Acyclic Diamino Carbene Complexes of Manganese(I): Synthesis, Deprotonation, and Subsequent Multiple Insertion Reaction of Alkynes

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Received September 12, 2008

The cationic isocyanide complexes *fac*-$[Mn(CNR)(CO)_3(bipy)]^+$ (**1**) react with NH_2CH_3 to give acyclic diaminocarbene (ADC) complexes *fac*-$[Mn(ADC)(CO)_3(bipy)]^+$ (**2**), which when treated with KOH yield neutral formamidinyl (ADC-H) derivates *fac*-$[Mn(ADC\text{-}H)(CO)_3(bipy)]$ (**3**). These undergo multiple insertion reactions of methyl propiolate or phenyl acetylene into the metal−carbon bond to afford compounds **4** and **5** containing a new η^4-azacyclohexadienyl ligand, with the loss of the bipy chelating ligand.

Introduction

The chemistry of N-heterocyclic carbene (NHC) metal complexes has received widespread interest in recent years mainly owing to its application in homogeneous catalysis.[1] Less attention has been paid to their analogous acyclic diaminocarbene (ADC) complexes, although this type of derivative has been known for more than four decades.[2] However, isolation of free ADCs[3] and recent recognition that ADC palladium complexes have activities comparable to those of NHCs in some catalytic processes[4] have furnished a new impetus to the field. Methods for synthesizing ADC complexes involve nucleophilic addition of primary or secondary amines to coordinated isocyanides[2,5] or reaction of free ADC with the appropriate metallic fragment.[3,6] Specific routes implying deprotonation of tetrazolium ions with carbonylferrate[7] and reaction of tetramethylformamidinium dichloride with $Fe_2(CO)_9$[8] have also been described.

ADC complexes containing N−H residues can be easily deprotonated to afford formamidinyl derivatives[9] and on occasion liberated from the metal center yielding the corresponding formamidines,[2a,9b] which have also been obtained upon reductive elimination from hydrido formamidinyl Pt(II) derivatives.[9b] ADC complexes appear also to be involved in the catalytic formation of carbodiimides from isocyanides and amines on gold metal surfaces.[10] Apart from the above, the reactivity of ADC complexes or their deprotonated forms remains practically unexplored.

In this context, we describe herein the synthesis of cationic ADC complexes of manganese(I) of general formula *fac*-$[Mn(ADC)(CO)_3(bipy)]^+$ by 1,2-addition of NH_2Me to a variety of coordinated arylisocyanide ligands, their deprotonation reaction yielding formamidinyl derivatives, and the subsequent multiple insertion reaction of methyl propiolate and phenyl acetylene into the metal−carbon bond to afford a new type of azacyclohexadienyl ligand.

Results and Discussion

When dichloromethane solutions of the cationic isocyanide complexes *fac*-$[Mn(CNR)(CO)_3(bipy)]^+$ (**1a**, R = phenyl; **1b**, R = 2-naphthyl; **1c**, R = xylyl; **1d**, R = 2-chloro-6-methylphenyl) are treated with an excess of gaseous methylamine at room temperature, the acyclic diaminocarbene complexes *fac*-$[Mn\{(C(NHR)NHMe\}(CO)_3(bipy)]^+$ (**2a**−**d**) are formed within a few minutes (Scheme 1). The reaction was monitored by IR spectroscopy showing the disappearance of the ν_{CN} band of the coordinated isocyanide ligand (2171−2176 cm^{-1}) together with the ν_{CO} bands of the carbonyl ligands appearing at lower frequencies than those in the parent compounds (about 30 cm^{-1} on average, see Table 1). The IR spectra of these derivatives in KBr also reveal the presence of ν_{N-H} bands in the range 3300−3400 cm^{-1}, as well as a ν_{C-N} band around 1530 cm^{-1} characteristic of diaminocarbene ligands.

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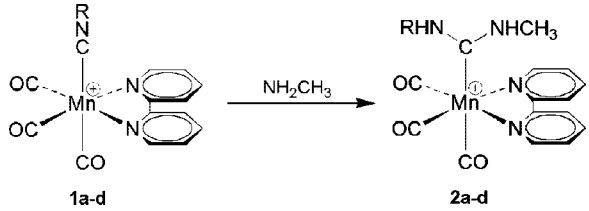
10.1021/om800888r CCC: $40.75
Publication on Web 01/09/2009

Scheme 1. Synthesis of the Manganese Diaminocarbene Complexes 2a−d [a]



1a-d 2a-d

[a] **2a**, R = phenyl; **2b**, R = 2-napthyl; **2c**, R = xylyl; **2d**, R = 2-chloro-6-phenyl.

The multiple-bond character of the two $C_{carbene}-N$ bonds causes restricted rotation around these bonds;[2a] consequently four conformers may result depending upon the relative disposition of the substituents on the nitrogen atoms (Figure 1). The ^{1}H NMR spectra (Table 1 and experimental section) show the presence of two isomers in the case of **2a**,**b** and just one isomer in the case of **2c**,**d**. Thus, a doublet signal is observed for the NMe group around 3.1 ppm for complexes **2c**,**d**, whereas two doublets at about 3.1 and 2.7 ppm are present in the case of complexes **2a**,**b**. Owing to steric reasons, the two amphi configurations *ZE* and *EZ* (forms a and b in Figure 1) appear to be clearly favored[2a] and should be those formed in complexes **2a**,**b**. The bulkier xylyl and 2-chloro-6-methylphenyl substituents in complexes **2c**,**d** cause strong steric hinderance so that one of these two conformers appears to be largely preferred. An X-ray diffraction study carried out on **2d** (Figure 2) shows that this complex displays a diaminocarbene conformation corresponding to that of form a in Figure 1, that is with the bulky 2-chloro-6-methylphenyl group located in a *syn* disposition with respect to the metallic fragment and *anti* with respect to the N(H)Me group. The preference of form a could be tentatively explained taking into account the longer value of the $Mn-C_{carbene}$ bond distance (2.097(2) Å) compared with the $C_{carbene}-N$(H)Me bond length (1.330(3) Å), which would allow a smaller steric repulsion between the 2-chloro-6-methylphenyl substituent and the metallic fragment than would exist between this group and the N(H)Me residue in the isomeric form b. Among the other structural parameters of **2d**, it is worth noting the C1−N1 (1.339(3) Å) and C1−N2 (1.330(3) Å) bond lengths, which are intermediate between single and double bond, thus justifying the absence of free rotation around those bonds in the ADC complexes **2a**−**d**. On the other hand, the $Mn-C_{carbene}$ (2.097(2) Å) distance in **2d** is appreciably longer than that found (2.054−2.078(3) Å) in similar N-heterocyclic carbene complexes of formula *fac*-[Mn(NHC)(CO)$_3$(bipy)]$^+$, recently prepared by our group.[11,12] These structural data, together with the fact that in the IR spectra the ν_{CO} bands for compounds **2a**−**d** appear at slightly higher frequencies than those for the analogous NHC compounds (3 cm^{-1} on average, see Table 1 and refs 11 and 12), seem to indicate that the ADC ligands described herein have slightly weaker basicities than their NHC counterparts, contrary to what is found in the literature for other ADC ligands.[13]

