Synthesis of N-Heterocyclic Carbene Complexes of Manganese(I) by Coupling Isocyanide Ligands with Propargylamines and Propargylic Alcohols§

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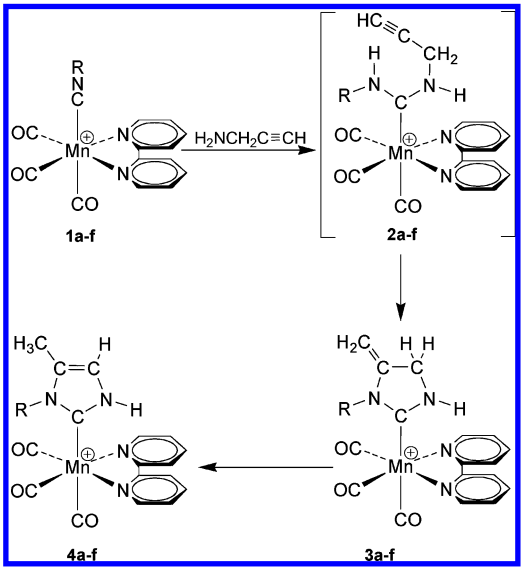
A variety of N-heterocyclic carbene (NHC) complexes of general formula *fac*-[Mn(NHC)(CO)$_3$(bipy)]$^+$ have been prepared by reaction of the manganese(I) isocyanide complexes *fac*-[Mn(CNR)(CO)$_3$(bipy)]$^+$ with propargylamines and propargylic alcohols and characterized by spectroscopic and X-ray diffraction methods.

Introduction

No doubt the chemistry of N-heterocyclic carbenes (NHCs) has been one of the most active areas of research in organometallic chemistry in recent years.[1] Isolation by Arduengo et al. of the first stable, crystalline NHC was a milestone in this chemistry,[2] which was followed soon afterward by the recognition of the great potential of NHC complexes in transition metal homogeneous catalysis.[3] The synthesis of NHC complexes is generally accomplished by reaction of the corresponding imidazolium salts with the appropriate metallic fragment, with either a basic ligand attached to the metal or an external base acting as the deprotonating agent.[1b] Alternatively, direct reaction of free NHC with the metal complex precursor can be employed,[1b] as well as transmetalation reaction from NHC complexes of silver(I).[4] A synthetic route to NHC complexes involving four-component condensation reactions with cyano transition metal complexes has also been reported.[5]

Reaction of coordinated isocyanides with amines is a well-known method for the synthesis of diaminocarbene complexes.[6] The extension of this procedure to haloamines leads to the preparation of cyclic diaminocarbenes.[7] Furthermore intramolecular cyclization of amino-functionalized isocyanides leading to benzannulated NHC complexes has also been described in the literature.[8] In relation with this, we have recently communicated a new experimental approach to the synthesis of NHC complexes based on the metal-assisted coupling of isocyanides and propargylamine.[9] We report now in this paper a detailed account of the synthesis of manganese(I) complexes bearing NHC ligands of imidazoline-2-ylidene and imidazolidine-2-ylidene types and their analogous N,O-heterocyclic carbenes, by coupling different arylic and alkylic isocyanide ligands with a variety of propargylamines and propargylic alcohols.

Scheme 1. Proposed Mechanism for the Formation of NHC Complexes



Results and Discussion

N,N-Heterocyclic Carbene Complexes. Reaction of the cationic isocyanide complexes *fac*-[Mn(CNR)(CO)$_3$(bipy)]$^+$ (**1a**,

§ Dedicated to the memory of Professor Lorenzo Pueyo.

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Table 1. Selected IR Spectral and ^{1}H and ^{13}C NMR Spectroscopic Data

