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## Coupling of isocyanides to alkynes on manganese

Craig L. Homrighausen<sup>1</sup>, John J. Alexander<sup>\*</sup>, Jeanette A. Krause Bauer

Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221, USA

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Dedicated to Professor Andrew A. Wojcicki in recognition of his contributions to inorganic chemistry

### Abstract

Novel six-membered nitrogen-containing heterocycles bonded to manganese are produced from the reaction of  $[p-RC_6H_4CH_2C(O)Mn(CO)_4(CNC_6H_4-p-R')]$  (1) R' = Me or OMe, R = H or Cl with various alkynes. Trapping of the alkynes by an unsaturated manganese-mono(iminoacyl) group generated in situ leads to formation of:  $[1-(p-tolyl)-2-(p-chlorobenzyl)-3,4,5,6-tetraphenyl-\eta^5-azacyclohexadienyl]manganese tricarbonyl (2a), <math>[1-(p-methoxy)-2-benzyl-3,4,5,6-tetraphenyl-\eta^5-azacyclohexadie-nyl]manganese tricarbonyl (2b), <math>[1-(p-tolyl)-2-(p-chlorobenzyl)-3,5-dihydro-4,6-diphenyl-\eta^5-azacyclohexadienyl]manganese tricarbonyl (3b), <math>[1-(p-tolyl)-2-(p-chlorobenzyl)-3,5-dihydro-4,6-diphenyl-\eta^5-azacyclohexadienyl]manganese tricarbonyl (3b), <math>[1-(p-tolyl)-2-(p-chlorobenzyl)-3,5-dimethyl-4,6-bis(carbomethoxy)-\eta^5-azacyclohexadienyl]manganese tricarbonyl (3b), <math>[1-(p-tolyl)-2-(p-chlorobenzyl)-3,6-dimethyl-4,5-bis(carbomethoxy)-\eta^4-azacyclohexadienyl]manganese tricarbonyl (5b), <math>[1-(p-tolyl)-2-(p-chlorobenzyl)-3,6-bis(carbomethoxy)-q^5-azacyclohexadienyl]manganese tricarbonyl (5b), <math>[1-(p-tolyl)-2-(p-chlorobenzyl)-3,6-bis(carbomethoxy)-q^4-azacyclohexadienyl]manganese tricarbonyl (5b), <math>[1-(p-tolyl)-2-(p-chlorobenzyl)-3,6-bis(carbomethoxy)-q^4-azacyclohexadienyl]manganese tricarbonyl (5b), <math>[1-(p-tolyl)-2-(p-chlorobenzyl)-3,6-bis(carbomethoxy)-q^4-azacyclohexadienyl]manganese tricarbonyl (5b), <math>[1-(p-tolyl)-2-(p-chlorobenzyl)-3,6-bis(carbomethoxy)-q^4-azacyclohexadienyl]manganese tricarbonyl (5c) and <math>[1-(p-tolyl)-2-(p-chlorobenzyl)-3,6-bis(carbomethoxy)-q^4-azacyclohexadienyl]manganese tricarbonyl (5c) and <math>[1-(p-tolyl)-2-(p-chlorobenzyl)-3,4,5,6-tetrakis(carbomethoxy)-\eta^4-azacyclohexadienyl]manganese tricarbonyl (6). All these products result from coupling of one iminoacyl group and two molecules of alkyne. Surprisingly, reaction of 1 with hexafluoro-2-butyne led to formation of an unsaturated five-membered manganacycle <math>[1,1,1,1-tetracarbonyl-2,3-bis(trifluoromethyl)-4-(p-chlorobenzyl)-5-p-tolyl]-5-azamanganacyclopentadien$ 

Keywords: Isocyanides; Alkynes; Manganese; Coupling

### 1. Introduction

Transition-metal-mediated coupling reactions between alkynes and carbon monoxide have resulted in a large variety of organic compounds [1] along with a myriad of organometallic complexes [2]. Studies of metal-mediated coupling reactions between alkynes and isocyanides have been far fewer [3].

Isocyanides, CNR, are isolobal with CO and hence might be expected to display similar chemistry [4]. Indeed, many such similarities are apparent. For example, isocyanides often replace terminal carbonyl ligands. Isocyanides are also known to insert into metal-carbon bonds to produce complexes containing the iminoacyl (C(=NR)) group [5]. In fact, we and others have shown that aromatic isocyanides insert into metal-carbon bonds preferentially to carbon monoxide [6,7].

Previous studies in our group have demonstrated that a dimeric manganese diazabutadiene complex is produced upon refluxing the (p-tolyl)isocyanide-substituted manganese acyl complex [p-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C(O)Mn-(CO)<sub>4</sub>(CNC<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub>)] in THF (Scheme 1) [7].

An unsaturated manganese-mono(iminoacyl) intermediate was proposed to occur along the pathway to the diazabutadiene dimer. More recently, when the product mixture from the reaction of p-chlorobenzyl manganese pentacarbonyl and 2,6-dimethylphenyl isocyanide was placed under an atmosphere of carbon dioxide, a carbamate-bridged manganese dimer was produced (Scheme 2) [8]. In the proposed mechanism an unsaturated manganese-mono(iminoacyl) intermedi-

<sup>\*</sup> Corresponding author. Tel.: +1-513-556 9200; fax: +1-513-556 9239.

<sup>&</sup>lt;sup>1</sup> Present address: Eltron Research Inc., 4600 Nautilus Court South, Boulder, CO 80301-3241, USA.



ate reacts via nucleophilic attack on carbon dioxide by the imino nitrogen lone pair initiating formation of a bridging carbamate ligand.

These observations prompted us to investigate reactivity of the manganese acyl complexes  $[p-RC_6H_4CH_2C(O)Mn(CO)_4(CNC_6H_4-p-R')]$  (1) with alkynes. We wish to report that we have been able to trap with alkynes the unsaturated manganese-mono(iminoacyl) group generated in situ to produce novel nitrogencontaining heterocycles bonded to manganese.

### 2. Results and discussion

2.1. Reactions of alkynes with 
$$p$$
-  
 $RC_6H_4CH_2C(O)Mn(CO)_4(CNC_6H_4-p-R')$  (1)

### 2.1.1. Formation of $\eta^5$ -azacyclohexadienyl complexes

Reaction of *p*-tolyl ( $\mathbf{R'} = \mathbf{Me}$ ) or *p*-methoxyphenyl ( $\mathbf{R'} = \mathbf{OMe}$ ) isocyanide with (*p*-chlorobenzyl)manganese pentacarbonyl or (phenylacetyl)manganese pentacarbonyl gave the expected acyl complexes **1a**, **1b**, and **1c**. When 2 equiv. of alkyne were allowed to react with these acyl complexes in warm THF,  $\eta^5$ -nitrogen-substituted azacyclohexadienyl complexes **2a**, **2b**, **3a**, **3b**, and **4** were produced (Scheme 3).



Scheme 2.



Lower yields were obtained from generation of the acyl complex in situ followed by addition of the alkyne and warming in THF.

2.1.1.1. Diphenylacetylene. When **1a** was heated in THF in the presence of 2 equiv. of diphenylacetylene, complex **2a** was isolated. Complex **2a** contains an  $\eta^5$ -azacyclohexadienyl ligand resulting from the coupling of two molecules of diphenylacetylene and a *p*-tolyl(iminoacyl) group on manganese. The [1-(*p*-tolyl)-2-*p*-(chlorobenzyl)-3,4,5,6-tetraphenyl- $\eta^5$ -azacyclohexadienyl] ligand functions as a six-electron donor to manganese. Complex **2a** is isoelectronic with cymantrene, CpMn(CO)<sub>3</sub>.

Spectral data (Table 1) are consistent with the structure proposed for 2a. The IR spectrum displays three bands in the terminal CO stretching region in a pattern characteristic of fac-geometry. The absence of a band at 2164  $\text{cm}^{-1}$  indicates that the terminal isocyanide of the starting p-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C(O)Mn(CO)<sub>4</sub>- $(CNC_6H_4-p-CH_3)$  (1a) is no longer present. The <sup>1</sup>H NMR spectrum has signals in the aromatic region due to the phenyl rings, as well as a methyl singlet at 2.25 ppm due to the p-tolyl group. The diastereotopic benzylic protons appear as an AB quartet centered around 3.68 ppm having J = 15 Hz. The <sup>13</sup>C spectrum of 2a is only somewhat informative; it contains signals in the aromatic region due to the phenyl rings. Signals at 20.5 and 40.1 ppm arise from methyl and methylene carbons, respectively, and five signals at 70.6, 81.8, 106.8, 108.8, and 110.4 ppm are assigned to the five carbons of the  $\eta^5$ -azacyclohexadienyl ligand. These five signals are in the same range as those previously reported for unsymmetrically substituted  $\eta^5$ -cyclopentadienyl ligands on manganese as well as  $\eta^5$ -cyclohexadienyl manganese tricarbonyl [9]. The <sup>13</sup>C spectrum displays one signal for the three carbonyl carbons which remains unchanged down to -56 °C in CDCl<sub>3</sub> [10], indicating facile CO exchange.

2.1.1.2. Structure of  $[1-p-(methoxyphenyl)-2-benzyl-3,4,5,6-tetraphenyl-\eta^5-azacyclohexadienyl]manganese tricarbonyl (2b). The molecular structure of 2b was$ 

determined by single-crystal X-ray diffraction analysis. An ORTEP drawing for **2b** is presented in Fig. 1.

Selected bond lengths and angles are presented in Table 2. The structure of **2b** can be described as highback piano stool geometry. The dihedral angle between the planes defined by C4-C5-C6-C7-C8 and by C8-N1-C4 is 53.3(2)°. Angles C<sub>carbonyl</sub>-Mn-C<sub>carbonyl</sub> range from 84.3(2) to 94.0(2)° while the angles C<sub>carbonyl</sub>-Mn- $C_{ring}$  range from 86.1(1) to 173.5(1)°. The five-carbon segment of the  $\eta^5$ -azacyclohexadienyl ligand is essentially planar with a mean deviation from planarity of 0.032 Å. Bond lengths between C4–C5, C5–C6, C6–C7, and C7–C8 of 1.422(4), 1.441(4), 1.445(4), 1.405(4) Å, respectively, are intermediate between carbon-carbon single and double bonds implying delocalization throughout the five-carbon skeleton of the ring. Bond lengths between N1-C4 of 1.460(3) Å and N1-C8 of 1.455(3) Å are typical of nitrogen-carbon single bonds. Angles C4-N1-C8, C4-N1-C40, C8-N1-C40 of 103.6(2), 114.7(2) and 117.8(2)°, respectively, define a distorted tetrahedral geometry about nitrogen with the lone pair at the fourth vertex. Adams and Huang have reported a related structure of a metalated pyridine formed by a 1,4-cycloaddition of an alkyne to the enamine grouping in a five-membered cyclomangana enamine ring of a dimeric manganese complex [3a].

