization, resulting in a less selective dimerization.

The ratio of products formed in both dimerizations could be simulated using the different initial concentrations and the same relative rates of isomerization to dimerization of  $k_2(\text{dimer})/k_1(\text{isom}) = 2.3 \text{ M}^{-1}$ . The (observed, *calculated*) product ratios for dimerization of 0.75 M **11** were: **15** (0.54, 0.60): **16** (0.36, 0.31): **17** (0.10, 0.09); and for dimerization of 0.30 M **12** were: **15** (0.20, 0.14): **16** (0.35, 0.39): **17** (0.45, 0.47). The close agreement between the observed and calculated ratios supports our NMR assignments and rate assumptions. It is remarkable that our 'house of cards' is surprisingly robust.

Substantial variation in Z/E ratios was observed: for example, although the ratio of 17-*E*:17-*Z* remained relatively constant at approximately 3:1, the 15-*E*:15-*Z* ratio varied from 2:1 to 4:1, and the 16-*E*:16-*Z* ratio changed from 1.8:1 to 1:1.6 in the thermolyses of 11 and 12. We do not know whether the observed Z/E ratios are kinetically controlled or whether some isomerization has occurred. In the case of rhenium enediyne complex 5-*Z*, exposure to air resulted in isomerization of 5-*Z* to 5-*E* [4b].

The rates of dimerization of manganese alkynylcarbene complexes are faster than those of the corresponding rhenium complexes, allowing dimerization at lower temperature (65 °C for Mn, 120 °C for Re). There is an even greater difference between the rates of isomerization of manganese and rhenium alkynylcarbene complexes. The ratio of isomerization to dimerization is small for rhenium and results in high regioselectivity of dimerization. In contrast, the similar rates of isomerization to dimerization of manganese alkynylcarbene complexes results in low regioselectivity of dimerization.

### 2.4. Formation of cyclic enediyne manganese complexes

Intramolecular dimerization of tethered bis-(alkynylcarbene) complexes occurs well below room temperature in both rhenium [4b] and manganese systems. The reaction of a slight excess of  $[Cp(OC)_2Mn \equiv$  $(CPh]^+BCl_4^-$  (18) with the bis-alkynylzinc compound  $BrZnC \equiv CCH_2CH_2C \equiv CZnBr$  in  $CH_2Cl_2 - THF$  at -78 °C initially produced a dark red solution, consistent with formation of a manganese bis-(alkynylcarbene) complex (Scheme 7). However, all attempts to isolate this complex failed because of rapid isomerization to the light red-orange manganese enediyne com- $[Cp(OC)_2Mn]_2[\eta^2,\eta^2-PhC\equiv CC(CH_2CH_2CH_2)=$ plex CC=CPh] (19). When a sample taken from the -78 °C reaction mixture was analyzed immediately by thin layer chromatography, only the bright red coupled product 19 was seen; there was no evidence for a dark red faster moving manganese carbene complex. The enediyne complex 19 was isolated by column chromatography in 71% yield (based on 1,6heptadiyne). Infrared spectroscopy of 19 showed the expected two carbonyl bands at 1982 and 1916  $\rm cm^{-1}$ . The <sup>1</sup>H NMR spectrum of **19** was broadened by paramagnetic impurities, and could not be readily assigned.

The enediyne complex **19** was also thermally labile and released the enediyne upon mild heating in toluene at 90 °C over 16 h. Preparative TLC provided 1,2bis(phenylethynyl)cyclopentene (**20**) as an off-white solid in 70% yield.

### 2.5. Summary

We have shown that the dimerization of manganese alkynylcarbene complexes occurs at temperatures lower than those required for the corresponding rhenium complexes. Unlike the thermally stable rhenium enediyne complexes, manganese enediyne complexes release the free enediyne upon moderate heating. The



reactions of manganese alkynylcarbene complexes provide a facile synthesis of the Z-enediyne skeleton.