compd	IR (CH_2Cl_2, cm^{-1})[a] ν(CO)	^{1}H NMR,[b] δ	$^{13}C\{^{1}H\}$ NMR,[b] δ ($C_{carbene}$)
1a	2050vs, 1990s, 1957s 2175m ν(CN)		
1b	2052vs, 1996s, 1962s 2172m ν(CN)		
1c	2050vs, 1990s, 1957s 2176m ν(CN)		
1d	2050vs, 1989s, 1957s 2171m ν(CN)	1.97 (6H, s, CH_3)	
1e	2051vs, 1993s, 1959s 2171m ν(CN)	2.14 (3H, s, CH_3)	
1f	2050vs, 1983s, 1951s 2212m ν(CN)	4.78 (2H, s, CH_2)	
3b	2034vs, 1955s, 1928s	4.37 (2H, s, NCH_2) 4.23 (1H, d, $^{3}J_{HH} = 3$, $=CH_2$) 3.77 (1H, d, $^{3}J_{HH} = 3$, $=CH_2$)	222.4
3f	2032vs, 1951s, 1923s	4.91 (2H, d, $^{4}J_{HH} = 6$, CH_2 Bz) 4.40 (1H, s, $=CH_2$) 4.17 (1H, s, $=CH_2$) 3.83 (2H, s, NCH_2)	
4a	2028vs, 1944s, 1925s	9.76 (1H, s, NH) 6.94 (1H, s, $=$CH) 1.74 (3H, s, CH_3)	184.7
4b	2030vs, 1949s, 1926s	9.65 (1H, s, NH) 7.03 (1H, s, $=$CH) 1.85 (3H, s, CH_3)	189.0
4c	2029vs, 1945s, 1923s	10.02 (1H, s, NH) 7.02 (1H, s, $=$CH) 1.79 (3H, s, CH_3)	184.7
4d	2029vs, 1945s, 1925s	9.60 (1H, s, NH) 7.09 (1H, s, $=$CH) 1.76 (6H, s, CH_3 xylyl) 1.72 (3H, s, CH_3)	
4e	2029vs, 1946s, 1925s	9.54 (1H, s, NH) 7.08 (1H, d, $^{4}J_{HH} = 1$, $=$CH) 2.08 (3H, s, CH_3 Ph) 1.77 (3H, s, CH_3)	
4f	2031vs, 1949s, 1921s	9.70 (1H, s, NH) 6.78 (1H, s, $=$CH) 4.89 (2H, s, CH_2 Bz) 1.88 (2H, s, CH_3)	
5b	2035vs, 1957s, 1928s	4.61 (2H, s, CH_2) 4.22 (1H, s, $=CH_2$) 3.66 (3H, s, NCH_3) 3.41 (1H, s, $=CH_2$)	217.7
6a	2025vs, 1939s, 1917s	6.35 (1H, s, $=$CH) 4.02 (3H, s, NCH_3) 1.54 (3H, s, CH_3)	181.9
8a	2040vs, 1964s, 1934s	5.14 (2H, t, $^{4}J_{HH} = 3$, OCH_2) 4.51 (1H, q, $^{2}J_{HH} = {}^{4}J_{HH} = 3$, $=CH_2$) 3.99 (1H, q, $^{2}J_{HH} = {}^{4}J_{HH} = 3$, $=CH_2$)	241.0
8b	2043vs, 1969s, 1936s	5.05 (2H, t, $^{4}J_{HH} = 3$, OCH_2) 4.51 (1H, q, $^{2}J_{HH} = {}^{4}J_{HH} = 3$, $=CH_2$) 4.07 (1H, q, $^{2}J_{HH} = {}^{4}J_{HH} = 3$, $=CH_2$)	245.9
8c	2040vs, 1964s, 1934s	5.18 (2H, t, $^{4}J_{HH} = 3$, OCH_2) 4.55 (1H, q, $^{2}J_{HH} = {}^{4}J_{HH} = 3$, $=CH_2$) 4.06 (1H, q, $^{2}J_{HH} = {}^{4}J_{HH} = 3$, $=CH_2$)	241.2
9a	2038vs, 1960s, 1933s	1.77 (3H, s, CH_3)	215.9
9b	2041vs, 1965s, 1935s	7.65 (1H, s, $=$CH) 1.84 (3H, s, CH_3)	219.0
10b	2043vs, 1969s, 1937s	4.48−4.46 (1H, m, $=CH_2$) 4.15−4.13 (1H, m, $=CH_2$) 1.21 (3H, d, $^{3}J_{HH} = 7$, CH_3)	243.2
11a	2038vs, 1960s, 1933s	2.08 (2H, s, CH_3) 1.64 (3H, s, CH_3)	213.3
11b	2043vs, 1969s, 1937s	1.78 (3H, s, CH_3), 1.73 (3H, s, CH_3)	
12a	2039vs, 1962s, 1934s	4.96 (2H, quint, $^{4}J_{HH} = {}^{5}J_{HH} = 3$, OCH_2) 4.80 (1H, qt, $^{3}J_{HH} = 8$, $^{4}J_{HH} = 3$, CH) 0.77 (3H, dt, $^{3}J_{HH} = 8$, $^{5}J_{HH} = 3$, CH_3)	241.3
12b	2042vs, 1968s, 1935s	4.99 (2H, quint, $^{4}J_{HH} = {}^{5}J_{HH} = 2$, OCH_2) 4.84 (1H, q, $^{3}J_{HH} = 7$, CH) 0.97 (3H, d, $^{3}J_{HH} = 7$, CH_3)	246.4

[a] Abbreviations: v = very, s = strong, m = medium. [b] NMR spectra recorded in CD_2Cl_2 at rt.

R = phenyl; **1b**, R = 2,6-difluorophenyl; **1c**, R = 2-naphthyl; **1d**, R = xylyl; **1e**, R = 2-chloro-6-methylphenyl; **1f**, R = benzyl)[10] with an excess of propargylamine in THF results in the formation of the carbene complexes **4a**−**f** (Scheme 1). The

Table 2. Crystallographic Data for 3a, 4b, and 8a

	3b	4b	8a
formula	$C_{23}H_{16}ClF_2MnN_4O_7$	$C_{23}H_{16}ClF_2MnN_4O_7$	$C_{23}H_{17}ClMnN_3O_8$
fw	588.79	588.79	553.79
color/habit	yellow/prism	yellow/prism	yellow/prism
cryst dimensions, mm^3	0.58 × 0.30 × 0.30	0.43 × 0.30 × 0.30	0.58 × 0.42 × 0.17
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	*Pcab*
a, Å	9.5104(9)	10.9964(13)	13.223(4)
b, Å	19.863(4)	17.422(3)	14.573(3)
c, Å	13.515(3)	13.6750(15)	24.6375(16)
β, deg	107.984(9)	104.356(11)	90
V, $Å^3$	2428.3(7)	2538.0(6)	4747.6(18)
Z	4	4	8
T, K	200	200	298
D_{calcd}, g cm^{-3}	1.611	1.541	1.550
μ, mm^{-1}	0.722	0.691	0.723
F(000)	1192	1192	2256
θ range, deg	3.74−27.51	5.04−27.50	3.59−27.49
no. of rflns collected	49 238	49 195	44 718
no. of indep rflns/R_{int}	5581/0.0650	5786/0.0508	5432/0.0904
no. of obsd rflns ($I>2\sigma(I)$)	3923	4306	3286
no. of data/restraints/params	5581/0/351	5786/0/347	5432/0/333
R_1/wR_2 ($I>2\sigma(I)$)[a]	0.0447/0.0895	0.0384/0.0893	0.0462/0.0975
R_1/wR_2 (all data)[a]	0.0804/0.1014	0.0635/0.0977	0.1021/0.1242
GOF (on F^2)[a]	1.028	1.037	1.023
largest diff peak and hole, e $Å^{-3}$	+0.473/−0.488	+0.592/−0.468	+0.361/−0.397