Complexes **2a**−**d** are instantaneously deprotonated when treated with an excess of KOH in dichloromethane to give the neutral formamidinyl complexes **3a**−**d** (Scheme 2) in quantitative yields, a process that is accompanied by a strong color change from yellow to red. The two step synthesis of formamidinyl complexes by reaction of coordinated isocyanides with amines and subsequent deprotonation reaction is well-known in the literature,[9] although these derivatives can also be obtained by direct insertion of isocyanides in the metal−nitrogen bond of amido complexes.[14]

Deprotonation of **2a**−**d** to afford **3a**−**d** occurs in the N(H)aryl group rather than in the N(H)Me residue, due to the more acidic character of the former. This is corroborated by the maintenance of the doublet signal of the methyl group in the ^{1}H NMR spectra of compounds **3** (Table 2) (in the case of **3a**,**b** a broad singlet is observed), as well as by the presence of the N(H)Me fragment in the insertion product with alkyne molecules, as we will comment below. Naturally, the IR spectra of **3a**−**d** in the ν(CO) region show the characteristic pattern of a *fac*-geometry, but at lower frequencies (30 cm^{-1} on average, Table 1) than the parent complexes **2a**−**d**.

The deprotonation reaction of **2a**−**d** proved to be fully reversible, so the addition of an equivalent of HBF_4 to **3a**−**d** gives the acyclic diaminocarbene complexes again. In fact, this reversible process is useful in the purification of compounds **2a**,**b** (see Experimental Section).

In view of the lack of precedents in the literature, we found it interesting to begin the study of the reactivity of ADC and formamidinyl complexes toward unsaturated molecules such as alkynes. It must be pointed out that a rare case of migratory insertion of alkynes in NHC complexes of ruthenium(II) has been described.[15] In our case, the ADC carbene complexes **2a**−**d** do not react with a variety of alkynes such as dimethyl acetylenedicarboxylate (DMAD), methyl propiolate, or phenyl acetylene, even under forcing conditions, whereas the deprotonated derivatives **3a**−**d** readily react with those alkynes. In the case of methyl propiolate and phenyl acetylene, the reaction is selective and affords the multiple insertion products **4a**−**d**, and **5a**−**c**, respectively, as we will discuss in subsequent lines. For the alkyne DMAD, the reaction is not selective giving a complex and untreatable mixture of species.

The heating of compounds **3** with 2 equiv of methyl propiolate in toluene at 60 °C for 15 min or with 4 equiv of phenyl acetylene in toluene at 90 °C for 20 min gave rise to the formation of complexes **4** and **5**, respectively (Scheme 3), involving liberation of the bipy ligand. Chromatography on grade IV acidic alumina and elution with 1/3 dichloromethane/hexane removed the bipy from the mixture, while elution with 1/1 dichloromethane/hexane gave a yellow band of **4a**−**d** or **5a**−**c**, which were isolated as yellow solids. A plausible mechanism for the formation of these complexes is shown in Scheme 3. Thus, two successive insertion reactions of the alkyne into the carbon−metal bond of the formamidinyl ligand[16] in a head-to-tail fashion give rise to the alkenyl intermediates I and II. The last undergoes electrocyclic rearrangement yielding complex III, forming a new azacyclohexadienyl ligand acting in an η^1 manner. The additional donor capability of the cyclic

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(16) In order to allow coordination of the alkyne molecule previous to each insertion process, a reversible change in the coordination mode of the bipy ligand from bidentate to monodentate could be proposed. See, for instance: Memering, M. N.; Dobson, G. R. *Inorg. Chem.* **1973**, *12*, 2490.

Table 1. Selected Spectroscopic Data (IR and ^{1}H NMR) for Compounds 1−5

compound	IR (CH_2Cl_2, cm^{-1}), ν(CO)[a]	^{1}H NMR,[b] δ
1a	2050vs, 1990s, 1957vs; 2175w ν(CN)	
1b	2050vs, 1990s, 1957vs; 2176w ν(CN)	
1c	2050vs, 1989s, 1957vs; 2171w ν(CN)	
1d	2051vs, 1993s, 1959vs; 2171w ν(CN)	
2a	2031vs, 1949s, 1924s	Isomer A: 6.57 (2H, br s, NH); 3.08 (3H, d, $^3J_{HH}$ = 5.4, NCH_3). Isomer B: 6.41 (2H, br s, NH); 2.68 (3H, d, $^3J_{HH}$ = 5.4, NCH_3)
2b	2031vs, 1948s, 1924s	Isomer A: 6.72 (2H, br s, NH); 3.09 (3H, d, $^3J_{HH}$ = 4.8, NCH_3). Isomer B: 6.59 (2H, br s, NH); 2.75 (3H, d, $^3J_{HH}$ = 4.8, NCH_3)
2c	2033vs, 1952s, 1924s	6.22 (1H, s, NH); 6.17 (1H, s, NH); 3.14 (3H, d, $^3J_{HH}$ = 5.0, NCH_3)
2d	2033vs, 1953s, 1924s	6.28 (1H, s, NH); 6.13 (1H, s, NH); 3.21 (3H, d, $^3J_{HH}$ = 5.1, NCH_3)
3a	2001vs, 1912s, 1892s	4.43 (1H, s, NH); 2.52 (3H, br s, NCH_3)
3b	2001vs, 1912s, 1892s	4.62 (1H, s, NH); 2.62 (3H, br s, NCH_3)
3c	2000vs, 1906s, 1891s	4.42 (1H, d,, $^3J_{HH}$ = 4.0, NH); 2.61 (3H, d, $^3J_{HH}$ = 4.0, NCH_3)
3d	2002vs, 1910s, 1893s	4.48 (1H, s, NH); 2.54 (3H, d, $^3J_{HH}$ = 4.4, NCH_3)
4a	2004 vs, 1926s, 1910s	5.21 (1H, s, NH); 2.93 (3H, d, $^3J_{HH}$ = 2.5, NCH_3)
4b	2004vs, 1926s, 1911s	5.30 (1H, s, NH); 2.92 (3H, d, $^3J_{HH}$ = 4.8, $NHCH_3$)
4c	2002vs, 1923s, 1908s	4.75 (1H, s, NH); 2.93 (3H, br s, NCH_3)
4d	2003vs, 1924s, 1909s	4.72 (1H, s, NH); 2.96 (3H, d, $^3J_{HH}$ = 5.1, NCH_3)
5a	1982vs, 1896s, 1886sh	5.18 (1H, s, NH); 3.03 (3H, d, $^3J_{HH}$ = 3.0, NCH_3)
5b	1982vs, 1897s, 1885sh	5.28 (1H, s, NH); 3.00 (3H, d, $^3J_{HH}$ = 3.1, NCH_3)
5c	1979vs, 1890s, 1881sh	4.55 (1H, s, NH); 3.06 (3H, br s, NCH_3)

[a] Abbreviations: vs = very strong, s = strong, w= weak, sh = shoulder. [b] NMR spectra recorded in CD_2Cl_2.

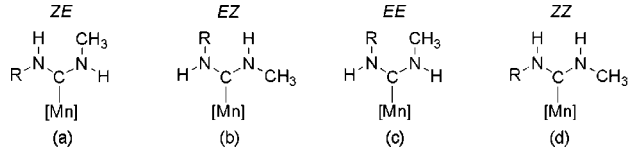

Figure 1. Schematic representation of the four possible isomers for carbene complexes **2a**−**d**.