## 3. Experimental

# 3.1. General

All air sensitive materials were manipulated under nitrogen in a glovebox or by standard high-vacuum and Schlenk-techniques. Hexane and THF were distilled from Na and benzophenone. Dichloromethane was distilled from CaH<sub>2</sub>. Phenylacetylene, 4-ethynyltoluene, 1,6-heptadiyne, BuLi (1.6 M, hexanes), and ZnBr<sub>2</sub> were purchased from Aldrich. [Cp(CO)<sub>2</sub>Mn=CPh]BCl<sub>4</sub>, [Cp(CO)<sub>2</sub>Mn=CTol]BCl<sub>4</sub>, and their methylcyclopentadienyl analogues were synthesized according to modified literature procedures [9].

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Bruker AC 250 or AC 300 or Varian Unity 500 spectrometer. IR spectra were recorded on a Mattson Polaris FT IR spectrometer. Mass spectra were obtained on a Kratos MS-80 or Micromass AutoSpec spectrometer.

## 3.2. $Cp(CO)_2Mn=C(Tol)(C\equiv CPh)$ (9)

Addition of BrZnC=CPh [from LiC=CPh (22 mg, 0.20 mmol) and ZnBr<sub>2</sub> (45 mg, 0.20 mmol) in 0.5 ml THF] to an orange solution of  $[Cp(CO)_2Mn \equiv CTol]BCl_4$ in 1 ml THF at -35 °C produced a red-brown solution which was directly placed on a preparative thin layer chromatography plate. A red-brown band (silica,  $C_6H_{14}$ ,  $R_f = 0.3$ ) was isolated. The brown-red solid was redissolved in a little CH<sub>2</sub>Cl<sub>2</sub> in a vial and layered with  $C_5H_{12}$ . Red-brown crystals of 9 (32 mg, 44%) suitable for an X-ray crystal structure analysis were obtained. Presumably due to paramagnetic impurities, lines in the <sup>1</sup>H NMR spectrum were too broad to analyze ( $\omega_{1/2} \approx 1000$  Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz): δ 21.54 (CH<sub>3</sub>), 87.56 (C=C), 94.05 (C<sub>5</sub>H<sub>5</sub>), 105.27 (C=C), 126.28 (aromatic), 129.14 (aromatic), 129.25 (aromatic), 129.40 (aromatic), 131.29 (aromatic), 134.19 (aromatic), 140.69 (aromatic), 153.21 (aromatic), 234.30 (CO), 301.11 (Mn=C). A Cp impurity was seen at  $\delta$  85.58.

All other manganese alkynyl carbene complexes were prepared in a similar way.

# 3.3. $(\eta^5 - C_5 H_4 Me)(CO)_2 Mn = C(Tol) C \equiv CTol (10)$

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, all signals broad):  $\delta$  7.95 (2H, Tol), 7.43 (2H, Tol), 7.20 (4H, Tol), 5.08 (2H, Cp'), 4.97 (2H, Cp'), 2.36 (Me), 2.33 (Me), 1.95 (Me). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  152.68, 139.87, 139.35, 134.16, 130.92, 129.53, 128.85, 126.02 (aromatic); 122.06 (MeC of Cp'); 107.58, 105.08, (C=C); 94.73, 93.36, (Cp); 21.72, 21.47, 13.53 (Me). IR (C<sub>6</sub>H<sub>14</sub>, cm<sup>-1</sup>): 1974, 1918.

# 3.4. $(\eta^{5}-C_{5}H_{4}Me)(CO)_{2}Mn=C(Ph)C=CTol (11)$

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  7.95 (d, J = 8.0 Hz, 2H, Tol), 7.46–7.36 (m, 5H, Ph), 7.22 (d, J = 8.0 Hz, 2H, Tol), 5.11–5.09 (m, 2H, Cp'), 5.00–4.98 (m, 2H, Cp'), 2.38 (s, TolCH<sub>3</sub>), 1.97 (s, 3H, CpCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (62.9 MHz, CDCl<sub>3</sub>)  $\delta$  300.91 (C=Mn); 233.90 (CO); 155.62, 139.49, 135.00, 130.98, 129.55, 128.97, 128.07, 125.26 (aromatic); 122.01 (MeC of Cp'); 107.69 (Cp'); 105.65, 94.81 (C=C); 94.53, 93.44 (Cp'); 21.72, 13.51 (Me). IR (C<sub>6</sub>H<sub>14</sub>, cm<sup>-1</sup>): 1978, 1920.