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; GOF $= \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.

reaction was monitored by IR spectroscopy, which shows the disappearance of the νCN band of the coordinated isocyanide ligands (2171−2212 cm^{-1}) once the reaction is finished. In parallel, the νCO bands of the carbonyl ligands undergo an appreciable shift to low frequencies (see Table 1). This indicates that the NHC ligands are better electron donors than their parent isocyanide ligands. Compounds of type **4** were fully characterized by spectroscopic and analytical methods (see Table 1 and Experimental Section); additionally in the case of **4b** an X-ray diffraction study was undertaken (Figure 1), and the corresponding structural features will be discussed in detail below. The formation of the new carbene ligands is evidenced by the presence of a low-field signal around 185 ppm in the $^{13}C\{^1H\}$ NMR spectra, corresponding to the carbene carbon atom. In the ^1H NMR spectra the new methyl group of the heterocycle appears as a singlet at about 1.8 ppm, and the proton of the N−H group displays a typical high-frequency singlet signal (9.54−10.02 ppm). Also of note is the presence of the vinyl proton resonance in the range 6.78−7.09 ppm.

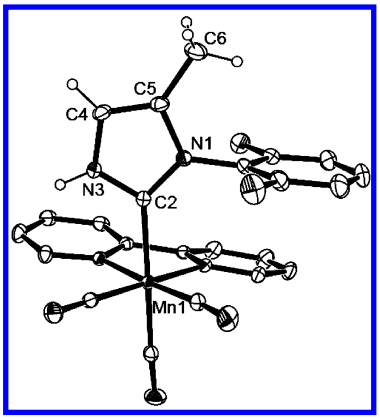

Figure 1. Molecular structure of **4b**, shown with 30% thermal ellipsoids. Hydrogen atoms of the bipy ligand and 2,6-difluorophenyl substituent are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mn1−C2 = 2.078(2), N1−C2 = 1.377(3), C2−N3 = 1.354(3), N3−C4 = 1.398(3), C4−C5 = 1.354(3), C5−N1 = 1.417(3), C5−C6 = 1.501 (3); Mn1−C2−N1 = 133.3(1), Mn1−C2−N3 = 124.3(2), N1−C2−N3 = 102.3(2), C2−N3−C4 = 113.3(2), N3−C4−C5 = 106.7(2), C4−C5−N1 = 105.2(2), C5−N1−C2 = 112.5(2).

The proposed mechanism for the formation of the NHC complexes **4** is shown in Scheme 1. As nucleophilic addition of amines to isocyanides is a typical reaction of isocyanide complexes,[6,7] it seems obvious that the first step of the reaction involves the nucleophilic attack of propargylamine to this ligand to afford the acyclic diaminocarbene complexes of type **2**. These species would then undergo an intramolecular hydroamination to give the cyclic carbenes **3**, which in a final step are transformed to complexes **4** by a 1,3 proton shift from the endocyclic methylene group to the exocyclic one. Supporting this mechanism, the intermediate derivatives **3** could be detected in the course of the reaction and, in the case of **3b** and **3f**, were conveniently isolated as pure species by controlling the reaction time and the amount of propargylamine added. The reaction time for the formation of derivatives **3** varies from 5 min (compound **3b**) to 2 days (compound **3f**), showing that nucleophilic attack of propargylamine to the isocyanide is favored for aryl isocyanides containing electron-withdrawing substituents. The transformation of complexes of type **3** into **4** is base-promoted; in fact **3b**,**f** are stable in solution for days and are not transformed into **4b**,**f** unless a base is added (propargylamine or triethylamine).

The IR spectra of **3b** and **3f** show νCO bands at slightly higher frequencies than **4b** and **4f**, indicating that the imidazolidine-2-ylidene carbenes in **3** are slightly poorer electron donors than the imidazoline-2-ylidene carbenes in **4**. On the other hand, the carbene-carbon signal in the $^{13}C\{^1H\}$ NMR spectrum of **3b** is shifted 33 ppm downfield with respect to **4b**, which is a typical trend observed in the literature when comparing saturated versus unsaturated NHC ligands.[11] It is also worth noting the presence of signals for both the methylene and vinylidene CH_2 protons in the ^1H NMR spectra of **3b** and **3f** in the expected range (see Table 1). Furthermore, in the case

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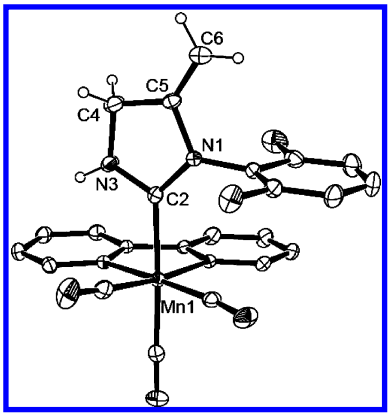
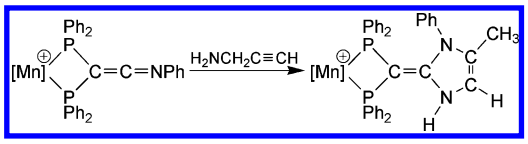


Figure 2. Molecular structure of **3b**, shown with 30% thermal ellipsoids. Hydrogen atoms of the bipy ligand and 2,6-difluorophenyl substituent are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mn1−C2 = 2.068(3), N1−C2 = 1.375(3), C2−N3 = 1.338(3), N3−C4 = 1.458(3), C4−C5 = 1.481(4), C5−N1 = 1.437(3), C5−C6 = 1.350(4); Mn1−C2−N1 = 132.2(2), Mn1−C2−N3 = 122.6(2), N1−C2−N3 = 105.1(2), C2−N3−C4 = 114.9(2), N3−C4−C5 = 102.2(2), C4−C5−N1 = 104.6(2), C5−N1−C2 = 113.1(2).