2.1.1.3. Phenylacetylene. Four regioisomeric products are possible from the reaction of 1 with phenylacetylene (Scheme 4): A, B, C, and D resulting from head-to-tail, tail-to-tail, head-to-head, and tail-to-head coupling, respectively.

When **1a** was stirred at 60 °C in THF in the presence of 2 equiv. of phenylacetylene, IR analysis showed the disappearance of 1a and the presence of product 3a. Spectral data (Table 1) are consistent with the formation of regioisomer D. The IR spectrum displays three bands in the terminal CO region. The  $\eta^5$ -azacyclohexadienyl ligand proton resonances appear as singlets at 6.00 and 5.04 ppm. Evidence for the assignment of regioisomer **D** as the structure of 3a was obtained by employing the  $^{1}H^{-1}H$  COSY experiment [11]. Regioisomer C was ruled out on the basis of the <sup>1</sup>H NMR spectrum. The spectrum lacks signals indicative of three-bond coupling between protons on adjacent carbons of the azacyclohexadienyl ligand which would be anticipated for C. The COSY spectrum (Fig. 2) displays symmetrically disposed crosspeaks (X) between the benzylic protons and the azacyclohexadienyl proton at 5.04 ppm.

Crosspeaks (Y) are also present between the two azacyclohexadienyl protons. These two sets of symmetrically disposed crosspeaks (X) and (Y) can be explained by considering that electron delocalization throughout the five-carbon skeleton of the azacyclohexadienyl ligand provides a mechanism by which the nuclear spins (four bonds removed in both cases) can

Compound	IR <sup>a,b</sup> (cm <sup><math>-1</math></sup> )	<sup>1</sup> H NMR <sup>c</sup>	<sup>13</sup> C NMR <sup>d,e</sup>
2a	2017 (vs), 1962 (m), 1936 (s)	7.53–6.29 (m) (C <sub>6</sub> H <sub>5</sub> , C <sub>6</sub> H <sub>4</sub> ), 3.68 (AB, q, J = 15 Hz) (CH <sub>2</sub> ), 2.24 (s) (CH <sub>3</sub> )	221.5 (CO), 152.9, 140.2, 136.9, 134.9, 134.3, 134.1, 132.6, 132.4, 132.1, 131.6, 130.8, 129.9, 129.3, 128.9, 128.5, 128.3, 128.1, 128.0, 127.7, 127.5, 127.4, 127.1, 127.0, 126.7, 125.9, 117.6 (Ph), 110.4, 108.8, 106.8, 81.8, 70.6 (η <sup>5</sup> -azacyclohexadienyl), 40.1 (CH <sub>2</sub> ), 20.5
2b	2015 (vs), 1957 (s), 1928 (m)	7.23–6.39 (m) (C <sub>6</sub> H <sub>5</sub> , C <sub>6</sub> H <sub>4</sub> ), 3.69 (AB, q, J = 15 Hz) (CH <sub>2</sub> ), 3.73 (s) (OCH <sub>3</sub> )	(Me) 221.9 (CO), 154.6, 148.4, 138.5, 135.3, 134.5, 132.1, 131.9, 130.2, 127.9, 127.7, 127.6, 127.5, 127.3, 126.7, 125.8, 119.8 (Ph), 113.6, 108.8, 107.2, 87.9, 74.8 ( $\eta^{5}$ -azacyclohexadienyl), 55.4 (OMe), 40.5 (CH <sub>2</sub> )
3a	2019 (s), 1955 (s), 1947 (sh, m)	7.67–6.75 (m) (C <sub>6</sub> H <sub>5</sub> , C <sub>6</sub> H <sub>4</sub> ), 6.05 (s) (H), 5.01 (s) (H), 3.86 (AB, q, $J = 17.5$ Hz) (CH <sub>2</sub> ), 2.20 (s) (CH <sub>2</sub> )	150.8, 139.2, 136.6, 133.8, 132.1, 131.8, 129.3, 128.9, 128.4, 127.0, 126.9, 123.6 118.5 (Ph), 99.2, 89.6, 87.5, 86.4, 77.3 ( $\eta^{5}$ - aracycloheradienyl) 39.9 (CHa) 20.5 (Me)
3b	2018 (vs), 1954 (s), 1946 (sh, m)	(c13) 7.70–6.65 (m) ( $C_6H_5$ , $C_6H_4$ ), 6.03 (s) (H), 4.93 (s) (H), 3.80 (s) (CH <sub>2</sub> ), 3.69 (s) (OCH <sub>3</sub> )	155.3, 145.4, 138.4, 136.3, 133.5, 132.7, 131.3, 128.6, 128.4, 128.3, 127.9, 126.7, 126.5, 123.3, 120.9 (Ph), 113.5, 98.4, 88.5, 85.6, 78.7 (n <sup>5</sup> -azacyclohexadienyl), 54.9 (OMe), 39.2 (CH <sub>2</sub> )
4	2036 (vs), 1977 (s), 1959 (s)	7.43-6.55 (m) (C <sub>6</sub> H <sub>4</sub> ), 3.94 (s) (OCH <sub>3</sub> ), 3.74 (s) (OCH <sub>3</sub> ), 3.45 (AB, q, $J = 15$ Hz ) (CH <sub>2</sub> ), 2.48 (s) 2.24 (s) 2.03 (s) (CH <sub>3</sub> )	(171.6, 167.7 (C=O), 147.9, 136.0, 133.7, 132.9, 130.9, 129.5, 128.3, 119.6 (Ph), 114.9, 107.5, 101.3, 92.9, 65.4 (η <sup>5</sup> -azacyclo-hexadienyl), 53.2, 51.4 (OMe), 36.6 (CH <sub>2</sub> ), 20.7, 17.9, 17.3 (Me)
5a	2015 (vs), 1946 (s), 1936 (s)	7.46–6.47 (m) (C <sub>6</sub> H <sub>4</sub> ), 4.02 (s) (OCH <sub>3</sub> ), 3.69 (s) (OCH <sub>3</sub> ), 3.17 (AB, q, $J = 16$ Hz) (CH <sub>2</sub> ), 2.66 (s) 2.35 (s) 1.81 (s) (CH <sub>3</sub> )	
5b	2016 (vs), 1941 (s), 1927 (s)	7.18–6.51 (m) ( $C_6H_4$ ), 3.84 (AB, q, $J = 15$ Hz) (CH <sub>2</sub> ), 3.60 (s) (OCH <sub>3</sub> ), 3.35 (s) (OCH <sub>3</sub> ), 2.57 (s) 2.43 (s) 2.28 (s) (CH <sub>3</sub> )	185.4 (C=N <sup>(+)</sup> ), 169.0, 168.6, (C=O), 139.4, 138.7, 133.3, 132.5, 130.0, 129.8, 128.8, 124.9 (Ph), 109.9, 99.7, 85.7, 65.8 ( $\eta^{4}$ -azacyclohexadienyl), 51.0, 50.5 (OMe), 37.2 (CH <sub>2</sub> ), 29.6, 21.1, 17.3 (Me)
5c	2007 (vs), 1930 (s), 1919 (s),	7.28-6.71 (m) (C <sub>6</sub> H <sub>4</sub> ), 3.88 (s) (OCH <sub>3</sub> ), 3.74 (s) (OCH <sub>3</sub> ), 3.48 (AB, q, $J = 5$ Hz) (CH <sub>2</sub> ), 2.75 (s) 2.37 (s) 1.53 (s) (CH <sub>3</sub> )	
6	2028 (vs), 1956 (s), 1949 (sh, m)	7.19–6.67 (m) (C <sub>6</sub> H <sub>4</sub> ), 3.96 (AB, q, $J = 15$ Hz) (CH <sub>2</sub> ), 3.96 (s) 3.80 (s), 3.63 (s) 3.42 (s) (OCH <sub>3</sub> ), 2.35 (s) (CH <sub>3</sub> )	187.3 (C=N <sup>(+)</sup> ), 167.4, 166.9, 166.5, 166.2 (C=O), 140.0, 137.6, 133.4, 131.6, 130.3, 128.8, 125.0, 113.0 (Ph), 108.7, 98.7, 79.0, 60.3 ( $\eta^4$ -azacyclohexadienyl), 53.7, 53.4, 51.7, 51.3 (OMe), 37.0 (CH <sub>2</sub> ), 29.7, 21.3 (Me)
7	2090 (m), 2010 (s, sh), 2006 (vs), 1980 (s)	7.19–6.62 (m) (C <sub>6</sub> H <sub>4</sub> ), 3.89 (s) (CH <sub>2</sub> ), 2.34 (s) (CH <sub>3</sub> )	$(CH_2)$ , 2.1., 2.1.5 (RR) 215.4, 209.2 (CO), 183.9 (C=N), 149.5, 137.2, 133.9, 132.9, 130.4, 128.9,120.1, 38.8 (CH <sub>2</sub> ), 20.9 (CH <sub>3</sub> )

Spectral data for compounds 2a, 2b, 3a, 3b, 4, 5a-c, 6 and 7

<sup>a</sup> In hexane. vs, very strong; s, strong; m, medium; sh, shoulder.

<sup>b</sup> CO stretching frequencies.

<sup>c</sup> In CDCl<sub>3</sub> shifts reported in ppm downfield from internal TMS standard. m, multiplet; s, singlet; d, doublet; q, quartet.

<sup>d</sup> Shifts reported in ppm relative to central deuterated chloroform peak.

<sup>e</sup> No resonance around 200 ppm for the carbonyl carbons of **3a**, **3b**, **4**, and **5b** could be discerned, probably due to a combination of relaxation time and quadrupolar coupling effects.

communicate. This form of *J*-coupling could be considered somewhat analogous to the four-bond coupling observed in allylic systems [11b,12]. Moreover, regioisomer **D** is the only isomer in which four-bond separation exists for both sets of coupled nuclei. The <sup>13</sup>C spectrum of **3a** contains signals in the aromatic region due to the phenyl rings. Signals at 20.5 and 39.9 ppm due to the methyl and methylene carbons, respectively are observed. Five signals at 77.3, 86.4, 87.5, 89.6, and 99.2 ppm are assigned to the five  $\eta^5$ -azacyclohexadienyl carbons. The signals attributed to carbons C3 (89.6 ppm) and C5 (86.4 ppm) were unambiguously identified using a 2D HETCOR experiment [13]. Signals for quaternary carbons in the 2, 4, and 6 positions are not detected by the 2D HETCOR experiment.