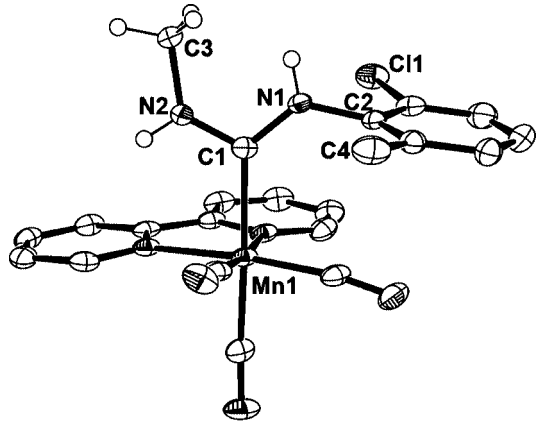

Figure 2. Molecular structure of **2d** (50% thermal ellipsoids) showing only one of the two positions adopted by disordered Cl and CH_3 substituents in the 2-chloro-6-methylphenyl group. Selected interatomic distances (Å) and angles (deg): Mn1−C1 = 2.097(2), C1−N1 = 1.339(3), C1−N2 = 1.330(3), N1−C2 = 1.428(3), N2−C3 = 1.466(3); Mn1−C1−N1 = 129.0(2), Mn1−C1−N2 = 118.1 (2), N1−C1−N2 = 112.9(2), C1−N1−C2 = 128.6(2), C1−N2−C3 = 126.4(2).

ligand forces substitution of bipy affording complexes **4** and **5**, which contain the azaheterocycle η^4-coordinated to the metal center. It must be noted that related η^4-azacyclohexadienyl complexes have recently been described resulting from the coupling of alkynes to iminoacyl ligands on manganese.[17]

The structure of these complexes **4** and **5** depicted in Scheme 3 was determined by spectroscopic methods (Table 1 and Experimental Section) and by X-ray diffraction analysis (**4d** and

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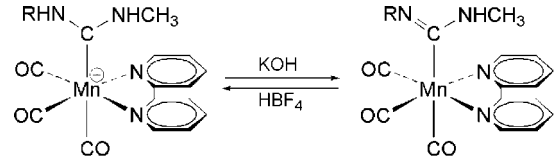
Scheme 2. Reversible Deprotonation Reaction of Compounds 2a−d



2a-d **3a-d**

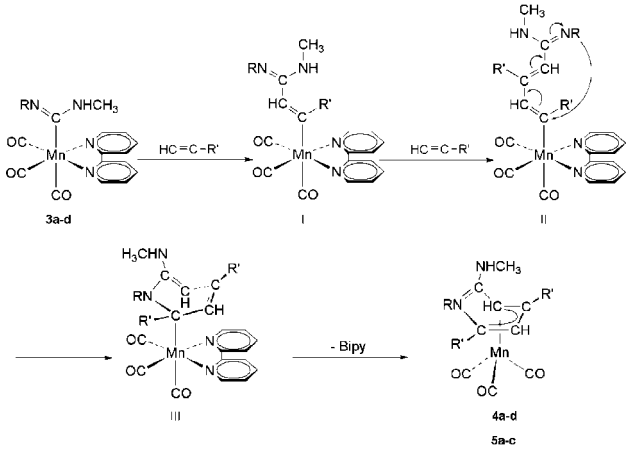
5c, Figures 3 and 4, respectively). The IR spectra in the ν_{CO} region show typical *fac*-tricarbonyl patterns; the relative low frequencies of the ν_{CO} bands showing a high donor ability of the cyclic ligand, specially in the case of **5a**−**c**, lacking electron-withdrawing carboxylate groups. The NMR and X-ray data of **4** and **5** suggest that these complexes are better considered as containing within the azaheterocycle a butenediyl fragment η^4-coordinated to Mn(+1) (form b in Figure 5) rather than a butadiene fragment η^4-coordinated to Mn(−1) (form a in Figure 5). This is evidenced by the strong difference in the chemical shift of the two C−H protons in the azaheterocycle, one of them being close to vinylic in character (range 6.4−6.9 ppm), whereas the other one appears at much lower frequency (at about 3 ppm), as a consequence of its alkylic (carbanionic) character. A similar behavior is observed in the $^{13}C\{^1H\}$ NMR chemical shifts of the corresponding C−H carbon atoms, appearing at about 80 (vinylic) and 30 (carbanionic) ppm, respectively (see Experimental Section). The single-crystal X-ray diffraction study carried out on complexes **4d** (Figure 3) and **5c** (Figure 4) showed that both compounds have very similar structures, forming the same regioisomer of the azacyclohexadienyl ligand. The four carbon atoms of the cycle directly bonded to manganese arise from two alkyne molecules, which are coupled in a head-to-tail mode. The azaheterocycle is completed with the imine residue of the original formamidinyl ligand. The azaheterocycle is bent, with dihedral angles between C1−C2−C3−C4 and C4−C5−N1−C1 planes of 43.7(5)° (**4d**) and 44.4(2)° (**5c**). The C1−C2 (1.438(5) Å (**4d**), 1.446(2) Å (**5c**)) and C3−C4 (1.454(5) Å (**4d**), 1.469(2) Å (**5c**)) distances are appreciable longer than the C2−C3 distances (1.395(2) Å (**4d**), 1.403(2) Å (**5c**)), supporting the butenediyl description of the four carbon atom segment bonded to manganese (form b, Figure 5). In agreement with this consideration, the Mn1−C2 and Mn1−C3 bond lengths are slightly shorter than the Mn1−C1

Table 2. Crystallographic Data for 2d, 4d, and 5c

	2d	4d	5c
formula	$C_{22}H_{19}Cl_2MnN_4O_7$	$C_{20}H_{18}ClMnN_2O_7 \cdot CH_2Cl_2$	$C_{29}H_{25}MnN_2O_3 \cdot 0.5CH_2Cl_2$
FW	577.25	573.68	546.92
color/habit	yellow/prism	yellow/prism	yellow/prism
cryst dimensions (mm^3)	0.17 × 0.14 × 0.08	0.25 × 0.20 × 0.04	0.58 × 0.42 × 0.17
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	9.76710(10)	12.376(2)	14.7044(6)
b, Å	12.0128(2)	11.822(2)	10.3457(3)
c, Å	20.2660(3)	16.339(3)	17.4489(7)
β, deg	95.4160(10)	94.657(3)	105.016(2)
V, $Å^3$	2367.20(6)	2382.6(7)	2563.81(16)
Z	4	4	4
T, K	100(2)	110(2)	100(2)
D_{calcd}, g cm^{-3}	1.62	1.599	1.417
μ, mm^{-1}	0.836	0.936	0.654
F(000)	1176	1168	1132
θ range, deg	1.97−26.43	1.65−26.45	1.62 − 27.88
no. of rflns collected	36093	20548	44778
no. indep reflns/R_{int}	4864/0.0505	4902/0.0712	6116/0.0339
no. of obsd reflns ($I > 2\sigma(I)$)	3866	3208	4990
no. data/restraints/params	4864/0/337	4902/1/328	6116/0/358
R1/wR2 ($I > 2\ \sigma(I)$)[a]	0.0363/0.0785	0.0516/0.1203	0.0366/0.0847
R1/wR2 (all data)[a]	0.0519/0.0829	0.0878/0.1322	0.0498/0.0908
GOF (on F^2)[a]	1.030	1.088	1.052
largest diff peak/hole (e $Å^{-3}$)	+0.458/−0.456	+0.704/−0.778	+0.421/−0.369

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

Scheme 3. Proposed Mechanism for the Formation of Compounds 4a−d and 5a−c[a]



[a] **4a**, R = phenyl, R′ = CO_2CH_3; **4b**, R = 2-napthyl, R′ = CO_2CH_3; **4c**, R = xylyl, R′ = CO_2CH_3; **4d**, R = 2-chloro-6-methyl, R′ = CO_2CH_3; **5a**, R = R′ = phenyl; **5b**, R = 2-napthyl, R′ = phenyl; **5c**, R = xylyl, R′ = phenyl.