# 3.5. $(\eta^5 - C_5 H_4 Me)(CO)_2 Mn = C(Tol) C \equiv CPh$ (12)

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  7.98 (d, J = 7.3 Hz, 2H, Tol), 7.6–7.3 (m, 5H, Ph), 7.22 (d, J = 7.7 Hz, 2H, Tol), 5.10 (br s, 2H, Cp'), 4.99 (br s, 2H, Cp'), 2.34 (s, TolCH<sub>3</sub>), 1.97 (s, CpCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (62.9 MHz, CDCl<sub>3</sub>):  $\delta$  quaternary carbons not found above noise. 130.79, 128.89, 128.80, 128.72, 126.0 (aromatic); 94.80, 93.46 (Cp'); 21.48, 13.53 (Me). IR (C<sub>6</sub>H<sub>14</sub>, cm<sup>-1</sup>): 1975, 1915.

# 3.6. Thermolysis of $(\eta^5 - C_5 H_4 Me)(CO)_2 Mn = C(Tol) - C \equiv CTol (10)$ at 65 °C

A solution of **10** (253 mg, 0.619 mmol) in 1.0 ml C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> was heated at 65 °C for 19 h. TLC analysis revealed one red spot (10% ether/hexanes,  $R_f = 0.6$ ) and extensive baseline decomposition. Column chromatography (silica gel, 10% ether/hexanes) gave [( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)(OC)<sub>2</sub>Mn]<sub>2</sub>[ $\eta^2$ , $\eta^2$ -TolC=CC(Tol)=C(Tol)C= CTol] (**13**) as a sticky red solid (75 mg, 30%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.87 (d, J = 7.8 Hz, H<sub>tol</sub>), 7.4–6.8 (series of overlapping d's, H<sub>tol</sub>), 4.8–4.0 (series of overlapping m, Cp'), 2.426, 2.389, 2.371, 2.340, 2.333, 2.311, 2.295, 2.247, 2.232 (overlapping Me of tolyl and

Cp' groups). IR ( $C_6H_{14}$ , cm<sup>-1</sup>): 1976, 1915. MS (ESI) m/z calc. for  $C_{50}H_{42}$  <sup>55</sup>Mn<sub>2</sub>O<sub>4</sub> [ $M^+$ ]: 816.1844. Found: 816.1837.

# 3.7. Thermolysis of $(\eta^5 - C_5 H_4 Me)(CO)_2 Mn = C(Tol) - C = CTol (10)$ at 100 °C

A solution of 10 (67 mg, 0.164 mmol) in 0.27 ml  $C_6H_5CH_3$  was heated at 100 °C for 8 h. A ~1:1 mixture of Z-:E-TolC=CC(Tol)=C(Tol)C=CTol (14) (15 mg, 42%) was isolated as a yellow solid by preparative TLC (5% EtOAc/hexanes). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  7.89 (d, J = 8.5 Hz, 2H, H<sub>tol</sub>), 7.44 (d, J = 8.5 Hz, 2H, H<sub>tol</sub>), 7.22 (d, J = 7.8 Hz, 6H, H<sub>tol</sub>), 7.13  $(d, J = 8.5 Hz, 2H, H_{tol}), 7.10 (d, J = 8.3 Hz, 2H, H_{tol}),$ 7.02 (d, J = 8.0 Hz, 2H, H<sub>tol</sub>), 2.429 (s, 3H, Me), 2.368 (s, 3H, Me), 2.343 (s, 3H, Me), 2.316 (s, 3H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  138.49, 137.95, 137.51, 136.42, 134.85, 131.53 (CH), 131.26 (CH), 129.60 (CH), 129.15 (CH), 129.09 (CH), 129.04 (CH), 128.73 (CH), 128.42 (CH), 127.57, 120.44, (C<sub>Tol</sub>), 98.36, 96.57, 91.60, 90.75, (C=C) 21.53 (2 CH<sub>3</sub>), 21.39 (CH<sub>3</sub>), 21.27 (CH<sub>3</sub>). Not all quaternary carbons were identified. MS (EI) m/z calc. for C<sub>34</sub>H<sub>28</sub> [ $M^+$ ]: 436.2191. Found: 436.2185.