2.1.1.4. Structure of  $[1-p-(methoxyphenyl)-2-p-(chlorobenzyl)-3,5-dihydro-4,6-diphenyl-<math>\eta^5$ -azacyclohexadienyl]manganese tricarbonyl (**3b**). The molecular structure of **3b** (derived from **1b**) was determined by single-crystal X-ray diffraction analysis. An ORTEP drawing for **3b** is presented in Fig. 3.

Selected bond lengths and angles are presented in Table 2. The main structural features of **3b** are similar to those of **2b**. The dihedral angle of 44.8(3)° between the planes defined by C4–C5–C6–C7–C8 and by C8–N1–C4 differs from that in **2b** (55.6°) by 10.8°. This could be attributed to the difference in steric demands imposed by the greater number of phenyl groups in **2b**. The five-carbon segment of the  $\eta^5$ -azacyclohexadienyl ligand is essentially planar with a mean deviation from planarity



Fig. 1. ORTEP drawing for complex **2b**. Hydrogen atoms omitted for clarity.

of 0.016 Å. As in **2b**, bond lengths between C4–C5, C5–C6, C6–C7, and C7–C8 are intermediate between carbon–carbon single and double bonds implying delocalization throughout the five-carbon skeleton of the ring. Angles C4–N1–C8, C4–N1–C28, C8–N1–C28 of 103.8(3), 116.0(3) and 117.2(3)°, respectively, are consistent with distorted tetrahedral geometry about nitrogen with the lone pair at the fourth vertex.

2.1.1.5. Methyl 2-butynoate. The reaction of the unsymmetrical alkyne methyl 2-butynoate with **1a** could also be expected to lead to four regioisomeric products





analogous to **A**, **B**, **C**, **D** of Scheme 4 depending on the coupling mode of the alkynes. In fact, we have isolated and characterized all four regioisomeric products, **4**, **5a**, **5b** and **5c** (vide infra). When **1a** was stirred at 65 °C in THF in the presence of 2 equiv. of methyl 2-butynoate, IR analysis showed the disappearance of **1a** and the presence of a complex mixture. Chromatography on grade II acidic alumina eluting with 60/40 methylene chloride/hexane gave a yellow band eventually identified as  $[1-(p-tolyl)-2-(p-chlorobenzyl)-3,5-dimethyl-4,6-bis(carbomethoxy)-\eta<sup>5</sup>-azacyclohexadienyl]manganese tricarbonyl ($ **4**). Spectral data (Table 1) are consistent with the structure depicted for**4**in Scheme 3.

2.1.1.6. Structure of  $[1-(p-tolyl)-2-(p-chlorobenzyl)-3,5-dimethyl-4,6-bis(carbomethoxy)-\eta^5-azacyclohexa$ dienyl]manganese tricarbonyl (4). The molecular structure of 4 was determined by a single-crystal X-raydiffraction study. An ORTEP drawing for 4 is presented $in Fig. 4. The <math>\eta^5$ -heterocycle features tail-to-head

Table 2

Selected bond distances (Å) and angles (°) and their estimated standard deviations for compounds 2b, 3b, 4 and 7

	2b	3b	4		7
Bond distances					
N1-C4	1.460(3)	1.470(5)	1.446(3)	N1-C5	1.296(2)
N1-C8	1.455(3)	1.457(5)	1.453(3)	C5-C6	1.471(2)
C4-C5	1.422(4)	1.418(5)	1.422(3)	C6-C7	1.356(2)
C5-C6	1.441(4)	1.430(5)	1.438(3)	C6-C8	1.512(2)
C6-C7	1.445(4)	1.451(5)	1.443(3)	C7-C9	1.507(2)
C7-C8	1.405(4)	1.386(5)	1.405(3)	Mn1-C1	1.821(2)
Mn-C4	2.165(3)	2.205(4)	2.144(2)	Mn1-C2	1.847(2)
Mn-C5	2.150(3)	2.137(4)	2.140(2)	Mn1-C3	1.872(2)
Mn-C6	2.151(3)	2.157(4)	2.154(2)	Mn1-C4	1.852(2)
Mn-C7	2.145(3)	2.134(4)	2.158(2)	Mn1-N1	2.031(1)
Mn-C8	2.246(3)	2.228(4)	2.208(3)	Mn1-C7	2.039(1)
Bond angles					
C1-N1-C4	114.7(2)	116.0(3)	116.8(2)	Mn1-N1-C5	118.2(1)
C1-N1-C8	117.8(2)	117.2(3)	117.9(2)	Mn1-N1-C10	121.7(1)
C4-N1-C8	103.6(2)	103.8(3)	103.6(2)	Mn1-C7-C6	114.8(1)
C7-C8-N1	117.0(3)	119.6(3)	115.9(2)	C10-N1-C5	120.1(1)
$N1 - C8 - C^2$	115.5(3)	113.9(3)	117.6(2)	N1-C5-C6	113.8(1)
$C7 - C8 - C^2$	125.5(3)	123.0(4)	122.5(2)	C5-C6-C7	114.2(1)

(1) C40 for 2b, C28 for 3b, C24 for 4. (2) C33 for 2b, C21 for 3b, C17 for 4.



Fig. 2.  ${}^{1}H - {}^{1}H$  COSY spectrum for complex 3a.



Fig. 3. ORTEP drawing for complex 3b. All hydrogen atoms except those on C5 and C7 removed for clarity.



Fig. 4. ORTEP drawing for complex 4. Hydrogen atoms removed for clarity.

coupling of the two alkynes analogous to regioisomer **D** of Scheme 4. Selected bond lengths and angles are presented in Table 2. In 4, the dihedral angle between the planes defined by C4–C5–C6–C7–C8 and by C8–N1–C4 is 52.9(2)°. As observed in the related structures, the  $\eta^5$ -azacyclohexadienyl ligand is essentially planar with a mean deviation from planarity of 0.024 Å. The other structural features of 4 are similar to those of 2b and 3b.

### 2.1.2. Formation of $\eta^4$ -azacyclohexadienyl complexes

2.1.2.1. Methyl 2-butynoate. As described above, the reaction of **1a** with 2 equiv. of methyl 2-butynoate led to a complex mixture as determined by IR analysis. Chromatography on grade II acidic alumina and elution with 60/40 methylene chloride/hexane removed **4**, while elution with 75/25 methylene chloride/hexane gave a second (orange) band. Removal of solvent in vacuo and recrystallization from methylene chloride/hexane (1/2) gave an orange solid. <sup>1</sup>H NMR analysis showed 10 methyl signals in the same region of the spectrum as the methyl groups for compound **4**. Therefore, the mixture was believed to contain two regioisomeric azacylohexadienyl complexes. Fractional recrystallization from hexane at -78 °C gave **5b** and **5c** (vide infra).

Elution with THF gave a third (yellow) band. Removal of solvent in vacuo and recrystallization from methylene chloride/hexane (1/2) gave a yellow solid (**5a**). Spectral data (Table 1) were consistent with data for the previously described  $\eta^5$ -azacyclohexadienyl complexes. The small amounts of compound **5a** isolated have prevented acquisition of a <sup>13</sup>C NMR spectrum. Only upon completion of a single crystal X-ray diffraction study (vide infra) was discovered that compound **5a** is an  $\eta^4$ -azacyclohexadienyl complex (Scheme 5).

2.1.2.2. Structure of  $[1-(p-tolyl)-2-(p-chlorobenzyl)-3,6-dimethyl-4,5-bis(carbomethoxy)-\eta^4-azacyclohexa$ dienyl]manganese tricarbonyl (5a). The molecular structure of 5a was determined by a single-crystal X-raydiffraction study. An ORTEP drawing for 5a is presentedin Fig. 5. Selected bond lengths and angles are presented $in Table 3. The complex contains an <math>\eta^4$ -azacyclohex-



Fig. 5. ORTEP drawing for complex **5a**. Hydrogen atoms removed for clarity.

adienyl ligand, formed from the coupling of a (ptolyl)iminoacyl group and two molecules of methyl 2butynoate in tail-to-tail fashion on manganese. The four-carbon segment of the n<sup>4</sup>-azacyclohexadienyl ligand consists of three carbons arising from alkynes plus the iminoacyl C; it is essentially planar with a mean deviation from planarity of 0.009 Å. The dihedral angle is  $48.2(1)^{\circ}$  between the planes defined by C5–C6–C7– C8 and by C5-C4-N1-C8. Bond lengths between C4-C5, C5-C6, and C7-C8 of 1.465(3), 1.482(3), 1.462(3) Å, respectively, could be described as short C-C single bonds while the bond distance for C6–C7 of 1.401(3) Å may best be described as a long carbon-carbon double bond (vide infra). The bond length between N1 and C4 of 1.307(3) Å is indicative of an N–C double bond. The through-space distance between C4 and manganese is 2.991 Å, well outside the accepted bonding distance of manganese-carbon single bonds. Angles C4-N1-C8, C4-N1-C24, C8-N1-C24 of 116.3(2), 122.6(2) and 120.0(2)°, respectively, demonstrate trigonal planar geometry about nitrogen.



Scheme 5.

Table 3 Selected bond distances (Å) and angles (°) and their estimated standard deviations for compounds 5a, 5b, 5c and 6

	5b	5c	5a	6
Bond distances				
N1-C4	1.465(3)	1.311(3)	1.307(3)	1.471(3)
N1-C8	1.305(3)	1.486(4)	1.480(3)	1.304(3)
C4-C5	1.464(4)	1.459(4)	1.465(3)	1.458(3)
C5-C6	1.394(4)	1.479(4)	1.482(3)	1.406(3)
C6-C7	1.491(4)	1.402(4)	1.401(3)	1.478(3)
C7-C8	1.458(3)	1.460(4)	1.462(3)	1.464(3)
Mn-C4	2.079(3)	2.976 <sup>a</sup>	2.991 <sup>a</sup>	2.090(2)
Mn-C5	2.089(3)	2.145(3)	2.147(2)	2.078(2)
Mn-C6	2.089(3)	2.058(3)	2.082(2)	2.058(2)
Mn-C7	2.130(2)	2.104(3)	2.068(2)	2.149(2)
Mn-C8	2.985 <sup>a</sup>	2.105(3)	2.104(2)	2.995 <sup>a</sup>
Bond angles				
C24-N1-C4	118.9(2)	122.2(2)	122.6(2)	120.0(2)
C24-N1-C8	123.0(2)	119.7(2)	120.0(2)	123.9(2)
C4-N1-C8	115.1(2)	117.1(2)	116.3(2)	115.0(2)
C7-C8-N1	114.5(2)	112.0(2)	110.7(2)	115.0(2)
N1-C8-C17	121.2(3)	115.8(2)	114.8(2)	122.0(2)
C7-C8-C17	123.5(3)	118.4(2)	119.0(2)	122.4(2)

<sup>a</sup> Indicates through space distance.