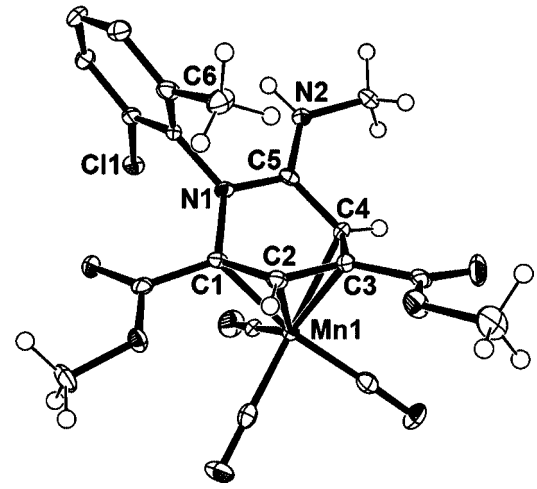


Figure 3. Molecular structure of **4d** (50% thermal ellipsoids) showing only one of the two positions adopted by disordered Cl and CH_3 substituents in the 2-chloro-6-methylphenyl group. Selected interatomic distances (Å) and angles (deg): Mn1−C1 = 2.124(3), Mn1−C2 = 2.075(4), Mn1−C3 = 2.065(4), Mn1−C4 = 2.125(4), Mn1−C5 = 2.934(5), C1−C2 = 1.438(5), C2−C3 = 1.395(5), C3−C4 = 1.454(5), C4−C5 = 1.437(5), C5−N1 = 1.344(4), C5−N2 = 1.329(4), C1−N1 = 1.474(4); C1−C2−C3 = 113.0(3), C2−C3−C4 = 115.2 (3), C3−C4−C5 = 114.6(3), C4−C5−N1 = 115.7(3), C5−N1−C1 = 114.4(3), N1−C1−C2 = 115.8(3).

and Mn1−C4 ones in these complexes (see Figures 3 and 4). Also of note is the short N1−C5 bond length (1.344(4) and 1.335(2) Å for **4d** and **5c**, respectively), showing its multiple bond character.

Conclusion

We have described herein the synthesis of acyclic diamino carbene (ADC) complexes of manganese(I) by reaction of NH_2Me with a variety of coordinated isocyanide ligands. In these complexes, the carbene ligands are easily deprotonated affording the corresponding formamidinyl derivatives, which undergo regiospecific multiple insertion reactions of alkynes into the metal−carbon bond to form azacyclohexadienyl ligands η^4-coordinated to the metal center. Spectroscopic and structural data suggest that these cyclic ligands can be considered as containing a butenediyl framework within the heterocycle. Works aiming to insert other unsaturated molecules into the metal−carbon bond of the formamidinyl derivatives are currently in progress in our group.

Experimental Section

General Remarks. All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled over appropriate drying agents under dry nitrogen prior to use. Compounds *fac*-$[Mn(CO)_3(CNR)(bipy)][ClO_4]$

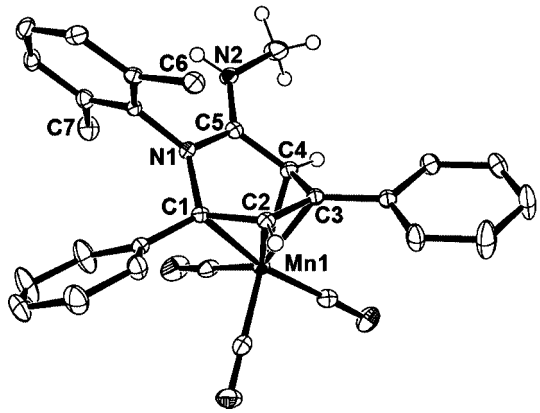


Figure 4. Molecular structure of **5c** (50% thermal ellipsoids). Selected interatomic distances (Å) and angles (deg): Mn1−C1 = 2.1101(16), Mn1−C2 = 2.0852(16), Mn1−C3 = 2.0849(16), Mn1−C4 = 2.1332(17), Mn1−C5 = 2.9380(20), C1−C2 = 1.446(2), C2−C3 = 1.403(2), C3−C4 = 1.469(2), C4−C5 = 1.446(2), C5−N1 = 1.335(2), C5−N2 = 1.330(2), C1−N1 = 1.490(2); C1−C2−C3 = 114.57(15), C2−C3−C4 = 113.14(14), C3−C4−C5 = 115.56(14), C4−C5−N1 = 115.95(15), C5−N1−C1 = 114.34(13), N1−C1−C2 = 114.04(14).

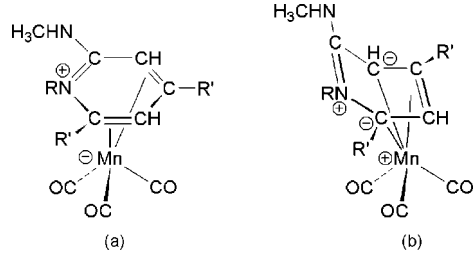
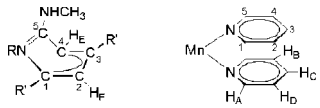


Figure 5. Two extreme representations of the bond between manganese and the η^4-azacyclohexadienyl ligand in the complexes **4** and **5**.

(**1a**−**d**·ClO_4) were prepared according to a reported protocol.[18] NMR spectra were recorded on Bruker 300 and 400 MHz spectrometers. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, dt = doublet of triplets, m = multiplet, br = broad. Coupling constants, *J*, are given in Hz. Methyl propiolate and phenyl acetylene were purchased from Aldrich and used without previous purification.

Safety note: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of such materials should be prepared, and these should be handled with great caution.