# 3.8. Thermolysis of $(\eta^5 - C_5 H_4 Me)(CO)_2 Mn = C(Ph)C \equiv CTol (11)$ at 100 °C

A solution of 11 (292 mg, 0.74 mmol) in 1.0 ml  $C_6H_5CH_3$  was heated at 90 °C for 30 min. TLC analysis showed complete disappearance of 11 (deep red,  $R_{\rm f} =$ 0.33, 5% EtOAc/hexanes) and appearance of a new light red spot, presumably enediyne complex (light red,  $R_{\rm f} =$ 0.28). After 6 h at 90 °C, TLC showed a new yellow spot at  $R_{\rm f} = 0.35$ . Flash chromatography (5% EtOAc/ hexanes) followed by preparative TLC gave a mixture of enedivnes 15, 16, and 17 (60 mg, 40%) as a yellow wax. Partial Data: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.99 (t, J = 8 Hz, Tol), 7.92 (d, J = 8 Hz, Tol), 7.6–7.0 (m, Ph), 2.429 (0.360 H,15-E), 2.423 (0.166 H, 16-E), 2.366 (0.026 H, 17-Z), 2.360 (0.065 H, 16-Z), 2.337 (0.065 H, 16-Z), 2.330 (0.077 H, 17-E), 2.314 (0.174 H, 15-Z), 2.304 (0.116 H, 16-E) (Me's). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  138.64, 138.12, 137.66, 136.24, 134.65 (Ar, quat), 131–127 (overlapping peaks, aromatic), 98.19, 96.38, 92.06, 91.21, 90.55 (C=C); 21.547, 21.399 (2C), 21.275 (Me). HRMS m/z calc. for C<sub>32</sub>H<sub>24</sub>: 408.1878. Found: 408.1894.

# 3.9. Thermolysis of $(\eta^5 - C_5 H_4 Me)(CO)_2 Mn = C(Tol) - C = CPh$ (12) at 100 °C

A solution of **12** (113 mg, 0.29 mmol) in 1.0 ml  $C_6H_5CH_3$  was heated at 90 °C for 6 h. Flash chromatography (5% EtOAc/hexanes) followed by preparative

TLC gave a mixture of enediynes **15**, **16**, and **17** (15 mg, 26%) as a yellow solid. Partial Data: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.0–7.9 (m), 7.6–7.0 (series of m, aromatic), 2.429 (0.110H, **15-***E*), 2.423 (0.067H, **16-***E*), 2.366 (0.117H, **17-***Z*), 2.360 (0.108H, **16-***Z*), 2.337 (0.108H, **16-***Z*), 2.330 (0.332H, **17-***E*), 2.314 (0.037 H, **15-***Z*), 2.304 (0.067 H, **16-***E*) (Me's).

# 3.10. $[Cp(OC)_2Mn]_2[\eta^2,\eta^2-PhC \equiv CC(CH_2CH_2CH_2) = CC \equiv CPh]$ (19)

BuLi (1.6 M, hexanes, 0.47 ml, 0.752 mmol) was added to a solution of 1,6-heptadiyne (0.043 ml, 0.376 mmol) at -78 °C followed by slow warming to room temperature to give a fine suspension of dilithioheptadiyne. After 10 min, ZnBr<sub>2</sub> (0.1743 g, 0.774 mmol) was added to give a thick white suspension of BrZnC=  $CCH_2CH_2CH_2C \equiv CZnBr$ . The suspension was then cannula transferred into a solution of  $[Cp(CO)_2Mn \equiv$ CPh]BCl<sub>4</sub> (18) (348.5 mg, 0.834 mmol) in 70 ml  $CH_2Cl_2$  at -78 °C. The color of the carbyne solution changed from yellow to red. After 20 min at -78 °C, a TLC sample was taken. The deep red solution visibly lightened in the capillary tube and TLC analysis showed only the enediyne complex 19. Evaporation of solvent followed by flash chromatography (silica, 20% ether/ hexanes) gave 19 (165 mg, 71%) as a bright red solid. NMR analysis was complicated by facile decomposition of the sample, leading to broad lines. <sup>1</sup>H NMR (500 MHz, 5 °C, CDCl<sub>3</sub>):  $\delta$  7.3–7.0 (m, Ph), 4.710 (s, Cp), 3.2-2.8 (m, CH<sub>2</sub>). 2.3-2.2 (m, CH<sub>2</sub>). IR (C<sub>6</sub>H<sub>14</sub>): 1982, 1916 cm<sup>-1</sup>. MS (ESI) m/z calc. for  $C_{35}H_{26}^{55}Mn_2O_4$ [*M*<sup>+</sup>]: 620.0592. Found: 620.0565.