Spectral data for **5a** (Table 1) are similar to data for the previously described  $\eta^5$ -azacyclohexadienyl complexes. The complex displayed <sup>1</sup>H NMR signals in the aromatic region due to the phenyl rings. Singlets at 4.02, 3.69, 2.66 and 2.35 ppm are attributed to the carbomethoxy methyl and azacylohexadienyl ring methyl groups, respectively. A singlet at 1.81 ppm is assigned to the *p*-tolyl methyl group. The diastereotopic benzylic protons appear as an AB quartet centered around 3.17 ppm having J = 16 Hz.



Fig. 6. ORTEP drawing for complex **5b**. Hydrogen atoms removed for clarity.

2.1.2.3. Structure of [1-(p-tolyl)-2-(p-chlorobenzyl)-4,5 - dimethyl - 3,6 - bis(carbomethoxy) -  $\eta^4$  - azacyclohexadienvl [manganese tricarbonvl (5b). The molecular structure of **5b** was determined by a single-crystal X-ray diffraction analysis. An ORTEP drawing for 5b is presented in Fig. 6. Selected bond lengths and angles are presented in Table 3. The complex contains a  $\eta^4$ azacyclohexadienyl ligand, formed from the coupling of two molecules of methyl 2-butynoate in head-to-head fashion and a p-tolyl(iminoacyl) group on manganese. The four-carbon segment of the  $\eta^4$ -azacyclohexadienyl ligand consists of carbons arising from the two alkynes; it is essentially planar with a mean deviation from planarity of 0.003 Å. The dihedral angle is  $48.9(2)^{\circ}$ between the planes defined by C4-C5-C6-C7 and by C4-N1-C8-C7. Bond lengths between C4-C5, C6-C7, and C7-C8 of 1.464(4), 1.491(4), 1.458(3) Å, respectively, could be described as short C-C single bonds while the bond distance for C5-C6 of 1.394(4) may best be described as a long C-C double bond (vide infra). The bond length between N1 and C8 of 1.305(3) A is indicative of an N–C double bond. The throughspace distance between C8 and manganese is 2.985 Å, well outside the accepted bonding distance of manganese-carbon single bonds. Angles C4-N1-C8, C4-N1-C24, C8-N1-C24 of 115.1(2), 118.9(2) and 123.0(2)°, respectively, demonstrate trigonal planar geometry about nitrogen.

Spectral data for 5b (Table 1) are consistent with data for previously described azacyclohexadienyl complexes. The complex displayed <sup>1</sup>H NMR signals in the aromatic region due to the phenyl rings. Singlets at 3.60, 3.35, 2.57 and 2.43 ppm are attributed to the carbomethoxy methyl and azacylohexadienyl ring methyl groups, respectively. A singlet at 2.28 ppm is assigned to the *p*-tolyl methyl group. The diastereotopic benzylic protons appear as an AB quartet centered around 3.84 ppm having J = 15 Hz. The <sup>13</sup>C spectrum contains signals in the aromatic region due to phenyl rings. Signals at 21.1 and 37.2 ppm are due to *p*-tolyl methyl and methylene carbons, respectively. Signals at 51.0, 50.5, and at 169.0, 168.6 ppm were attributed to the carbomethoxy methyl and carbomethoxy carbonyl carbons, respectively. Four signals at 65.8, 85.7, 99.7 and 109.9 ppm were assigned to the  $\eta^4$ -azacyclohexadienyl ligand carbons. A signal at 185.4 ppm (not seen in the  ${}^{13}C$  spectra of the  $\eta^5$ derivatives) has been assigned to the quaternary carbon of the imine. It seems reasonable, based on deshielding arguments, that a quaternary carbon of an imine containing a nitrogen atom with a formal charge of (+1) would resonate further downfield from TMS than the carbonyl carbons of the azacyclohexadienyl ligand. Liu et al. recently reported that the <sup>13</sup>C resonance for the imine-carbon of a number of N-tert-butanesulfinyl imines ranges from  $\delta$  151.1 to 192.4 ppm [14]. The position of this signal suggests that the compound contains an  $\eta^4\mbox{-}azacyclohexadienyl ligand as shown in Scheme 5.$ 

2.1.2.4. Structure of  $[1-(p-tolyl)-2-(p-chlorobenzyl)-4,6-dimethyl-3,5-bis(carbomethoxy)-\eta^4-azacyclohexa$ dienyl]manganese tricarbonyl (5c). The small amountsof 5c isolated have prevented determination of a <sup>13</sup>CNMR spectrum. Only upon completion of a singlecrystal X-ray diffraction study (vide infra) was it $discovered this compound was a <math>\eta^4$ -azacyclohexadienyl complex (Scheme 5).

An ORTEP drawing for 5c is presented in Fig. 7. Selected bond lengths and angles are presented in Table 3. This complex also contains a  $\eta^4$ -azacyclohexadienyl ligand, formed from the coupling of a *p*-tolyl(iminoacyl) group and two molecules of methyl 2-butynoate in a head-to-tail fashion on manganese. The four-carbon segment of the  $\eta^4$ -azacyclohexadienyl ligand contains three carbons arising from alkynes plus the iminoacyl carbon; it is essentially planar with a mean deviation from planarity of 0.016 Å. The dihedral angle is  $46.6(2)^{\circ}$ between the planes defined by C5-C6-C7-C8 and by C5-C4-N1-C8. Bond lengths between C4-C5, C5-C6, and C7-C8 of 1.459(4), 1.479(4), 1.460(4) Å, respectively, could be described as short C-C single bonds while the bond distance for C6–C7 of 1.402(4) Å may best be described as a long C-C double bond (vide infra). The bond length between N1 and C4 of 1.311(3) Å is indicative of an N–C double bond. The throughspace distance between C4 and manganese is 2.976 Å, well outside the accepted bonding distance of manganese-carbon single bonds. Angles C4-N1-C8, C4-N1-C24, C8-N1-C24 of 117.1(2), 122.2(2) and 119.7(2)°, respectively, demonstrate trigonal planar geometry about nitrogen.



Fig. 7. ORTEP drawing for complex 5c. Hydrogen atoms removed for clarity.



2.1.2.5. Dimethylacetylene dicarboxylate (DMAD). When **1a** was warmed to 60  $^{\circ}$ C in the presence of 2 equiv. of DMAD for a 3-h period, IR analysis showed the complete disappearance of **1a** and appearance of the coupling product **6** (Scheme 6).

Spectral data (Table 1) for the product were consistent with data for the previously described  $\eta^4$ -azacyclohexadienyl complexes. The <sup>13</sup>C spectrum contains signals 60.3, 79.0, 98.7, and 108.7 ppm assigned to the  $\eta^4$ -azacyclohexadienyl ligand carbons. A signal at 187.3 ppm has been assigned to the quaternary carbon of the imine. The position of this signal suggests that **6** contains a  $\eta^4$ -azacyclohexadienyl ligand. It was not until completion of a single crystal X-ray diffraction study (vide infra) that we confirmed that this compound was indeed a  $\eta^4$ -azacyclohexadienyl complex.

## 2.1.3. Structure of $[1-(p-tolyl)-2-(p-chlorobenzyl)-3,4,5,6-tetrakis(carbomethoxy)-\eta^4-azacyclohexa$ dienyl]manganese tricarbonyl (6)

The molecular structure of 6 was determined by single-crystal X-ray diffraction analysis. An ORTEP drawing for 6 is presented in Fig. 8. Selected bond lengths and angles are presented in Table 3.



Fig. 8. ORTEP drawing for complex 6. Hydrogen atoms removed for clarity.

The complex contains a  $\eta^4$ -azacyclohexadienyl ligand resulting from the coupling of two molecules of DMAD and a (p-tolyl)iminoacyl group on manganese. All four carbons coordinated to Mn arise from alkynes. The dihedral angle is  $46.3(1)^{\circ}$  between the planes defined by C4-C5-C6-C7 and by C4-N1-C8-C7. The fourcarbon segment of the  $\eta^4$ -azacyclohexadienyl ligand is essentially planar with a mean deviation from planarity of 0.017 Å. Bond lengths between C4–C5, C6–C7, and C7-C8 of 1.458(3), 1.478(3), 1.464(3) Å, respectively, could be described as short C-C single bonds. The bond distance for C5-C6 of 1.406(3) Å may best be described as a long C-C double bond (vide infra). The bond length between N1 and C8 of 1.304(3) Å is indicative of an N-C double bond. Angles C4-N1-C8, C4-N1-C24, C8-N1-C24 of 115.0(2), 120.0(2) and 123.9(2)°, respectively, are indicative of trigonal planar geometry about nitrogen.

2.1.3.1. Electronic structure of  $\eta^4$ -azacyclohexadienyl complexes. Examination of the C-C bond lengths (Table 3) in the manganese-bound four-carbon segment of the ring for compounds **5a**, **5b**, **5c**, and **6** suggests that two formulations of the electronic structure are possible as depicted in Scheme 7.