For the NMR spectra, the atom labeling in 2,2′-bipyridine and in η^4-azacyclohexadienyl ligands are as follows:



[Mn{C(NHPh)(NHCH$_3$)}(CO)$_3$(bipy)][BF$_4$] (2a·BF$_4$). Through a solution of **1a**·ClO_4 (0.10 g, 0.20 mmol) in CH_2Cl_2 (10 mL), NH_2CH_3 was bubbled for 3 min. The solution was then evaporated to dryness, and the solid remaining was dissolved in CH_2Cl_2 (10 mL). After filtration, some KOH (0.25 g, 4.46 mmol) was added, and the resulting mixture was stirred for 15 min. The red solution was filtered off, and then HBF_4 (0.028 mL, 54% w, 0,20 mmol) was added to the solution, which immediately turned yellow. The solution was concentrated to 3 mL, and hexane (10 mL) was added to afford a yellow solid, which was dried under vacuum. Yield: 0.083 g (70%). Anal. (%) Calcd for $C_{21}H_{18}BF_4MnN_4O_3$: C 48.87, H 3.52, N 10.85. Found: C 48.70, H 3.36, N 10.51. IR (CH_2Cl_2): ν 2031 (vs), 1949 (s), 1924 (s) cm^{-1} (CO). IR (KBr): ν 3438 (w), 3306 (w) cm^{-1} (NH); 1536 (s) cm^{-1} (CN). ^{1}H NMR (300 MHz, CD_2Cl_2), Isomer A (25%): δ 9.16 (2H, d, $^3J_{HH}$ = 5.4, H_a bipy), 8.50 (2H, d, $^3J_{HH}$ = 8.1, H_d bipy), 8.22 (2H, td, $^4J_{HH}$ = 1.2, $^3J_{HH}$ = 7.9, H_c bipy), 7.78−7.72 (2H, m, H_b bipy), 7.36−7.29 (3H, m, Ph), 6.69 (2H, d, $^3J_{HH}$ = 7.2, H_{orto} Ph), 6.57 (2H, br s, NH), 3.08 (3H, d, $^3J_{HH}$ = 5.4, NCH_3). Isomer B (75%): δ 8.73 (2H, d, $^3J_{HH}$ = 5.4, H_a bipy), 8.28 (2H, d, $^3J_{HH}$ = 8.1, H_d bipy), 8.07 (2H, td,$^4J_{HH}$ = 1.2, $^3J_{HH}$ = 7.9, H_c bipy), 7.47 (2H, t, $^3J_{HH}$ = 7.3, H_b bipy), 7.36−7.29 (3H, m, Ph), 6.99 (2H, d, $^3J_{HH}$ = 7.2, H_{orto} Ph), 6.41 (2H, br s, NH), 2.68 (3H, d,$^3J_{HH}$ = 5.4, NCH_3).

[Mn{C(NHC$_{10}$H$_7$)(NHCH$_3$)}(CO)$_3$(bipy)][BF$_4$] (2b·BF$_4$). The procedure is analogous to that described above, using **1b**·ClO_4 (0.1 g, 0.18 mmol), NH_2CH_3 (bubbled through the solution for 10 min), KOH (0.25 g, 4.46 mmol), and HBF_4 (0.028 mL, 54% w, 0.20 mmol). Yield: 0.077 g (75%). Anal. (%) Calcd for $C_{25}H_{20}BF_4MnN_4O_3$: C 53.03, H 3.56, N 9.90. Found: C 52.99, H 3.65, N 9.98. IR (CH_2Cl_2): ν 2031 (vs), 1948 (s), 1924 (s) cm^{-1} (CO). IR (KBr): ν 3439 (w), 3325(w) cm^{-1} (NH); 1538 (s) cm^{-1} (CN). ^{1}H NMR (300 MHz, CD_2Cl_2), Isomer A (25%): δ 9.20 (2H, d, $^3J_{HH}$ = 4.9, H_a bipy), 8.53 (2H, d, $^3J_{HH}$ = 8.0, H_d bipy), 8.01−7.04 (11H, m, H_{arom} $C_{10}H_7$, H_c and H_b bipy), 6.72 (2H, br s, NH), 3.09 (3H, d, $^3J_{HH}$ = 4.8, NCH_3). Isomer B (75%): δ 8.61 (2H, d, $^3J_{HH}$ = 4.9, H_a bipy), 8.24 (2H, d, $^3J_{HH}$ = 8.0, H_d bipy), 8.01−7.04 (11H, m, H_{arom} $C_{10}H_7$, H_c and H_b bipy), 6.59 (2H, br s, NH), 2.75 (3H, d, $^3J_{HH}$ = 4.8, NCH_3).^{13}C NMR (75.5 MHz, CD_2Cl_2), Isomer A (25%): δ 219.4 (s, $C_{carbene}$), 216.5, 213.1 (br s, CO), 158.8 (s, C_1 bipy), 154.6 (s, C_2 bipy), 140.1−121.4 (C_3, C_4, C_5 bipy, CH_{arom} naphtyl), 34.7 (NCH_3). Isomer B (75%): δ 220.5 (s, $C_{carbene}$); 217.0, 213.1 (br s, CO); 155.5 (s, C_1 bipy), 153.7 (s, C_2 bipy), 140.1−121.4 (C_3, C_4, C_5 bipy, CH_{arom} naphtyl), 30.9 (NCH_3).

[Mn{C(NHXylyl)(NHCH$_3$)}(CO)$_3$(bipy)][ClO$_4$] (2c·ClO$_4$). Through a solution of **1c**·ClO_4 (0.1 g, 0.19 mmol) in CH_2Cl_2 (10 mL), NH_2CH_3 was bubbled for 20 min. The solvent was then evaporated to dryness, and the remaining mixture was stirred with 10 mL of CH_2Cl_2. The resulting suspension was filtered with kieselgur affording a yellow solution, which was concentrated to 4 mL. Addition of 10 mL of hexane with vigorous stirring gave a yellow solid, which was filtered off and dried under vacuum. Yield: 0.075 g (71%). Anal. (%) Calcd for $C_{23}H_{22}ClMnN_4O_7$: C 49.61, H 3.98, N 10.06. Found: C 49.61, H 4.02, N 9.92. IR (CH_2Cl_2): ν 2033 (vs), 1952 (s), 1924 (s) cm^{-1} (CO). IR (KBr): ν 3449 (w), 3280 (w) cm^{-1} (NH); 1532 (s) cm^{-1} (CN). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.19 (2H, d, $^3J_{HH}$ = 4.6, H_a bipy), 8.53 (2H, d, $^3J_{HH}$ = 7.9, H_d bipy), 8.25 (2H, t,$^3J_{HH}$ = 7.5, H_c bipy), 7.71 (2H, t,$^3J_{HH}$ = 6.2, H_b bipy), 7.14−6.98 (3H, m, xylyl), 6.22 (1H, s, NH), 6.17 (1H, s, NH), 3.14 (3H, d,$^3J_{HH}$ = 5.0, NCH_3), 1.66 (2H,s, CH_3 xylyl). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 221.7 (s, $C_{carbene}$); 215.5, 213.0 (br s, CO), 155.5 (s, C_1 bipy), 154.3 (s, C_2 bipy), 140.4 (s, C_3 bipy), 136.6 (s, C_{ipso} xylyl), 132.5, 129.7, 129.5 (s, CH_{arom} xylyl), 128.1(s, C_4 bipy), 124.7 (s, C_5, bipy), 35.1 (s, CH_3−NH), 17.7 (s, CH_3 xylyl).