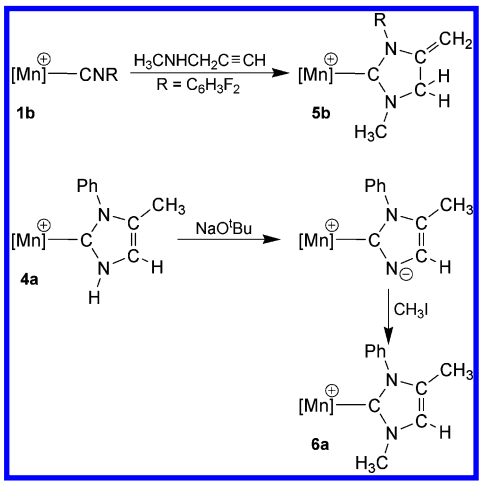
of **3b** an X-ray diffraction study was carried out (Figure 2), allowing a comparison of the structural parameters of this complex with those of the corresponding unsaturated heterocyclic carbene **4b** (Figure 1). For **3b** the distances C2−N1 (1.375(3) Å) and C2−N3 (1.338(3) Å) are intermediate between single and double bond as a consequence of the implication of the lone pairs of both nitrogen atoms in those bonds. The slightly longer value of the C2−N1 bond length with respect to C2−N3 can be attributed to the conjugation of the N1 lone pair with the exocyclic double bond, which deviates some electron density toward that bond; in fact the N1−C5 bond length is slightly shorter than a single bond (1.437(3) Å). For complex **4b** the different bond lengths within the heterocycle are, in variable degree, intermediate between single and double bond, reflecting the existence of electronic delocalization in the heterocycle. The N1−C2−N3 bond angle for **3b** (105.1(2)°) is opened somewhat relative to the unsaturated analogue **4b** (102.3(2)°). Curiously both angles are in the range of values usually found in free carbenes of imidazolidine2-ylidene and imidazoline-2-ylidene types, respectively,[11,12] being slightly smaller than those normally encountered in coordinated carbenes of both types.[1b,12,13] Finally, the C2−Mn bond distances for **3b** and **4b** are 2.068(3) and 2.078(2) Å, respectively.

The cyclization process of **2** involving a terminal alkyne proposed in Scheme 1 is noteworthy, as the hydroamination reactions of unactivated akynes described in the literature take place only in a catalytic manner.[14] In those reactions, coordination of the alkyne to metals, such as Rh(I), Pd(II), or Cu(I), promotes the nucleophilic attack of the amine, allowing the catalytic hydroamination to occur.[15] In our case, the Mn(I) ion has a closed octahedral coordination sphere, avoiding the direct

Scheme 2. Generation of Imidazoline-Functionalized Diphosphine Ligand; $[Mn]^+ = [Mn(CO)_4]^+$



Scheme 3. Preparation of N-Methylated NHC Complexes; $[Mn]^+ = fac\text{-}[Mn(CO)_3(bipy)]^+$



intermediacy of the metallic center in the process. Although the acyclic derivatives **2** have not been detected in the reaction course, it could also be tentatively proposed a tautomerization reaction in these species from the terminal alkyne to the corresponding allene previous to the cyclization process, as apparently the hydroamination reaction could take place more easily in the latter, according to related processes described in the literature.[16]

It is also worth remarking that we had already observed a similar cyclization process of propargylamine with coordinated diphosphinoketenimine ligands to afford imidazoline-functionalized diphosphines (Scheme 2),[17] so that in a certain sense the isocyanide complexes **1** behave as ketenimine functionalities.

With the aim of preparing unsymmetrically substituted NHC ligands we extended the reaction above to *N*-methylpropargylamine. This proved to be much less reactive than propargylamine; in fact in these reactions only the imidazolidine-2-ylidene complex **5b** could be obtained (see Scheme 3) and with much longer reaction time (1 day) than for **3b** (5 min). Tautomerization of **5b** to the corresponding unsaturated carbene (imidazoline-2-ylidene) complex was not possible in this case even after adding a great excess of triethylamine as an external base.

The formation of an N-methylated NHC ligand was also observed by deprotonation of complex **4a** with KO*t*Bu and further treatment of the neutral intermediate with MeI (Scheme 3). In this way complex **6a** is obtained and fully characterized by spectroscopic methods (Table 1), the signal at 4.02 ppm in the ^{1}H NMR spectrum showing clearly the presence of the new methyl group added to the molecule.

N,O-Heterocyclic Carbene Complexes. In a similar process to that described above complexes **1** reacted with propargylic alcohol, generating N,O-heterocyclic carbene ligands. In this

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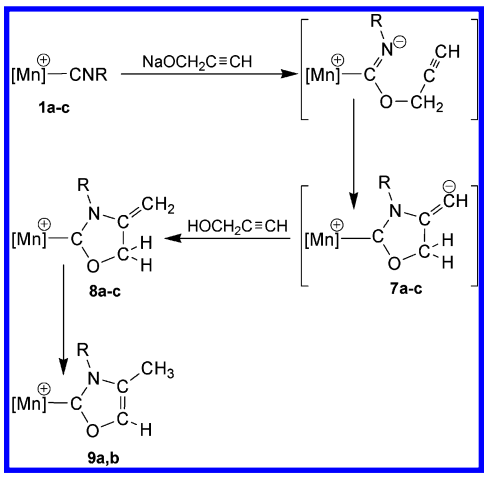
Scheme 4. Postulated Mechanism for the Formation of N,O-Heterocyclic Carbene Complexes; $[Mn]^+$ = *fac*-$[Mn(CO)_3(bipy)]^+$