### 3.11. 1,2-Bis(phenylethynyl)cyclopentene (20)

A solution of **19** (60 mg, 0.097 mmol) in 0.98 ml C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> was heated at 90 °C for 14 h. Preparative thin layer (5% EtOAc/hexanes) gave 20 (24 mg, 85% pure by NMR, 70% yield) as a slightly yellow solid. Complex 20 was contaminated with ~ 15% CpMn(CO)<sub>3</sub> [<sup>1</sup>H NMR:  $\delta$  4.759 (s); <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  82.78]. CpMn(CO)<sub>3</sub> did not interfere with the spectroscopic identification of 20 by comparison with the literature data [12]. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.56–7.46 (m, 2H, Ph), 7.40-7.30 (m, 3H, Ph), 2.70 (t, J = 7.5 Hz, 4H,  $CH_2CH_2CH_2$ ), 2.03 (pentet, J = 7.5 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 131.88 (dt,  ${}^{1}J_{CH} = 163$  Hz,  ${}^{3}J_{CH} = 7$  Hz,  $C_{Ph}$ ), 130.69 (m, C=C), 128.78 (dt,  ${}^{1}J_{CH} = 163$  Hz,  ${}^{1}J_{CH} = 6$  Hz, C<sub>Ph</sub>), 128.76 (d,  ${}^{1}J_{CH} = 162$  Hz, C<sub>Ph</sub>), 123.76 (t,  ${}^{3}J_{CH} = 7$  Hz,  $C_{Ph}$ ), 96.80 (t,  ${}^{3}J_{CH} = 5$  Hz,  $C \equiv CPh$ ), 86.62 (s,  $C \equiv CPh$ ), 37.41 (t,  ${}^{1}J_{CH} = 132$  Hz,  $CH_2CH_2CH_2$ ), 23.52 (t,  ${}^{1}J_{CH} =$ 131 Hz,  $CH_2CH_2CH_2$ ). HRMS m/z calc. for  $C_{21}H_{16}$ : 268.1252. Found: 268.1247.

### 4. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 186957 for compound 9. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.edu or www: http:// www.ccdc.cam.ac.uk).

### References

- For reviews of heteroatom substituted alkynylcarbene complexes, see: (a) R. Aumann, H. Nienaber, Adv. Organomet. Chem. 41 (1997) 163;
  - (b) W.D. Wulff, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, Pergamon Press, Oxford, 1995; vol. 12, chapter 5.3;
  - (c) J.W. Herndon, Coord. Chem. Rev. 181 (1999) 177;
  - (d) M.A. Sierra, Chem. Rev. 100 (2000) 3591;
  - (e) A. de Meijere, H. Schirmer, M. Duetsch, Angew. Chem., Int. Ed. Engl. 39 (2000) 3964 and references therein;
  - (f) J.W. Herndon, Coord. Chem. Rev. 206/207 (2000) 237;
  - (g) J.W. Herndon, Tetrahedron 56 (2000) 1257.
- [2] For Group 7 Fischer alkynylcarbene complexes, see: (a) W. Weng, J.A. Ramsden, A.M. Arif, J.A. Gladysz, J. Am. Chem. Soc. 115 (1993) 3824;

(b) W. Weng, A.M. Arif, J.A. Gladysz, Angew. Chem., Int. Ed. Engl. 32 (1993) 891;

(c) M.R. Terry, C. Kelley, N. Lugan, G.L. Geoffroy, B.S. Haggerty, A.L. Rheingold, Organometallics 12 (1993) 3607;

(d) W. Weng, T. Bartik, J.A. Gladysz, Angew. Chem., Int. Ed. Engl. 33 (1994) 2199;

(e) C.P. Casey, S. Kraft, D.R. Powell, M. Kavana, J. Organomet. Chem. 617/618 (2001) 723. See also Refs. [3,4,7].