[Mn{C(NHC$_7$H$_6$Cl)(NHCH$_3$)}(CO)$_3$(bipy)][ClO$_4$] (2d·ClO$_4$). The procedure was completely analogous to that described above, using **1d**·ClO_4 (0.1 g, 0.18 mmol) and a bubbling time of 15 min. Yield: 0.087 g (82%).Crystals of **2d**·ClO_4 suitable for X-ray diffraction study were obtained by slow diffusion of hexane into CH_2Cl_2 solution of the compound. Anal. (%) Calcd for $C_{22}H_{19}Cl_2MnN_4O_7$: C 45.78, H 3.32, N 9.71. Found: C 45.30, H 3.30, N 9.69. IR (CH_2Cl_2): ν 2033 (vs), 1953 (s), 1924 (s) cm^{-1} (CO). IR (KBr): ν 3445 (w), 3286 (w) cm^{-1} (NH), 1528 (s) cm^{-1} (CN). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.17 (2H, d, $^3J_{HH}$ = 5.4, H_a bipy), 8.49 (2H, d, $^3J_{HH}$ = 8.0, H_d bipy), 8.27−8.18 (2H, m, H_c bipy),

(18) Garcia Alonso, F. J.; Riera, V.; Villafañe, F.; Vivanco, M. *J. Organomet. Chem.* **1984**, *276*, 39.

7.74−7.67 (2H, m, H_b bipy), 7.23−7.15 (3H, m, H_{arom} C_7H_6Cl), 6.28 (1H, s, NH), 6.13 (1H, s, NH), 3.21 (3H, d, $^3J_{HH}$ = 5.1, NCH_3), 1.83 (2H, s, CH_3 C_7H_6Cl).

[Mn{C(=NPh)(NHCH$_3$)}(CO)$_3$(bipy)] (3a). To a solution of **2a**.BF_4 (0.1 g, 0.019 mmol) in CH_2Cl_2 (10 mL), some KOH (0.50 g, 8.91 mmol) was added, and the mixture stirred for 20 min. The color of the solution changed from yellow to red. Then the solution was filtered off and concentrated to 3 mL. Hexane (10 mL) was slowly added to give a red solid, which was filtered off and dried under vacuum. Yield: 0.070 g (84%). Anal. (%) Calcd for $C_{21}H_{17}MnN_4O_3$: C 58.89, H 4.00, N 13.08. Found: C 58.30, H 4.05, N 13.09. IR (CH_2Cl_2): ν 2001 (vs), 1911 (s), 1892 (s) cm^{-1} (CO). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.72 (2H, d, $^3J_{HH}$ = 5.0, H_a bipy), 7.96 (2H, d, $^3J_{HH}$ = 7.9, H_d bipy), 7.80 (2H, t, $^3J_{HH}$ = 7.5, H_c bipy), 7.12 (2H, t, $^3J_{HH}$ = 5.7, H_b bipy), 6.78 (2H, t, $^3J_{HH}$ = 6.8, H_{meta} Ph), 6.62 (1H, t, $^3J_{HH}$ = 6.8, H_{para} Ph), 6.17 (2H, d, $^3J_{HH}$ = 6.7, H_{orto} Ph), 4.43 (1H, s, NH), 2.52 (3H, br s, NCH_3).

[Mn{C(=NC$_{10}$H$_7$(NHCH$_3$)}(CO)$_3$(bipy)] (3b). The procedure was completely analogous to that described above, using **2b**.BF_4 (0.1 g, 0.18 mmol) and KOH (0.50 g, 8.91 mmol). Yield: 0.075 g (89%). Anal. (%) Calcd for $C_{25}H_{19}MnN_4O_3$: C 62.77, H 4.00, N 11.71. Found: C 62.30, H 4.11, N 11.49. IR (CH_2Cl_2): ν 2001 (vs), 1912 (s), 1892 (s) cm^{-1} (CO). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.69 (2H, d, $^3J_{HH}$ = 4.3, H_a bipy), 7.94 (2H, d, $^3J_{HH}$ = 8.1, H_d bipy), 7.74 (2H, t, $^3J_{HH}$ = 7.6, H_c bipy), 7.66 (1H, d, $^3J_{HH}$ = 8.1, $C_{10}H_7$), 7.45 (1H, d, $^3J_{HH}$ = 8.1, $C_{10}H_7$), 7.36−7.30 (2H, m, H_b bipy), 7.26−7.19 (1H, m, $C_{10}H_7$), 6.86 (2H, t, $^3J_{HH}$ = 5.8, $C_{10}H_7$), 6.66 (1H, s, $C_{10}H_7$), 6.40 (1H, dd, $^4J_{HH}$ = 1.6, $^3J_{HH}$ = 8.7, $C_{10}H_7$), 4.62 (1H, s, NH), 2.62 (3H, br s, CH_3).

[Mn{C(=NXylyl)(NHCH$_3$)}(CO)$_3$(bipy)] (3c). The procedure was analogous to the synthesis of **3a** using **2c**·ClO_4 (0.1 g, 0.18 mmol) and KOH (0.50 g, 8.91 mmol). Yield: 0.069 g (84%). Anal. (%) Calcd for $C_{23}H_{21}MnN_4O_3$: C 60.53, H 4.64, N 12.28. Found: C 60.30, H 4.55, N 12.19. IR (CH_2Cl_2): ν 2000 (vs), 1907 (s), 1891 (s) cm^{-1} (CO). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.05 (2H, d, $^3J_{HH}$ = 5.4, H_a bipy), 8.07 (2H, d, $^3J_{HH}$ = 8.1, H_d bipy), 7.87 (2H, t, $^3J_{HH}$ = 7.8, H_c bipy), 7.32 (2H, t, $^3J_{HH}$ = 6.4, H_b bipy), 6.64 (2H, d, $^3J_{HH}$ = 7.3, H_{meta} xylyl), 6.45 (1H, t, $^3J_{HH}$ = 7.3, H_{para} xylyl), 4.42 (1H, d, $^3J_{HH}$ = 4.0, NH), 2.61 (3H, d,$^3J_{HH}$ = 4.0, NCH_3), 1.28 (6H, s, CH_3 xylyl). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 226.7, 214.1 (br s, CO), 190.6 (s, $C_{carbene}$), 156.9 (s, C_1 bipy), 152.5 (s, C_2 bipy), 136.9 (s, C_3 bipy), 124.1 (s, C_4 bipy), 121.6 (s, C_5, bipy), 126.9, 119.0 (s, CH_{arom} xylyl), 32.9 (s, CH_3−NH), 18.0 (s, CH_3 xylyl).