2.1.3.2. Formulation A. If all the C-C bond lengths in the four-carbon segment are interpreted as intermediate between single and double bonds, this moiety would consist of a neutral delocalized skeleton with a hapticity of four, isolobal with butadiene. The Mn-C bond lengths of the  $\eta^4$ -four carbon skeleton in 5a, 5b, 5c and 6 do differ relatively in the same manner as the median Mn–C bond lengths in  $\eta^4$ -1,3-butadiene complexes  $(R_2C^1C^2RC^2RC^1R_2)$  where Mn-C<sup>1</sup> and Mn-C<sup>2</sup> are 2.135 and 2.071 Å, respectively, lending credence to this view [15]. The bond lengths between nitrogen and the non-metalated carbon (C4 in 5a and 5c and C8 in 5b and 6) are best described as carbon-nitrogen double bonds. This requires the formulation of a quaternary nitrogen atom with a positive formal charge. Since the molecule is overall neutral, then, in accordance with the effective atomic number rule, manganese must be



Scheme 7. Formulation of  $\eta^4$ -4 complexes.

assigned an oxidation state of (-I) (Scheme 7). In this view 5a, 5b, 5c and 6 would be diene-substituted pentacarbonyl manganates. However, the negative formal charge on manganese implies a buildup of electron density on the metal. The positions of CO bands in the IR spectrum are sensitive to electron density on the metal. For example,  $v_{CO}$  is approximately 1860 cm<sup>-1</sup> in [Mn(CO)<sub>5</sub>]<sup>-</sup> and might be expected to be even lower if two CO's were replaced by a diene which is a weaker  $\pi$ acid, although this effect would be mitigated by the formal positive charge on Mn. Brookhart et al. [16] have prepared Li<sup>+</sup>[Mn(CO)<sub>3</sub>(cyclohexadiene)]<sup>-</sup> which is expected to exhibit ion pairing; the CO stretches in this compound occur at 1929, 1896, 1853, 1832, 1811 and 1758 cm<sup>-1</sup>.

However, the positions of the CO bands for our complexes are in the same range as the previously described  $\eta^5$ -azacyclohexadienyl complexes. Since these complexes are straightforwardly formulated as Mn(I) species, a formulation for the  $\eta^4$ -complexes different from that just described seems to be required.

2.1.3.3. Formulation B. Reexamination of the bond lengths (Table 3) of the ring for compounds 5a, 5b, 5c and 6 suggests a different interpretation. Since the internal C-C bond lengths between C5-C6 in 5b, and 6 and C6–C7 in 5a and 5c are significantly shorter than the other C-C bonds of the four-carbon skeleton, they may be interpreted as long C-C double bonds. Then the end carbons of the four-carbon skeleton would be considered carbanionic in character. This results in a formal charge of -2 on the  $\eta^4$ -manganese-bound portion of the azacyclohexadienyl ligand. A positively charged quaternary nitrogen atom and manganese with an oxidation state of (+I) results in an overall neutral species (Scheme 7). This latter formulation is in agreement with the observed positions of the CO bands in the IR spectra for compounds 5a, 5b, 5c and 6. Furthermore, the Mn-C5, Mn-C8 bond lengths in 5a and 5c and the Mn-C4, Mn-C7 in 6 and 5b closely agree with the Mn-C(sp<sup>3</sup>) median bond distance of 2.173 Å [15] approaching the metallacyclopentene extreme.

The difference in the above two formulations is that between the description of a  $C_4H_6$  metal compound as containing a neutral  $\pi$ -bound butadiene complex as contrasted with a metallacyclopentene, Scheme 7. Formulation **B** seems reasonable based on the location of the R groups on the ring of the  $\eta^4$ -azacyclohexadienyl ligand. In complexes **5a**, **5b**, **5c**, and **6** the negative charge on the formal carbanionic (end) carbons could be stabilized by electron-withdrawing R groups.

Two important questions about these reactions are: (1) What may be the mechanism of formation? (2) What factors determine the  $\eta^5$ - or  $\eta^4$ -hapticity?



2.1.3.4. Reaction of **1a** with hexafluoro-2-butyne. In an attempt to determine if the change in hapticity from  $\eta^5$  to  $\eta^4$  occurs when electron-withdrawing alkynes are employed, complex **1a** was allowed to react with excess hexafluoro-2-butyne [CF<sub>3</sub>C=CCF<sub>3</sub>(g)] under 400 psi of argon. The results are shown in Scheme 8. Spectral data (Table 1) indicate that the product (7) is different from the previously described  $\eta^5$ - and  $\eta^4$ -azacyclohexadienyl complexes. Most notable is that the IR spectrum shows four bands in the terminal CO region typical of *cis*-disubstituted octahedral geometry. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were only somewhat informative; however, the high-resolution mass spectrum [ $M^+$  511] indicated that only one molecule of hexafluoro-2-butyne had been incorporated into 7.

Complex 7 is a mangana-azacyclopentadiene complex in which one molecule of hexafluoro-2-butyne has formally inserted into the manganese–iminoacyl carbon bond. Delis et al. have observed insertion of acetylene into the iminoacyl carbon–Pd bond of the cationic complexes  $[N^{\cap}NPd-(C(=NR)Me]X$  where  $(N^{\cap}N =$ bipy, phen;  $R = 2,6-Me_2C_6H_3$ ;  $X = BF_4$ ) [5a]. Spectral data (Table 1) are consistent with the structure depicted



Fig. 9. ORTEP drawing for complex 7. Hydrogen atoms removed for clarity.



for 7, which was determined by a single-crystal X-ray diffraction analysis. An ORTEP drawing for 7 is presented in Fig. 9. Selected bond lengths and angles are presented in Table 2. Compound 7 exhibits structural features consistent with those of other reported manganese metallacycles [1b,17]. The bond length between N1–C5 of 1.296(2) Å is indicative of an N–C double bond. The C6–C7 bond distance of 1.356(2) Å provides evidence for a C–C double bond, demonstrating that the alkyne has been transformed to an olefinic species.

2.1.3.5. Mechanism of  $\eta^5$ -azacyclohexadienyl complex formation. Scheme 9 depicts three possible pathways for  $\eta^5$ -azacyclohexadienyl complex formation.

Common to all pathways is thermal decarbonylation of the starting acyl **1** which produces **9**, which undergoes a rapid and preferential insertion of isocyanide into the Mn-benzyl carbon bond producing unsaturated **10**. Complex **10** then takes up a molecule of alkyne producing **11**. Complex **11** undergoes insertion of alkyne into the Mn-iminoacyl carbon bond producing the fivemembered manganacyclic intermediate **12** analogous to **7**. Deshong et al. [2b] have reported that alkynes are capable of inserting into Mn-acyl carbon bonds to produce five-membered metallacyles in which the acyl oxygen occupies a coordination site on manganese analogous to 12. Here the paths branch. The route to paths A and B (Scheme 9) involves nucleophilic displacement of the iminoacyl nitrogen by another molecule of alkyne producing 13. Complex 13 then undergoes ring formation via one of two pathways. In pathway A, attack by the iminoacyl nitrogen lone pair upon the coordinated alkyne converts 13 to 14. Electrocyclic rearrangement leads to a species such as 19. Loss of CO and a rearrangement similar to ring slippage generates 8. Motz and Alexander [18] have observed attack upon a coordinated isocyanide by an iminoacyl nitrogen lone pair followed by rearrangement to generate a mangana-azacyclobutene ring. Alternatively, 13 could undergo ring formation via pathway B in which the coordinated alkyne inserts into the manganese-vinyl carbon bond producing 15. Electrocyclic rearrangement leads to a species such as 19a'. CO loss and rearrangement leads to 8. Washington et al. [19] have proposed insertion of a coordinated alkyne into an osmium-vinyl bond of a metallaacylcyclobutene ring, followed by reductive coupling in order to account for generation of metalated cyclopentadienones. In pathway C, 12 undergoes substitution of CO by alkyne, generating 16. Insertion of the coordinated alkyne into the manganese-vinyl carbon bond produces 17. Complex 17 attains an 18-electron configuration via  $\pi$ -donation from one olefinic unit of the unsaturated metallocycle. Electrocyclic rearrangement generates 8. Intermediates somewhat analogous to 17 have been postulated in the mechanism for the cobalt-catalyzed trimerization of alkynes and nitriles to produce pyridines [20]. However,  $\pi$ -donation from one olefinic unit is not required for cobalt to attain an 18-electron configuration. We have shown (vide infra) that complex 7 can be transformed to a six-membered coupling product implying that compounds analogous to 7 are intermediates along the reaction pathway. 'Unhooking' one of the coordinated C's from 8 can lead to  $\eta^4$ -products.

2.1.3.6. Reaction of 7 with phenyl acetylene. In an attempt to demonstrate that an intermediate such as 7 occurs along the pathway to the azacyclohexadienyl complexes, 7 was treated with phenylacetylene in refluxing THF for 5 days. IR analysis showed almost complete disappearance of 7 and the appearance of the coupling product **20** (Scheme 10).



Scheme 10. The regiochemistry and hapticity of **8** remain to be determined.

Our results are not yet complete enough to verify the regiochemistry or hapticity of **20**. It is hoped that an X-ray diffraction study on complex **20** will also provide the answer to the second question regarding the change in hapticity from  $\eta^5$  to  $\eta^4$ , which is believed to occur when electron-withdrawing alkynes are used in the coupling reaction.

2.1.3.7.  $\eta^4$ - versus  $\eta^5$ -Coordination. The preference for  $\eta^4$ - as opposed to  $\eta^5$ -coordination can be rationalized by the notion that electron-withdrawing alkynes such as dimethyl acetylene dicarboxylate are capable of stabilizing the formally carbanionic carbons of a metallacyclopentene (formulation B, Scheme 7). Support for this view comes from the fact that PhC=CPh (containing electron-rich phenyl groups) gives an  $\eta^5$ -product whereas DMAD (containing electron-poor carbomethoxy groups) gives an  $\eta^4$ -product. In cases where all ring substituents are not the same, composition of the  $\eta^4$ -group seems to be dictated by a preference for placing electron-withdrawing groups at formally carbanionic carbons. If electron-withdrawing ability is considered to decrease in the order  $-CO_2Me > CH_2C_6H_4Cl > -CH_3$ , we can rationalize the fact that, given the regiochemistry of alkyne couplings, methylcontaining carbons are not part of the  $\eta^4$ -moieties in **5a** and 5c. Instead, the original iminoacyl C containing a –  $CH_2C_6H_4Cl$  group is included in the  $\eta^4$ -moiety.

Interestingly, this interpretation does not find strong confirmation in the values of IR CO stretching frequencies. All the tricarbonyl compounds contain the expected three CO stretching bands: an A mode and the two components of the split E mode (from  $C_{3\nu}$  idealized symmetry). The average of the three frequencies spans a range of only 11 cm<sup>-1</sup> from the tetraphenyl compound (**2b**;  $\eta^5$ ; 1967 cm<sup>-1</sup>) to the tetrakis(carbomethoxy) compound (**6**;  $\eta^4$ ;1978 cm<sup>-1</sup>). This is perhaps an example of the Electroneutrality Principle. Moreover, comparison of the spectra of **5a** and **5c**, both of which are  $\eta^4$  and both of which have  $-CO_2Me$  and  $-CH_2C_6H_4Cl$  at the formally 'alkyl' coordinated C's and which differ only in the regiochemistry at the C-C formally double bond, reveals average values of  $v_{CO}$  of 1966 and 1952 cm<sup>-1</sup>, respectively.