- [3] C.P. Casey, S. Kraft, M. Kavana, Organometallics 20 (2001) 3795.
- [4] (a) C.P. Casey, S. Kraft, D.R. Powell, J. Am. Chem. Soc. 122 (2000) 3771;

(b) C.P. Casey, S. Kraft, D.R. Powell, J. Am. Chem. Soc. 124 (2002) 2584.

[5] (a) C.P. Casey, R.L. Anderson, J. Chem. Soc., Chem. Commun. (1975) 895; (b) C.P. Casey, T.J. Burkhardt, C.A. Bunnell, J.C. Calabrese, J. Am. Chem. Soc. 99 (1977) 2127;

- (c) C.P. Casey, S.W. Polichnowski, J. Am. Chem. Soc. 99 (1977) 6097;
- (d) H. Fischer, J. Schmid, J. Mol. Catal. 46 (1988) 277;
- (e) H. Fischer, S. Zeuner, K. Ackermann, J. Schmid, Chem. Ber. 119 (1986) 1546;
- (f) S. Fischer, K. Ackermann, Chem. Commun. (1984) 684;

(g) F. Hohmann, S. Siemoneit, M. Nieger, S. Kotila, K.H. Dotz, Chem. Eur. J. 3 (1997) 853.

- [6] M.A. Sierra, J.C. del Amo, M.J. Mancheño, M. Gómez-Gallego, J. Am. Chem. Soc. 123 (2001) 851.
- [7] S. Kraft, Ph.D. Thesis, University of Wisconsin-Madison, Madison, 2001.
- [8] Y. Ortin, Y. Coppel, N. Lugan, R. Mathieu, M.J. McGlinchey, Chem. Commun. (2001) 1690.
- [9] E.O. Fischer, E.W. Meineke, F.R. Kreißl, Chem. Ber. 110 (1977) 1140.
- [10] X-ray crystal data for  $C_{23}H_{17}MnO_2$ : triclinic,  $P\bar{1}$ , a = 7.7162(6) Å, b = 8.2328(8) Å, c = 15.3872(12) Å,  $\alpha = 97.730(2)^{\circ}$ ,  $\beta = 102.651(3)^{\circ}$ ,  $\chi = 104.937(2)^{\circ}$ , V = 902.42(13) Å<sup>3</sup>, Z = 2, T = 133(2) K,  $D_{calc} = 1.400$  mg m<sup>-3</sup>, R(F) = 0.0352 for 3735 independent reflections ( $2.61 \le \theta \le 28.27^{\circ}$ ). All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure as idealized contributors. All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI). Further details are available from Supporting Information.
- [11] Tetraaryl-substitited enediynes have been prepared previously. (a)
   K. Isagawa, K. Mizuno, T. Majima, Tetrahedron Lett. 40 (1999) 9051;

(b) M. Periasamy, G. Srinivas, G.V. Karunakar, P. Bharathi, Tetrahedron Lett. 40 (1999) 7577;

(c) T. Shimizu, D. Miyasaka, N. Kamigata, J. Org. Chem. 66 (2001) 7202;

(d) T. Shimizu, D. Miyasaka, N. Kamigata, J. Org. Chem. 66 (2001) 1787;

(e) T. Shimizu, D. Miyasaka, N. Kamigata, Org. Lett. 2 (2000) 1923;

See also (f) O.I. Yurchenko, N.V. Komarov, T.N. Dybova, J. Org. Chem. USSR (Engl. Transl.) 12 (1976) 223.

[12] (a) C. Kosinski, A. Hirsch, F.W. Heinemann, F. Hampel, Eur. J. Org. Chem. (2001) 3879;
(b) G.B. Jones, J.M. Wright, G. Plourde, II, A.D. Purohit, J.K.

Wyatt, G. Hynd, F. Fouad, J. Am. Chem. Soc. 122 (2000) 9872 (and references therein).