case however a mixture of $HOCH_2C{\equiv}CH$ and $NaOCH_2C{\equiv}CH$ must be employed, as the propargylic alcohol itself is not nucleophilic enough for the reaction to take place. By controlling the reaction time complexes of type **8** (Scheme 4), containing an exocyclic carbon−carbon double bond (oxazolidine-2-ylidene carbenes), were isolated, which were transformed into the corresponding unsaturated cyclic carbenes **9** (oxazoline-2-ylidene carbenes) with longer reaction times. The mechanism proposed in Scheme 4 for the formation of these complexes is comparable to that described before for the formation of N,N-heterocyclic carbenes (Scheme 1). The IR spectra of **8** and **9** show νCO bands at higher frequencies than those of **3** and **4**, so that it can be deduced that the N,O-heterocyclic carbenes feature weaker basic character than the N,N-heterocyclic carbenes, which is probably due to the higher electronegativity of oxygen with respect to nitrogen. Moreover, the bands of compounds **9** in these spectra appear at slightly lower frequencies than those of **8**, showing once again the stronger basic character of the unsaturated carbene ligands with respect to the saturated ones. The ^{1}H NMR spectra of these complexes (Table 1) display signals of the singlet resonance of the newly formed methyl group (**9a**,**b**) and the two quartet signals for the methylene and vinylidene CH_2 protons (**8a**−**c**). Finally, the ^{13}C-{^{1}H} NMR spectra show the typical low-field signal for the carbene carbon atom.

The structure of complex **8a** in the solid state was elucidated by an X-ray diffraction study (Figure 3). Among the different structural parameters it is worth pointing out the C2−N1 (1.335(4) Å) and C2−O3 (1.340(3) Å) bond lengths, which indicate some multiple-bond character, showing once more the implication of the heteroatom lone pair in those bonds. On the other hand, the Mn−C1 distance (2.042(3) Å) in this oxazolidine-2-ylidene carbene complex is shorter than the corresponding distance in the imidazolidine-2-ylidene derivative **3b** (2.068(3) Å), leading to the apparent contradiction that a minor donor character of the carbene ligand causes a stronger interaction of the carbene with the metallic center. No doubt much more data are necessary to ascertain this statement, but it seems clear that π-back-donation from the metal to the carbene ligand must not be neglected in these complexes, as it has been pointed out in recent papers.[18]

It should be noted that, contrary to imidazol-2-ylidene, free oxazol-2-ylidene carbenes are not isolable, being of special interest the development of new reaction pathways for the synthesis of their transition metal complexes,[19] as that described herein. Related benzoxazol-2-ylidene carbene complexes can be prepared by intramolecular cyclization of 2-hydroxyphenyl isocyanide coordinated to transition metals.[20] However this implies a multiple-step process, as free 2-hydroxyphenyl isocyanide is not stable and the hydroxy group must be protected before coordination.

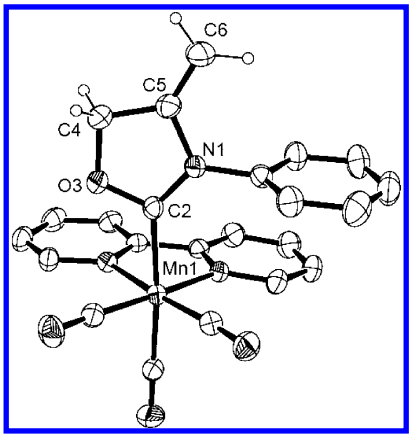


Figure 3. Molecular structure of **8a**, shown with 30% thermal ellipsoids. Hydrogen atoms of the bipy ligand and phenyl substituent are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mn1−C2 = 2.042(3), N1−C2 = 1.335(4), C2−O3 = 1.340(3), O3−C4 = 1.464(4), C4−C5 = 1.496(4), C5−N1 = 1.438(4), C5−C6 = 1.319(5); Mn1−C2−N1 = 135.0(2), Mn1−C2−O3 = 116.5(2), N1−C2−O3 = 108.5(2), C2−O3−C4 = 111.5(2), O3−C4−C5 = 103.5(2), C4−C5−N1 = 103.3(2), C5−N1−C2 = 113.0(2).

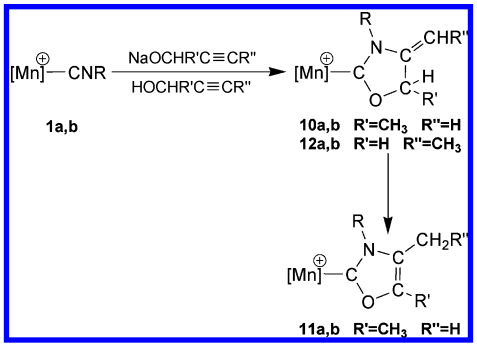
The use of substituted propargylic alcohol enlarges the synthetic possibilities of the methodology above. Thus reaction of complexes **1** with 3-butyn-2-ol allows the synthesis of N,O-heterocyclic carbene complexes fully substituted on the different atoms of the heterocycle, as is exemplified with the preparation of complexes **10b**, **11a**, and **11b** (Scheme 5). The ^{1}H NMR spectra of **11a**,**b** show the expected signals for the two methyl groups present as substituents in the new NHC ligands, whereas that of the isolable intermediate **10b** features as most relevant signals those corresponding to the methyl and vinylidene groups (Table 1). Analogously, the use of a propargylic alcohol containing an internal alkyne, such as 2-butyn-1-ol, leads to the formation of N,O-heterocyclic carbenes with a longer carbon chain as substituent in the heterocycle (Scheme 5). In this last case only the complexes containing oxazolidine-2-ylidene ligands (**12a** and **12b**) were obtained, being not possible to achieve the transformation of these complexes into the corresponding saturated tautomers.