Brookhart [16], Pauson [21], Sweigart [22], Rose-Munch [23] and their co-workers have reported the preparation of a large number of  $\eta^5$ -cyclopentadienyl and  $\eta^5$ -cyclohexadienyl complexes substituted at various positions on the rings; these were generally nucleophilic additions prepared by to [(arene) $Mn(CO)_3$ <sup>+</sup>. Trends in the IR spectra on varying ring substituents are not readily intelligible across a broad range of compounds. For example [21a], Cp- $Mn(CO)_3$  displays  $v_{CO}$  at 2015, 1945 and 1931 cm<sup>-1</sup> and  $\eta^{5}$ -[1,2-(CO<sub>2</sub>Me)-2-Ph-C<sub>5</sub>H<sub>2</sub>]Mn(CO)<sub>3</sub> at 2041, 1982 and 1975  $\text{cm}^{-1}$ , a trend in accord with expectation. In contrast [21b], the trend in the IR spectra of  $\eta^5$ -[1-Ph-2-Cl-C<sub>6</sub>H<sub>4</sub>]Mn(CO)<sub>3</sub> ( $\nu_{CO}$  at 2025, 1958 and 1948 cm<sup>-1</sup>) and  $\eta^5$ -[1-Ph-2-Cl-5-Me-C<sub>6</sub>H<sub>3</sub>]Mn(CO)<sub>3</sub> ( $\nu_{CO}$  at 2026, 1959 and 1947 cm<sup>-1</sup>) is not readily rationalized. In some cases the order of substituents in  $\eta^5$ -rings does not influence the CO stretching frequencies. For example [21b], [2-Cl-4-Me-C<sub>6</sub>H<sub>4</sub>]Mn(CO)<sub>3</sub> has  $\nu_{CO}$  at 2024, 1957 and 1943 cm<sup>-1</sup> and [2-Me-4-Cl-C<sub>6</sub>H<sub>4</sub>]Mn(CO)<sub>3</sub> has  $\nu_{CO}$ at 2025, 1955 and 1945 cm<sup>-1</sup>. In contrast, [2-NMe<sub>2</sub>-4-Me-C<sub>6</sub>H<sub>4</sub>]Mn(CO)<sub>3</sub> has  $\nu_{CO}$  at 1994 and 1911 cm<sup>-1</sup> and [2-Me-4-NMe<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>]Mn(CO)<sub>3</sub> has  $\nu_{CO}$  at 2007, 1928

Another possibility for explaining differences in the IR spectra of the carboxymethyl complexes is to examine how many groups are conjugated with the rings. This involves looking at the solid-state structures; there is, of course, no necessary correlation between these structures and solution structures. Even here, no trends are evident. The average values of  $v_{\rm CO}$  lie in the order 6 > 4 > 5a > 5b > 5c. The numbers of planar (conjugated) carbomethoxy groups in the solid state are three, one, one, two and one, respectively.

The results are consistent with kinetic control of the regiochemistry of coupling and electronic as well as steric control of the structure of the final product. Unraveling the influences of these effects will require examining coupling of a greater variety of unsymmetric alkynes.

#### 3. Conclusion

and 1918 cm<sup>-1</sup>.

Decarbonylation of the manganese acyl complex 1 followed by preferential insertion of aromatic isocyanides into manganese-alkyl carbon bonds generates an unsaturated manganese (mono)iminoacyl intermediate in situ. In the presence of alkynes both  $\eta^5$ - and  $\eta^4$ azacyclohexadienyl complexes are produced. When the manganese acyl complex was allowed to react with 2 equiv. of the unsymmetrical aliphatic alkyne phenylacetylene only one regioisomer was produced, suggesting that the coupling reaction is sensitive to steric factors. When the manganese acyl complex was treated with 2 equiv. of methyl-2-butynoate, all four possible regioisomers were formed. The relative isolated yields of 4 and 5a-c may not reflect their actual relative abundance in the reaction mixture. Because of overlapping IR bands no exact results are available. However, the relative amounts in the reaction mixture are  $5c > 4 \sim 5a + 5b$ , probably demonstrating no large steric influence on regioselectivity. Reaction of 1a with the electron-withdrawing alkyne  $CF_3C = CCF_3$  generates a five-membered unsaturated manganacycle 7 presumably because the very electron-withdrawing -CF<sub>3</sub> groups retard incorporation of a second equivalent of alkyne because of lower reactivity in nucleophilic displacement either of CO from 12 or of the imino nitrogen lone pair 13. See Scheme 9.

#### 4. Experimental

### 4.1. Procedures and materials

M.p.s were determined on a Mel-Temp apparatus using open-ended capillaries and are uncorrected. NMR spectra were recorded on a Bruker AM-250 spectrometer. Infrared solution spectra were recorded on a 1600 FTIR spectrophotometer. IR cells were 1.0 mm solution cells with NaCl windows. High-resolution mass spectra were recorded on a Kratos-80. Unless otherwise noted, all reactions were performed in dry glassware under an Ar atmosphere using standard Schlenk techniques.

Dimethylacetylene dicarboxylate and methyl 2-butynoate were purchased from Fischer Chemical Com-Phenylacetylene, pany and used as received. diphenylacetylene, p-chlorobenzyl chloride, hexafluoro-2-butyne, and deuterochloroform were purchased from Aldrich Chemical Company and dimanganese decacarbonyl from Strem Chemical Company. All were used as received. p-Methoxyphenyl isocyanide, p-tolyl isocyanide [24], p-chlorobenzyl manganese pentacarbonyl [7], and (p-tolyl isocyanide)[(pchlorophenyl)acetyl]manganese tetracarbonyl [7] were synthesized according to published procedures. Aluminum oxide 90, active acidic grade II (alumina) from EM science and Silica Gel 60, 230-400 mesh, were used for column chromatography. Tetrahydrofuran was distilled from sodium benzophenone ketyl. All other laboratory chemicals were reagent grade and used as received. The Parr Bomb used for the preparation of 7 was purchased from Parr Instrument Company, Inc.

### 4.1.1. X-ray diffraction studies of 2b, 3b, 4, 5a, 5b, 5c, 6 and 7

For X-ray examination and data collection, each crystal was coated with a light film of epoxy resin and mounted on a glass fiber. All data were collected using graphite-monochromated Mo K $\alpha$  radiation (Tables 4 and 5).

Intensity data for 2b, 3b, 5a and 7 were collected on a Siemens SMART 1K CCD diffractometer [25]. The detector was set at a distance of 5.00 cm from the crystal. A series of data frames measured at  $0.3^{\circ}$ increments of  $\omega$  were collected with three different  $2\theta$ and  $\phi$  values to calculate a preliminary unit cell. For data collection, frames were measured at  $0.3^{\circ}$  intervals of  $\omega$ . In order to correct for high-energy backgrounds in the images, data frames were collected as the sum of two exposures and non-correlating events were eliminated. The data frames were collected in distinct shells, with a maximum  $\theta$  value of approximately  $28^{\circ}$ . The initial 50–

Table 4						
Summary of crystallographic data	for	2b,	3b,	4	and	5c

	2b	3b	4	5c
Empirical formula	C46H34MnNO4	C34H25ClMnNO4	C <sub>28</sub> H <sub>25</sub> ClMnNO <sub>7</sub>	C <sub>28</sub> H <sub>25</sub> ClMnNO <sub>7</sub>
Molecular weight	719.7	601.9	577.9	577.9
Color, habit	yellow plates	yellow plates	yellow rods	orange rods
Temperature (K)	297	223	295	296
Space group	Pbca	$P2_1/c$	$P\overline{1}$	$P2_1/c$
a (Å)	11.1452(5)	12.092(2)	8.471(4)	16.232(3)
b (Å)	19.1470(8)	19.707(4)	11.598(3)	10.725(2)
<i>c</i> (Å)	34.911(2)	12.460(3)	14.867(5)	16.515(3)
α (°)	90.00	90.00	87.71(2)	90.00
β (°)	90.00	96.18(3)	85.12(3)	111.78(3)
γ (°)	90.00	90.00	71.67(3)	90.00
V (Å <sup>3</sup> )	7455.9(6)	2951.9(10)	1381.4(8)	2669.7(9)
Ζ	8	4	2	4
Absorption coefficient $(mm^{-1})$	0.399	0.576	0.620	0.642
Monochromator	graphite	graphite	graphite	graphite
Crystal size (mm)	$0.40 \times 0.35 \times 0.10$	$0.30 \times 0.20 \times 0.15$	$0.55 \times 0.35 \times 0.30$	$0.90 \times 0.25 \times 0.15$
$2\theta$ range (°)	4.26-52.74	3.96-56.44	3.7-55.12	4.64-55.12
Index ranges	$-13 \le h \le 13, -23 \le k \le 23,$ $-43/\le l \le 23$	$ -16 \le h \le 16, \ -26 \le k \le 26, \\ -10 \le l \le 16 $	$\begin{array}{l} 0 \leq h \leq 11, \ -14 \leq k \leq 15, \\ -19 \leq l \leq 19 \end{array}$	$\begin{array}{l} 0 \leq h \leq 21, \ 0 \leq k \leq 13, \\ -21 \leq l \leq 19 \end{array}$
Reflections collected	42 327	19985	6789	6365
Independent reflections	7611	7178	6357	6154
Min./max. transmis- sions	0.857/0.981	0.696/0.928	0.099/0.168	none
Variables	470	371	343	343
<i>R</i> indices $[I > 2\sigma(I)]$ <i>R</i> indices (all data) <i>R</i> <sub>int</sub> Extinction coefficient Res. elec. den. (e Å <sup>-3</sup> )	$R_1 = 0.0593, wR_2 = 0.0904$ $R_1 = 0.1302, wR_2 = 0.1109$ 0.1002 0.00037(6) 0.307	$R_1 = 0.0646, wR_2 = 0.1034$ $R_1 = 0.1965, wR_2 = 0.1504$ 0.0924 0.0014(3) 0.582	$R_1 = 0.0477, wR_2 = 0.1232$ $R_1 = 0.0705, wR_2 = 0.1452$ 0.0277 none 0.494	$R_1 = 0.0486, wR_2 = 0.1066$ $R_1 = 0.0890, wR_2 = 0.1359$ 0.0167 none 0.562

100 frames of the first data shell were recollected at the end of the data collection to correct for crystal decay. The data frames were processed using the program SAINT [25]. Data were corrected for decay and Lp effects. Semi-empirical absorption and beam corrections were applied using SADABS [26].