[Mn{C(=NC$_7$H$_6$Cl)(NHCH$_3$)}(CO)$_3$(bipy)] (3d). The procedure was identical to the synthesis of **3a** using **2d**·ClO_4 (0.1 g, 0.17 mmol) and KOH (0.50 g, 8.91 mmol). Yield: 0.071 g (86%). Anal. (%) Calcd for $C_{22}H_{18}ClMnN_4O_3$: C 55.42, H 3.81, N 11.75. Found: C 55.80, H 3.65, N 11.69. IR (CH_2Cl_2): ν 2002 (vs), 1910 (s), 1893 (s) cm^{-1} (CO). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.06 (1H, d, $^3J_{HH}$ = 5.4, H_a bipy), 8.98 (1H, d, $^3J_{HH}$ = 5.4, H_a bipy), 8.05 (1H, d, $^3J_{HH}$ = 7.9, H_d bipy), 8.04 (1H, d, $^3J_{HH}$ = 7.9, H_d bipy), 7.88 (1H, t, $^3J_{HH}$ = 7.5, H_c bipy), 7.86 (1H, t, $^3J_{HH}$ = 7.5, H_c bipy), 7.37−7.30 (2H, m, H_b bipy), 6.78 (1H, d, $^3J_{HH}$ = 7.9, H_{meta} C_7H_6Cl), 6.71 (1H, d, $^3J_{HH}$ = 7.3, H_{meta} C_7H_6Cl), 6.44 (1H, t, $^3J_{HH}$ = 7.7, H_{para} C_7H_6Cl), 4.48 (1H, s, NH), 2.54 (3H, d,$^3J_{HH}$ = 4.4, NCH_3), 1.51 (3H, s, CH_3 C_7H_6Cl).^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 225.5, 213.4 (br s, CO), 192.5 (s, $C_{carbene}$), 156.1, 156.0 (s, C_1 bipy), 152.4, 152.3 (s, C_2 bipy), 149.1 (C_{ipso} C_7H_6Cl), 136.8, 136.7 (s, C_3 bipy), 129.9 (C_{quat} C_7H_6Cl), 127.1, 124.2, 118.5 (s, CH_{arom} C_6H_5Cl), 124.2, 124.1 (s, C_4 bipy), 121.3, 121.2 (s, C_5, bipy), 32.0 (s, CH_3−NH), 18.2 (s, CH_3 C_7H_6Cl).

[Mn{η^4-C(CO$_2$CH$_3$)CH=(CO$_2$CH$_3$)CHC(NHCH$_3$)=N(Ph)} (4a). A solution of **3a** (0.1 g, 0.23 mmol) in toluene (60 mL) was heated to 60 °C with the help of a water bath, and when the temperature was stable 2 equiv of methyl propiolate (0.042 mL, d = 0.945 g/mL, 0.47 mmol) was added, and the mixture stirred for 15 min. After that, the solvent was removed under vacuum, and the residues were chromatographed on an alumina column (activity IV) at room temperature. Elution with CH_2Cl_2/hexane (1:4) gave the ligand 2,2′-bipyridine; next a second elution with CH_2Cl_2/hexane (1:1) gave a yellow fraction. Removal of solvents from the latter and crystallization in a mixture of CH_2Cl_2/hexane at −20 °C provided a yellow microcrystalline solid. Yield: 0.036 g (35%). Anal. (%) Calcd for $C_{19}H_{17}MnN_2O_7$: C 51.83, H 3.89, N 6.36. Found: C 51.80, H 3.85, N 6.29. IR (CH_2Cl_2): ν 2004 (vs), 1926 (s), 1910 (sh) cm^{-1} (CO). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.42−7.28 (3H, m, H_{arom} Ph), 7.04 (2H, d, $^3J_{HH}$ = 7.3, H_{arom} Ph), 6.72 (1H, d, $^4J_{HH}$ = 1.0, H_F), 5.21 (1H, s, NH), 3.90 (3H, s,CO_2CH_3), 3.46 (3H, s, CO_2CH_3), 3.02 (1H, d, $^3J_{HH}$ = 1.0, H_E), 2.93 (3H, d, $^2J_{HH}$ = 2.5, NCH_3).

[Mn{η^4-C(CO$_2$CH$_3$)CH=C(CO$_2$CH$_3$)CHC(NHCH$_3$)=N(C$_{10}$H$_7$)}(CO)$_3$] (4b). The procedure was identical to that above-described, but using **3b** (0.1 g, 0.21 mmol) and 0.037 mL of methyl propiolate (d = 0.945 g/mL, 0.042 mmol) with a reaction time of 10 min. Yield: 0.057 g (55%). Anal. (%) Calcd for $C_{23}H_{19}MnN_2O_7$: C 56.34, H 3.91, N 5.71. Found: C 56.24, H 3.96, N 5.59. IR (CH_2Cl_2): ν 2004 (vs), 1926 (s), 1911 (sh) cm^{-1} (CO). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.88−7.83 (3H, m, H_{arom} $C_{10}H_7$), 7.58−7.52 (3H, m, H_{arom} $C_{10}H_7$), 7.09 (1H, dd, $^4J_{HH}$ = 2.0,$^3J_{HH}$ = 8.5, H_{arom} $C_{10}H_7$), 6.78 (1H, d, $^4J_{HH}$ = 1.0, H_F), 5.30 (1H, s, NH), 3.92 (3H, s,CO_2CH_3), 3.42 (3H, s, CO_2CH_3), 3.07 (1H, d, $^4J_{HH}$ = 1.0, H_E), 2.92 (3H, d, $^2J_{HH}$ = 4.8, NCH_3).

[Mn{η^4-C(CO$_2$CH$_3$)CH=C(CO$_2$CH$_3$)CHC(NHCH$_3$)=N(xylyl)}(CO$_3$)] (4c). The procedure was analogous to the synthesis of **4a**, using **3c** (0.1 g, 0.22 mmol) and 0.039 mL of methyl propiolate (d = 0.945 g/mL, 0.44 mmol). Yield: 0.062 g (60%). Anal. (%) Calcd for $C_{21}H_{21}MnN_2O_7$: C 53.86, H 4.52, N 5.98. Found: C 53.82, H 4.40, N 5.83. IR (CH_2Cl_2): ν 2002 (vs), 1923 (s), 1908 (sh) cm^{-1} (CO).^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.15−7.13 (2H, m, H_{arom} xylyl), 7.02−6.99 (1H, m, H_{arom} xylyl), 6.83 (1H, d, $^4J_{HH}$ = 1.2, H_F), 4.75 (1H, s, NH), 3.90 (3H, s, CO_2CH_3), 3.45 (3H, s, CO_2CH_3), 3.00 (1H, d, $^4J_{HH}$ = 1.2, H_E), 2.93 (3H, br s, NCH_3), 2.43 (3H, s, CH_3 xylyl), 1.97 (3H, s, CH_3 xylyl). ^{13}C{^{1}H} NMR (300 MHz, CD_2Cl_2): δ 221.4 (br s, Mn−CO), 171.8 (s, C_5), 169.9, 168.5 (s, CO), 140.6 (s, C_{ipso} xylyl), 134.9, 133.9 (s, C_{orto} xylyl), 130.0, 129.6, 129.4 (s, C_{arom} xylyl), 90.1 (s, C_3), 87.2 (s, C_1), 78.1 (s, C_2), 52.7, 50.9 (s, OCH_3), 38.8 (s, NCH_3), 31,0 (s, C_4), 18.9, 18.8 (s, CH_3 xylyl).