(18) (a) Díez-González, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874. (b) Tafipolsky, M.; Scherer, W.; Öfele, K.; Artus, G.; Perdersen, B.; Herrmann, W. A.; McGrady, G. S. *J. Am. Chem. Soc.* **2002**, *124*, 5865. (c) Hu, X.; Tang, Y.; Gantzel, P.; Meyer, K. *Organometallics* **2003**, *22*, 612. (d) Boehme, C.; Frenking, G. *Organometallics* **1998**, *17*, 5801. (e) Gérard, H.; Clot, E.; Eisenstein, O. *New J. Chem.* **1999**, *23*, 495. (f) Huang, J.; Schanz, H.-J; Stevens, E. D.; Nolan, S. P. *Inorg. Chem.* **2000**, *39*, 1042.

(19) Reactions of *gem*-dicyano and cyanocarbethoxy epoxides with cyanometal acids yield oxazol-2-ylidene complexes: (a) See ref 5a, p 1270. (b) Kunz, R.; Grel, P. L.; Fehlhammer, W. P. *J. Chem. Soc., Dalton Trans.* **1996**, 3231.

(20) (a) Hahn, F. E.; Tamm M. *J. Chem. Soc., Chem. Commun.* **1993**, 842. (b) Hahn, F. E.; Tamm, M.; Lügger, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1356. (c) Hahn, F. E.; Tamm, M. *J. Organomet. Chem.* **1993**, *456*, C11. (d) Tamm, M.; Hahn, F. E. *Coord. Chem. Rev.* **1999**, *182*, 175−209. (e) Barluenga, J.; Aznar, F.; Weyershausen, B.; García-Granda, S.; Martín, E. *Chem. Commun.* **1996**, 2455.

Scheme 5. Preparation of N,O-Heterocyclic Carbene Complexes by Using Substituted Propargylic Alcohols; $[Mn]^+$ = *fac*-$[Mn(CO)_3(bipy)]^+$; a, R = Ph; b, R = 2,6-difluorophenyl



Conclusion

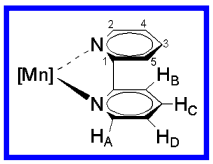
In this paper we have described a new method for the generation of N-heterocyclic carbenes, consisting of the coupling of coordinated isocyanide ligands with propargylamines and propargylic alcohols. The reaction proceeds through initial nucleophilic attack of the amine or the alkoxide to the isocyanide, followed by an intramolecular cyclization process that implies a formal hydroamination reaction of the alkyne residue. This approach allows the synthesis of Mn(I) complexes containing a variety of carbene ligands of imidazoline-2-ylidene and imidazolidine-2-ylidene types, as well as their analogous N,O-heterocyclic carbenes. Fine control of the nature of the carbene can be achieved by choosing the isocyanide ligand and the substituents on the propargylamine and propargylic alcohol frameworks.

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. Compound *fac*-$[Mn(CO)_3(CNPh)(bipy)]ClO_4$ (**1a**·ClO_4) was prepared according to a reported protocol.[10] NMR spectra were recorded on Bruker 300 and 400 MHz spectrometers. NMR multiplicities are abbreviated as follows: d = doublet, t = triplet, q = quartet, quint = quintet, qt = quartet of triplets, m = multiplet. Coupling constants *J* are given in Hz. Propargylamines and propargylalcohols were purchased from Aldrich and used without 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 the 2,2′-bipyridine ligand is as follows:



Synthesis of 1b−f·ClO_4. These compounds were obtained following a similar procedure to that used for the synthesis of **1a** with slight modifications. A mixture of $[Mn(CO)_3(bipy)Br]$ (0.10 g, 0.27 mmol) and $AgClO_4$ (0.066 g, 0.32 mmol) in acetone (10 mL) was stirred for 1 h in the dark and then filtered off to remove the AgBr formed. Then 1.2 equiv of the corresponding isocyanide was added to the filtrate, and the mixture stirred for 3 h. After removal of the solvent, the residue was dissolved in 3 mL of CH_2Cl_2. Addition of hexane (15 mL) caused the formation of a yellow solid, which was filtered off and dried under vacuum. **1b**·ClO_4: yield 0.135 g (95%). Anal. (%) Calcd for $C_{20}H_{11}N_3ClF_2MnO_7$: C 45.01, H 2.08, N 7.87. Found: C 44.97, H 1.93, N 8.00. IR (CH_2Cl_2): ν 2172 (m) (CN), 2034 (vs), 1955 (s), 1928 (s) cm^{-1} (CO). ^1H NMR (400 MHz, CD_2Cl_2): δ 9.00 (2H, d, $^3J_{HH}$ = 5, H_a bipy), 8.54 (2H, d, $^3J_{HH}$ = 8, H_d bipy), 8.28 (2H, t, $^3J_{HH}$ = 8, H_c bipy), 7.71 (2H, d, $^3J_{HH}$ = 7, H_b bipy), 7.41 (1H, t, $^3J_{HH}$ = 9, $C_6H_3F_2$), 7.00 (2H, t, $^3J_{HH}$ = $^3J_{HF}$ = 8, $C_6H_3F_2$). **1c**·ClO_4: yield 0.141 g (97%). Anal. (%) Calcd for $C_{24}H_{15}N_3ClMnO_7$: C 52.62, H 2.76, N 7.67. Found: C 52.20, H 2.42, N 7.63. IR (CH_2Cl_2): ν 2176 (m) (CN), 2050 (vs), 1990 (s), 1957 (s) cm^{-1} (CO). ^1H NMR (400 MHz, CD_2Cl_2): δ 9.08 (2H, d, $^3J_{HH}$ = 5, H_a bipy), 8.74 (2H, d, $^3J_{HH}$ = 8, H_d bipy), 8.30 (2H, t, $^3J_{HH}$ = 7, H_c bipy), 7.88−7.83 (4H, m, $C_{10}H_7$), 7.74 (2H, t, $^3J_{HH}$ = 6, H_b bipy), 7.61−7.58 (2H, m, $C_{10}H_7$), 7.25 (1H, d, $^3J_{HH}$ = 8, $C_{10}H_7$). **1d**·ClO_4: yield 0.112 g (80%). Anal. (%) Calcd for $C_{22}H_{17}N_3ClMnO_7$: C 50.26, H 3.26, N 7.99. Found: C 49.94, H 3.15, N 7.55. IR (CH_2Cl_2): ν 2171 (m) (CN), 2050 (vs), 1989 (s), 1957 (s) cm^{-1} (CO). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.99 (2H, d, $^3J_{HH}$ = 6, H_a bipy), 8.52 (2H, d, $^3J_{HH}$ = 8, H_d bipy), 8.22 (2H, t, $^3J_{HH}$ = 8, H_c bipy), 7.66 (2H, t, $^3J_{HH}$ = 7, H_b bipy), 7.13 (1H, t, $^3J_{HH}$ = 8, xylyl), 6.99 (2H, d, $^3J_{HH}$ = 8, xylyl), 1.97 (6H, s, CH_3 xylyl). **1e**·ClO_4: yield 0.143 g (98%). Anal. (%) Calcd for $C_{21}H_{14}N_3Cl_2MnO_7$: C 46.18, H 2.58, N 7.69. Found: C 46.35, H 2.27, N 7.74. IR (CH_2Cl_2): ν 2171 (m) (CN), 2051 (vs), 1993 (s), 1959 (s) cm^{-1} (CO). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.99 (2H, d, $^3J_{HH}$ = 5, H_a bipy), 8.86 (2H, d, $^3J_{HH}$ = 8, H_d bipy), 8.33 (2H, t, $^3J_{HH}$ = 8, H_c bipy), 7.71 (2H, t, $^3J_{HH}$ = 7, H_b bipy), 7.27−7.13 (3H, m, $C_6H_3ClCH_3$), 2.14 (3H, s, CH_3). **1f**·ClO_4: yield 0.115 g (85%). Anal. (%) Calcd for $C_{21}H_{15}N_3ClMnO_7$: C 49.29, H 2.95, N 8.21. Found: C 49.64, H 3.08, N 8.40. IR (CH_2Cl_2): ν 2212 (m) (CN), 2050 (vs), 1983 (s), 1951 (s) cm^{-1} (CO). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.89 (2H, d, $^3J_{HH}$ = 5, H_a bipy), 8.61 (2H, d, $^3J_{HH}$ = 8, H_d bipy), 8.23 (2H, t, $^3J_{HH}$ = 7, H_c bipy), 7.61 (2H, t,$^3J_{HH}$ = 7, H_b bipy), 7.34−7.33 (3H, m, Bz), 7.09−7.06 (2H, m, Bz), 4.78 (2H, s, CH_2).

Synthesis of 3b·ClO_4. A solution containing **1b** (0.10 g, 0.19 mmol) and propargylamine (0.480 mL, 7.5 mmol) in thf (10 mL) was stirred at room temperature for 5 min. The solvent was then evaporated to dryness and the remaining oil dissolved in CH_2Cl_2 (4 mL). Addition of hexane (12 mL) caused the precipitation of a yellow solid of the product, which was filtered off and dried under vacuum. Yield: 0.088 g (80%). Anal. (%) Calcd for $C_{23}H_{16}N_4ClF_2MnO_7$: C 46.92, H 2.74, N 9.52. Found: C 46.85, H 2.90, N 9.56. IR (CH_2Cl_2): ν 2034 (vs), 1955 (s), 1928 (s) cm^{-1} (CO). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.80 (2H, d, $^3J_{HH}$ = 5, H_a bipy), 8.35 (2H, d, $^3J_{HH}$ = 8, H_d bipy), 8.15 (2H, t, $^3J_{HH}$ = 7, H_c bipy), 7.61−7.11 (3H, m, H_b bipy, H_{para} $C_6H_3F_2$), 7.16−7.11 (3H, m, NH, H_{meta} $C_6H_3F_2$), 4.37 (2H, s, N−CH_2), 4.23 (1H, d, $^2J_{HH}$ = 3, =CH_2), 3.77 (1H, d, $^2J_{HH}$ = 3, =CH_2). ^{13}C NMR (100.7 MHz, CD_2Cl_2): δ 222.4 ($C_{carbene}$), 219.3, 212.7 (CO), 160.2 (d, $^1J_{FC}$ = 254, CF), 155.1 (C_1 bipy), 153.4 (C_2 bipy), 145.9 (C_{ipso} $C_6H_3F_2$), 139.4 (C_3 bipy),132.3 (C_{arom} $C_6H_3F_2$), 127.3 (C_4 bipy), 124.1 (C_5 bipy), 113.0 (d, $^2J_{FC}$ = 20, C_{meta} $C_6H_3F_2$), 84.6 (=CH_2), 51.0 (N−CH_2).