Intensity data for compounds 4, 5b, 5c and 6 were collected on a Siemens P3 diffractometer [25]. Lattice parameters were obtained by least-squares refinement of the angular settings from 40 reflections lying in a  $2\theta$  range of  $10-30^{\circ}$ . Intensity data were collected using  $\theta - 2\theta$  scans in the range  $3.5 \le 2\theta \le 55^{\circ}$ . A decay correction was applied to the unique reflections based on three standard reflections monitored every 300 reflections. Data were also corrected for Lp effects. For compounds 4 and 5b a semi-empirical absorption correction [26] based on measured  $\varphi$  scans was applied; no absorption corrections were applied for compounds 5c and 6.

Structures were solved by a combination of direct methods or Patterson analysis using SHELXTL v5.03 [27] and the difference Fourier technique and were refined by full-matrix least-squares on  $F^2$ . Non-hydrogen atoms were refined with anisotropic displacement parameters. A weighting scheme of the form  $w^{-1} = \sigma^2 (F_o^2) + (aP)^2 + bP$  was used, where  $P = 0.33333F_o^2 + 0.66667F_c^2$ . An

extinction correction of the form  $F_c^* = kF_c[1 + 0.001\chi F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$  was used for compounds **2b** and 3b. For compound 7 all hydrogen atoms were located directly from the difference map, while in all other structures hydrogen atom positions were located directly or calculated based on geometric criteria. All hydrogen atoms were allowed to ride on their respective atoms with the exception of compound 3b in which H5 and H7 were fixed where located. Hydrogen atom isotropic temperature factors were defined as U(C)a =U(H), where a = 1.5 for methyl hydrogens and a = 1.2for the remaining hydrogens. For compounds 5b and 7, methyl group was disordered and each conformation was set at 0.5 occupancy. Complex **5b** crystallizes with a molecule of solvent which appears to be a partial molecule of CH<sub>2</sub>Cl<sub>2</sub>. Attempts to model the solvent proved unsatisfactory, thus the solvent contribution was subtracted from the reflection data using the program SQUEEZE [28]

# 4.1.2. Preparation of $[1-(p-tolyl)-2-(p-chlorobenzyl)-3,4,5,6-tetraphenyl-\eta^5-azacyclohexadienyl]manganese tricarbonyl (2a)$

(p-Tolyl isocyanide)[(p-chlorophenyl)acetyl]manganese tetracarbonyl (1a) (0.211 g, 0.465 mmol) was

Table 5 Summary of crystallographic data for compounds **5a**, **5b**, **6**, and **7** 

	5b	5a	6	7
Empirical formula	C <sub>28</sub> H <sub>25</sub> ClMnNO <sub>7</sub>	C <sub>28</sub> H <sub>25</sub> ClMnNO <sub>7</sub>	C <sub>30</sub> H <sub>25</sub> ClMnNO <sub>11</sub>	C <sub>23</sub> H <sub>13</sub> ClF <sub>6</sub> MnNO <sub>4</sub>
Molecular weight	577.88	577.88	665.9	571.7
Color, habit	orange plates	orange plates	orange plates	yellow blocks
Temperature (K)	293	296	296	150
Space group	PĪ	$P2_1/c$	PĪ	PĪ
a (Å)	11.158(2)	10.1471(1)	10.650(2)	10.1503(2)
b (Å)	12.018(2)	14.2234(3)	10.691(2)	11.1541(3)
c (Å)	12.937(2)	18.6453(4)	13.854(3)	11.9960(3)
α (°)	111.77(1)	90.00	71.77(3)	69.408(1)
$\beta$ (°)	104.27(1)	94.342(1)	87.58(3)	72.022(1)
γ (°)	103.21(2)	90.00	83.15(3)	72.612(1)
$V(Å^3)$	1459.4(4)	2683.3(1)	1487.5(5)	1181.37(5)
Z	2	4	2	2
Absorption coefficient	0.587	0.638	0.596	0.750
$(mm^{-1})$				
Monochromator	graphite	graphite	graphite	graphite
Crystal size (mm)	$0.60 \times 0.55 \times 0.20$	$0.55 \times 0.40 \times 0.20$	$0.50 \times 0.30 \times 0.15$	$0.80 \times 0.80 \times 0.40$
$2\theta$ range (°)	3.64-56.12	4.54-56.62	4.04-55.12	5.02-56.4
Index ranges	$0 \le h \le 14, -15 \le k \le 15,$	$-13 \le h \le 6, -18 \le k \le 16,$	$0 \le h \le 13, -13 \le k \le 13,$	$-13 \le h \le 13, -14 \le k \le 14,$
	$-16 \le l \le 16$	$-24 \le l \le 23$	$-18 \le l \le 18$	$-15 \le l \le 15$
Reflections collected	7101	17 677	7220	13 146
Independent reflec-	6752	6617	6853	5739
tions				
Min./max. transmis-	0.727/0.999	0.720/0.998	none	0.475/0.694
sions				
Scan type	$\theta$ /2 $\theta$	ω	$\theta$ /2 $\theta$	$\theta/2\theta$
Variables	343	343	397	325
R indices $[I > 2\sigma(I)]$	$R_1 = 0.0525, wR_2 = 0.1425$	$R_1 = 0.0453, wR_2 = 0.1092$	$R_1 = 0.0400, wR_2 = 0.0913$	$R_1 = 0.0296, wR_2 = 0.0778$
R indices (all data)	$R_1 = 0.0796, wR_2 = 0.1425$	$R_1 = 0.0706, wR_2 = 0.1301$	$R_1 = 0.0637, wR_2 = 0.1058$	$R_1 = 0.0356, wR_2 = 0.0804$
R <sub>int</sub>	0.0194	0.0404	0.0160	0.0207
Extinction coefficient	none	none	none	none
Res. elec. den. (e Å $^{-3}$ )	0.305	0.346	0.313	0.331

dissolved in 20 ml of THF; diphenylacteylene (0.166 g, 0.930 mmol) was added, after which the reaction mixture was warmed and maintained at 50 °C for 8 h. IR analysis showed the disappearance of the starting materials and the presence of **2a**. The solvent was removed in vacuo and the resulting red residue dissolved in a minimum volume of CH<sub>2</sub>Cl<sub>2</sub> and loaded onto a grade II acidic alumina column (14.0 × 2.0 cm<sup>2</sup>). Elution with C<sub>6</sub>H<sub>14</sub> afforded **2a**; recrystallization from C<sub>6</sub>H<sub>14</sub> at -78 °C gave **2a** as a yellow solid. Yield: 0.156 g (46%), m.p. 177–180 (dec.) MS: *m/e* (relative intensity) 737 [*M*<sup>+</sup>, not observed], 709 [*M*<sup>+</sup> –CO] (5.9), 653 [*M*<sup>+</sup> – 3CO] (11.2), 598 [*M*<sup>+</sup> –Mn(CO)<sub>3</sub>] (100). *Anal.* Calc.: C, 74.80; H, 4.51; N, 1.89%. Found: C, 71.75; H, 4.19; N, 1.71%.

# 4.1.3. Preparation of $[1-(p-methoxyphenyl)-2-benzyl-3,4,5,6-tetraphenyl-\eta^5-azacyclohexadienyl]manganese tricarbonyl ($ **2b**)

(Phenylacetyl)manganese pentacarbonyl (0.307 g, 0.976 mmol) was dissolved in a minimum amount of THF, after which *p*-methoxyphenyl isocyanide (0.130 g, 0.976 mmol) and diphenylacetylene (0.870 g, 4.88 mmol)

dissolved in a minimum amount of THF were added by syringe. The reaction was refluxed for 20 h and deemed complete by IR analysis. Solvent was removed in vacuo; the resulting red residue was loaded onto a silica gel column. Elution with C<sub>6</sub>H<sub>14</sub>/CH<sub>2</sub>Cl<sub>2</sub> (9/1) removed small amounts of benzyl manganese pentacarbonyl. Elution with C<sub>6</sub>H<sub>14</sub>/CH<sub>2</sub>Cl<sub>2</sub> (1/1) afforded **2b**. Removal of the solvent in vacuo and repeated recrystallization from C<sub>6</sub>H<sub>14</sub>/CH<sub>2</sub>Cl<sub>2</sub> at -78 °C gave **2b** as an orange solid. Yield: 0.048 g (7%), m.p. 174–176 (dec.). MS: *m/e* (relative intensity) [*M*<sup>+</sup>] 719 (10), 691 [*M*<sup>+</sup> –CO] (35), 580 [*M*<sup>+</sup> –Mn(CO)<sub>3</sub>] (100).

### 4.1.4. Preparation of [1-(p-tolyl)-2-(p-chlorobenzyl)-3,5-dihydro-4,6-diphenyl-η<sup>5</sup>-azacyclohexadienyl]manganese tricarbonyl (**3a**)

(p-Tolyl isocyanide)[(p-chlorophenyl)acetyl]manganese tetracarbonyl (1a) (0.426 g, 0.972 mmol) was dissolved in THF (20 ml), and phenylacetylene (0.198 g, 0.213 ml, 1.94 mmol) was added by syringe, after which the reaction was warmed and maintained at 60 °C for 1.5 h. IR analysis showed the disappearance of the starting materials and the presence of 3a. The

solvent was removed in vacuo and the resulting orange residue dissolved in a minimum volume of CH<sub>2</sub>Cl<sub>2</sub> and loaded onto a grade II acidic alumina column (19.0 × 2.0 cm<sup>2</sup>). Elution with C<sub>6</sub>H<sub>14</sub> removed small amounts of (*p*-chlorobenzyl)manganese pentacarbonyl and small amounts of **3a**; elution with C<sub>6</sub>H<sub>14</sub>/CH<sub>2</sub>Cl<sub>2</sub> (4/1) removed **3a** as a yellow band. Removal of solvent in vacuo followed by repeated recrystallization from C<sub>6</sub>H<sub>14</sub>/Et<sub>2</sub>O (2/1) at -78 °C gave **3a** as a yellow solid. Yield: 0.43 g (76%), m.p. 155–157 (dec). MS: *m/e* (relative intensity) 585 [*M*<sup>+</sup>, not observed], 557 [*M*<sup>+</sup> –CO] (6), 501 [*M*<sup>+</sup> – 3CO] (16), 446 [*M*<sup>+</sup> –Mn(CO)<sub>3</sub>] (100). Anal. Calc.: C, 69.69; H, 4.30; N, 2.39. Found: C, 69.12; H, 4.66; N, 2.36%.