[Mn{η^4-C(CO$_2$CH$_3$)CH=C(CO$_2$CH$_3$)CHC(NHCH$_3$)=N(C$_7$H$_6$Cl)}(CO)$_3$] (4d). The procedure was completely analogous to the synthesis of **4a**, using **3d** (0.1 g, 0.21 mmol) and 0.037 mL of methyl propiolate (d = 0.945 g/mL, 0.42 mmol). Yield: 0.050 g (49%). Crystals of **4d** suitable for X-ray diffraction study were obtained by slow diffusion of hexane into CH_2Cl_2 solution of the compound. Anal. (%) Calcd for $C_{20}H_{18}ClMnN_2O_7$: C 49.15, H 3.71, N 5.73. Found: C 49.32, H 3.67, N 5.70. IR (CH_2Cl_2): ν 2003 (vs), 1924 (s), 1909 (sh) cm^{-1} (CO).^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.24−7.20 (3H, m, H_{arom} C_7H_6Cl), 6.86 (1H, d, $^4J_{HH}$ = 1.5, H_F), 4.72 (1H, s, NH), 3.90 (3H, s, CO_2CH_3), 3.48 (3H, s, CO_2CH_3), 2.99 (1H, d, $^4J_{HH}$ = 1.3, H_E), 2.96 (3H, d, $^3J_{HH}$ = 5.1, NCH_3), 2.50 (3H, s, CH_3 C_7H_6Cl).

[Mn{η^4-C(Ph)CH=C(Ph)CHC(NHCH$_3$)=N(Ph)}(CO$_3$)] (5a). To a solution of **3a** (0.05 g, 0.12 mmol) in toluene (30 mL), 4 equiv of phenyl acetylene (0.051 mL, d = 0.93 g/mL, 0.46 mmol) was added, and the mixture was heated to 90 °C with the help of an oil bath and stirred for 20 min. The solvent was then removed under vacuum, and the residues were chromatographed on an alumina column (activity IV) at room temperature. Elution with CH_2Cl_2/hexane (1:3) gave the ligand 2,2′-bipyridine; next a second elution with CH_2Cl_2/hexane (1:1) gave a yellow fraction. Removal of solvents from the latter and crystallization in a mixture of CH_2Cl_2/hexane at −20 °C provided a yellow microcrystalline solid. Yield: 0.022 g (43%). Anal. (%) Calcd for $C_{27}H_{21}MnN_2O_3$: C 68.07, H 4.44, N 5.88. Found: C 68.12, H 4.57, N 5.77. IR (CH_2Cl_2): ν 1982 (vs), 1896 (s), 1886 (sh) cm^{-1} (CO). ^{1}H NMR (400 MHz, CD_2Cl_2):

7.79 (2H, d, $^3J_{HH}$ = 7.0, H_{arom} Ph), 7.47−7.39 (5H, m, H_{arom} Ph), 7.24−7.12 (5H, m, H_{arom} Ph), 7.02−6.96 (3H, m, H_{arom} Ph), 6.44 (1H, s, H_F), 5.18 (1H, s, NH), 3.24 (1H, s, H_E), 3.03 (3H, d, $^3J_{HH}$ = 3.0, NCH_3). $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2): 225.6 (br, Mn-CO), 168.8 (s, C_5), 142.9, 141.5, 139.9 (s, C_{ipso} Ph), 129.5, 128.6, 127.8, 127.0, 126.9, 125.5, 124.9, 124.6 (s, C_{arom} Ph), 102.6 (s, C_3), 83.3 (s, C_1), 79.1 (s, C_2), 44.0 (s, NCH_3), 30.3 (s, C_2).

[Mn{η^4-C(Ph)CH=C(Ph)CHC(NHCH$_3$)=N(C$_{10}$H$_7$)}(CO$_3$)] (5b). The procedure was completely analogous to the synthesis of **5a**, using **3b** (0.05 g, 0.10 mmol) and 0.046 mL of phenyl acetylene (d = 0.93 g/mL, 0.42 mmol). The chromatography was similar to that described above for the compound **5a**. Yield: 0.031 g (56%). Anal. (%) Calcd for $C_{31}H_{23}MnN_2O_3$: C 70.72, H 4.40, N 5.32. Found: C 70.46, H 4.32, N 5.20. IR (CH_2Cl_2): ν 1982 (vs), 1897 (s), 1885 (sh) cm^{-1} (CO). ^1H NMR (300 MHz, CD_2Cl_2): 7.84−7.64 (6H, m, H_{arom} Ph and Naftil), 7.47−7.28 (8H, m, H_{arom} Ph and Naftil), 7.10−7.01 (3H, m, H_{arom} Ph and Naftil), 6.48 (1H, s, H_F), 5.28 (1H, s, NH), 3.22 (1H, s, H_E), 3.00 (3H, d, $^3J_{HH}$ = 3.1, NCH_3).

[Mn{η^4-C(Ph)CH=C(Ph)CHC(NHCH$_3$)=N(Xylyl)}(CO)$_3$] (5c). The procedure was analogous to the synthesis of **5a**, using **3c** (0.05 g, 0.11 mmol) and 0.048 mL of phenyl acetylene (d = 0.93 g/mL, 0.44 mmol). The chromatography was similar to that described for the compound **5a**. Yield: 0.031 g (56%). Crystals of **5c** suitable for X-ray diffraction study were obtained by slow diffusion of hexane into CH_2Cl_2 solution of the compound. Anal. (%) Calcd for $C_{29}H_{25}MnN_2O_3$: C 69.05, H 5.00, N 5.55. Found: C 69.35, H 4.92, N 5.40. IR (CH_2Cl_2): ν 1979 (vs), 1890 (s), 1881 (sh) cm^{-1} (CO). ^1H NMR (400 MHz, CD_2Cl_2): 7.83 (2H, d, $^3J_{HH}$ = 6.1, H_{arom} Ph), 7.48−7.39 (5H, m, H_{arom} Ph), 7.12−6.89 (6H, m, H_{arom} Ph and xylyl), 6.42 (1H, s, H_F), 4.55 (1H, s, NH), 3.06 (4H, br s, NCH_3 and CH_E), 2.49 (3H, s, CH_3 xylyl), 2.08 (3H, s, CH_3 xylyl). $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2): 225.0 (br s, Mn-CO), 170.7 (s, C_5), 140.5, 139.7, 138.4 (s, C_{ipso} Ph and xylyl), 134.8, 134.4 (s, C_{orto} xylyl), 129.3, 129.1, 128.9, 128.8, 128.5, 127.7, 127.4, 127.2, 126.2 (s, C_{arom} Ph and xylyl), 103.8 (s, C_3), 88.3 (s, C_1), 80.6 (s, C_2), 41.0 (s, NCH_3), 30.4 (s, C_4); 18.7, 18.3 (s, CH_3 xylyl).

Single-Crystal X-ray Structure Determination of Compounds. Suitable yellow single crystals of **2d**, **4d**, and **5c** for the X-ray diffraction study were selected. The data collection was carried out at 110 K. The crystals were mounted on a Smart-CCD-1000 BRUKER single-crystal diffractometer equipped with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Multiscan[19] absorption correction procedures were applied to the data. The structures were solved, using the WINGX package,[20] by direct methods (DIRDIF-99)[21] and refined by using full-matrix least-squared against F^2 (SHELXL-97).[22] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms except for the hydrogen atoms on C2 and C4 in compound **4d**. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme. The final residual electron density map showed no remarkable features.

Acknowledgment. This work was supported by the Spanish Ministerio de Educación y Ciencia (PGE and FEDER funding, Project CTQ2006-10035) and the Principado de Asturias (Project IB05-110). B.F.P. thanks the MEC for a FPU grant.

Supporting Information Available: Crystallographic data in CIF format of complexes **2d**, **4d**, and **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800888R

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