## 4.1.5. Preparation of $[1-(p-methoxyphenyl)-2-(p-chlorobenzyl)-3,5-dihydro-4,6-diphenyl-<math>\eta^5$ -azacyclohexadienyl[manganese tricarbonyl (**3b**)

(p-Chlorobenzyl)manganese pentacarbonyl (1.00 g, 3.12 mmol) and *p*-methoxyphenyl isocyanide (0.415 g, 3.12 mmol) were dissolved in a minimum volume of THF, after which the reaction mixture was stirred at ambient temperature for 18 h. IR analysis showed the presence of the expected (p-methoxyphenyl isocyanide)[(*p*-chlorophenyl)acetyl]manganese tetracarbonyl complex along with remaining (p-chlorobenzyl)manganese pentacarbonyl. Phenylacetylene (0.319 g, 0.343 ml, 6.24 mmol) was added by syringe, after which the solution was warmed and maintained at 40 °C for 72 h. The solvent was removed in vacuo; the resulting red residue was dissolved in a minimum volume of CH<sub>2</sub>Cl<sub>2</sub> and loaded onto a grade II acidic alumina column. Elution with C<sub>6</sub>H<sub>14</sub> afforded a red band. Elution with Et<sub>2</sub>O removed an orange band and elution with THF removed an orange band, all of which contained (pchlorobenzyl)manganese pentacarbonyl and 3b. Removal of the solvent in vacuo followed by extraction with  $C_5H_{12}$  and recrystallization at -78 °C gave **3b** as an orange solid. Yield: 0.240 g (13%), m.p. 129-131 (dec.). MS: m/e (relative intensity) 601  $[M^+$ , not observed], 573  $[M^+ - CO]$  (20), 517  $[M^+ - 3CO]$  (8), 462  $[M^+ - \text{Mn(CO)}_3]$  (100).

4.1.6. Preparation of  $[1-(p-tolyl)-2-(p-chlorobenzyl)-3,5-dimethyl-4,6-bis(carbomethoxy)-\eta^5-azacyclo$  $hexadienyl]manganese tricarbonyl (4), <math>[1-(p-tolyl)-2-(p-chlorobenzyl)-3,6-dimethyl-4,5-bis(carbomethoxy)-\eta^4-azacyclohexadienyl]manganese tricarbonyl (5a), <math>[1-(p-tolyl)-2-(p-chlorobenzyl)-4,5-dimethyl-3,6-bis(carbomethoxy)-\eta^4-azacyclohexadienyl]manganese tricarbonyl (5b) and <math>[1-(p-tolyl)-2-(p-chlorobenzyl)-4,6-(dimethyl)-3,5-bis(carbomethoxy)-\eta^5-azacyclohexadienyl]manganese tricarbonyl (5c)$ 

(p-Tolyl isocyanide)[(p-chlorobenzyl)acetyl]manganese tetracarbonyl (1a) (0.100 g, 0.229 mmol) wasdissolved in a minimum volume of THF, and methyl

2-butynoate (0.144 g, 0.048 ml, 0.478 mmol) was added by syringe, after which the reaction mixture was warmed and maintained at reflux for 2 h. IR analysis showed the disappearance of the starting materials and the presence of a complex mixture. The solvent was removed in vacuo, and the resulting orange residue was dissolved in a minimum volume of CH<sub>2</sub>Cl<sub>2</sub> and loaded onto a grade II acidic alumina column  $(17 \times 1.5 \text{ cm}^2)$ . Elution with  $C_6H_{14}/CH_2Cl_2$  (2/3) gave a yellow band. Removal of solvent in vacuo followed by recrystallization from  $CH_2Cl_2/C_6H_{14}$  (1/2) at -78 °C gave 4 as a yellow solid. Yield: 0.016 g (12%), m.p. 112 °C. MS: m/e (relative intensity) 577  $[M^+]$  (6.6), 493  $[M^+ - 3 \text{ CO}]$  (78), 438  $[M^+ - \text{Mn}(\text{CO})_3]$  (100). Elution with (1/4) C<sub>6</sub>H<sub>14</sub>/ CH<sub>2</sub>Cl<sub>2</sub> afforded an orange band. Removal of solvent in vacuo followed by recrystallization from CH2Cl2/  $C_6H_{14}$  (1/2) gave an orange solid. Yield: 0.030 g (23%). <sup>1</sup>H NMR analysis showed 10 methyl signals in the same region of the spectrum as the methyl groups for compound 4. Therefore, the mixture was believed to contain two regioisomeric azacylohexadienyl complexes. Fractional recrystallization from  $C_6H_{14}$  at -78 °C gave 5c as an orange solid. Yield: 0.005 g (4%), m.p. 172-175 (dec.). MS: m/e (relative intensity) 577  $[M^+, not$ observed], 493  $[M^+ - 3CO]$  (20), 438  $[M^+ - Mn(CO)_3]$ (30), and **5b** as a yellow solid. Yield: 0.019 g (14%), m.p. 107–108 (dec.). MS: m/e (relative intensity) 577  $[M^+]$ (10), 493  $[M^+ - 3CO]$  (20), 438  $[M^+ - Mn(CO)_3]$  (30).

Elution with 100% THF gave a yellow band. Removal of solvent in vacuo followed by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/C<sub>6</sub>H<sub>14</sub> (1/2) gave **5a** as a yellow solid. Yield: 0.009 g (7%), m.p. 191–192 (dec.). MS: m/e (relative intensity) 577 [ $M^+$ , not observed], 493 [ $M^+$  – 3CO] (20), 438 [ $M^+$  – Mn(CO)<sub>3</sub>] (30). Anal. Calc.: C, 58.20; H, 4.36; N, 2.42. Found: C, 57.96; H, 4.36; N, 2.35%.

## 4.1.7. Preparation of $[1-(p-tolyl)-2-(p-chlorobenzyl)-3,4,5,6-tetrakis(carbomethoxy)-\eta^4-azacyclohexa$ dienyl]manganese tricarbonyl (6)

(p-Tolyl isocyanide)[(p-chlorobenzyl)acetyl]manganese tetracarbonyl (1a) (0.222 g, 0.508 mmol) was dissolved in THF (8 ml); dimethylactetylene dicarboxylate (0.144 g, 0.125 ml, 1.02 mmol) was added by syringe, after which the reaction was warmed and maintained at 60 °C for a 3-h period. IR analysis showed the disappearance of the starting materials and the presence of 6. The solvent was removed in vacuo and the resulting orange residue dissolved in a minimum volume of CH2Cl2 and loaded onto a grade II acidic alumina column (15  $\times$  2.0 cm<sup>2</sup>). Elution with C<sub>6</sub>H<sub>14</sub>/ CH<sub>2</sub>Cl<sub>2</sub> (4/1) removed small amounts of (p-chlorobenzyl)manganese pentacarbonyl and small amounts of 6. Elution with  $CH_2Cl_2$  afforded **6** as an orange band. Removal of solvent in vacuo followed by repeated recrystallization from  $C_6H_{14}/Et_2O$  (2/1) at -78 °C, gave 6 as an orange solid. Yield: 0.241 g (71%), m.p.

168–171 (dec.). MS: m/e (relative intensity) 665  $[M^+]$ (15), 581  $[M^+ - 3CO]$  (57), 553  $[M^+ - 4CO]$  (100), 525  $[M^+ - 5CO]$  (10). Anal. Calc.: C, 54.12; H, 3.75; N, 2.10. Found: C, 54.78; H, 4.02; N, 2.02%.

# *4.1.8. Preparation of* [1,1,1,1*-tetracarbonyl-4,5-bis(trifluoromethyl)-3-(p-chlorobenzyl)-2-(p-tolyl)*]-2-azamanganacyclopentadiene (7)

(p-Tolyl isocyanide)[(p-chlorophenyl)acetyl]manganese tetracarbonyl (1a) (0.503 g, 1.108 mmol) was dissolved in THF (90 ml) and added to a 300-ml Parr bomb. The Parr bomb was sealed and hexafluoro-2butyne (excess) as determined by the Parr bomb pressure gauge was admitted to the bomb from a 10 ggas canister by employing an Aldrich lecture bottle regulator. The bomb was then pressurized to 400 psi with Ar. The temperature was increased to 52 °C and maintained for 4 h. IR analysis showed the almost complete disappearance of the starting material and the presence of 7. Removal of solvent in vacuo and extraction of the resulting red residue with C<sub>6</sub>H<sub>14</sub> followed by recrystallization from  $C_6H_{14}$  at -5 °C gave 7 as an orange solid. Yield: 0.140 g (22%), m.p. 105–106. MS: m/e (relative intensity) 571  $[M^+]$  (25),  $515 [M^+ - 2CO] (55), 487 [M^+ - 3CO] (40), 459 [M^+ -$ 4CO] (85). Anal. Calc.: C, 48.32; H, 2.27; N, 2.45. Found: C, 48.40; H, 2.41; N, 2.30%.

### 4.1.9. Reaction of 7 with phenylacetylene

To a THF solution of compound 7 (0.040 g, 0.070 mmol) was added phenylacetylene (0.007 g, 0.070 mmol). The solution was brought to reflux and maintained for 5 days. IR analysis indicated almost complete disappearance of 7 and the formation of the coupling product 7. Solvent was removed in vacuo and the resulting red residue was loaded onto a grade II acidic alumina column ( $13 \times 1.25 \text{ cm}^2$ ). Elution with C<sub>5</sub>H<sub>12</sub> removed an orange band, which contained compound 7, and the coupling product **20**. Repeated attempts at fractional crystallization from CH<sub>2</sub>Cl<sub>2</sub>/C<sub>6</sub>H<sub>14</sub> or C<sub>6</sub>H<sub>14</sub> were unsuccessful.

#### 5. Supplementary material

Crystallographic data for the structural analysis (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 175290–175297 for compounds **2b**, **3b**, **4**, **5a**–**c**, **6** and **7**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: int. code +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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