Synthesis of 3f·ClO_4. A mixture containing **1f** (0.10 g, 0.20 mmol) and propargylamine (0.501 mL, 7.82 mmol) in thf (10 mL) was stirred for 24 h at room temperature. After this period of time a new amount of propargylamine (0.250 mL, 3.90 mmol) was added, and the resulting solution was stirred for another 24 h. The solvent was then evaporated under vacuum, and the oil obtained was dissolved in CH_2Cl_2 (5 mL). Some toluene (15 mL) was added, and the resulting solution concentrated to 7 mL, inducing the appearance of a brown solid. After filtration, the solid was dissolved in CH_2Cl_2 (3 mL) and hexane added (12 mL), causing precipitation of a solid, which was filtered off and dried under vacuum. Yield: 0.080 g (72%). Anal. (%) Calcd for $C_{24}H_{20}N_4ClMnO_7$: C 50.85,

H 3.56, N 9.88. Found: C 50.39, H 3.37, N 9.94. IR (CH_2Cl_2): ν 2032 (vs), 1951 (s), 1923 (s) cm^{-1} (CO). ^1H NMR (300 MHz, CD_2Cl_2): δ 9.08 (2H, d, $^3J_{HH} = 6$, H_a bipy), 8.35 (2H, d, $^3J_{HH} = 8$, H_d bipy), 8.12 (2H, t, $^3J_{HH} = 9$, H_c bipy), 7.58 (2H, t, $^3J_{HH} = 6$, H_b bipy), 7.30−6.78 (6H, m, H_{arom}, NH), 4.91 (2H, d, $^4J_{HH} = 6$, CH_2 Bz), 4.40 (1H, s, =CH_2), 4.17 (1H, s, =CH_2), 3.83 (2H, s, N−CH_2).

Synthesis of 4a·ClO$_4$. To a solution of **1a**·ClO_4 (0.10 g, 0.20 mmol) in thf (10 mL) was added propargylamine (0.533 mL, 8.32 mmol). The resulting mixture was stirred for 4 h. The solvent was then evaporated to dryness under reduced pressure and CH_2Cl_2/toluene (1:4) (16 mL) added to the remaining oil. Then the mixture was stirred for 30 min. The resulting suspension was filtered off, affording a yellow solution, which was concentrated to 5 mL. Addition of hexane (10 mL) gave a yellow solid, which was dried under vacuum. Yield: 0.098 g (88%). Anal. (%) Calcd for $C_{23}H_{18}N_4ClMnO_7$: C 49.97, H 3.28, N 10.13. Found: C 50.26, H 3.55, N 10.12. IR (CH_2Cl_2): ν 2028 (vs), 1944 (s), 1925 (s) cm^{-1} (CO). ^1H NMR (300 MHz, CD_2Cl_2): δ 9.84 (1H, s, NH), 8.77 (2H, d, $^3J_{HH} = 6$, H_a bipy), 8.23 (2H, d, $^3J_{HH} = 8$, H_d bipy), 8.05 (2H, t, $^3J_{HH} = 8$, H_c bipy), 7.54−7.45 (5H, m, H_b bipy, H_{meta} Ph, H_{para} Ph), 7.08 (2H, d, $^3J_{HH} = 7$, H_{orto} Ph), 6.94 (1H, s, C=CH), 1.74 (3H, s, CH_3). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 221.1, 213.8 (br, CO); 184.7 ($C_{carbene}$), 155.1 (C_1 bipy), 153.8 (C_2 bipy), 139.3 (C_3 bipy), 138.1 (C_{ipso} Ph),132.7 (*C*-CH_3); 129.2, 128.5, 126.9 (C_{arom});127.8 (C_4 bipy), 123.9 (C_5 bipy), 117.9 (=CH), 10.4 (CH_3).

Synthesis of 4b·ClO$_4$. The procedure is completely analogous to that described above, using **1b**·ClO_4 (0.1 g, 0.19 mmol) and propargylamine (0.480 mL, 7.50 mmol) and with a stirring time of 24 h. Yield: 0.075 g (68%). Anal. (%) Calcd for $C_{23}H_{16}N_4ClF_2MnO_7$: C 46.92, H 2.72, N 9.52. Found: C 47.17, H 3.05, N 9.63. IR (CH_2Cl_2): ν 2030 (vs), 1949 (s), 1926 (s) cm^{-1} (CO). ^1H NMR (400 MHz, CD_2Cl_2): δ 9.65 (1H, s, NH), 8.85 (2H, d, $^3J_{HH} = 5$, H_a bipy), 8.34 (2H, d, $^3J_{HH} = 8$, H_d bipy), 8.14 (2H, t, $^3J_{HH} = 8$, H_c bipy), 7.63−7.55 (3H, m, H_{arom} $C_6H_3F_2$), 7.18 (2H, d, $^3J_{HH} = 8$, H_b bipy), 7.03 (1H, s, =CH), 1.85 (3H, s, CH_3). ^{13}C NMR (100.7 MHz, CD_2Cl_2): δ 220.8, 214,0 (br, CO); 189.0 ($C_{carbene}$), 159.9 (d, $^1J_{FC} = 254$, CF), 155.7 (C_1 bipy), 153.9 (C_2 bipy), 139.9 (C_3 bipy); 133,3, 133.1 (C_{arom} $C_6H_3F_2$);128.1 (C_4 bipy), 124.5 (C_5 bipy), 119.1 (=CH), 113.5 (d, $^2J_{FC} = 20$, C_{meta} $C_6H_3F_2$), 9.9 (CH_3).

Synthesis of 4c·ClO$_4$. This was similarly prepared from **1c** (0.10 g, 0.18 mmol) and propargylamine (0.501 mL, 7.30 mmol). Reaction time: 3 h. Yield: 0.070 g (64%). Anal. (%) Calcd for $C_{27}H_{20}N_4ClMnO_7$: C 53.79, H 3.34, N 9.29. Found: C 54.42, H 3.77, N 9.15. IR (CH_2Cl_2): ν 2029 (vs), 1945 (s), 1923 (s) cm^{-1} (CO). ^1H NMR (400 MHz, CD_2Cl_2): δ 10.02 (1H, s, NH), 8.72 (1H, d, $^3J_{HH} = 5$, H_a bipy), 8.68 (1H, d, $^3J_{HH} = 5$, H_a bipy), 8.21 (2H, d, $^3J_{HH} = 8$, H_d bipy), 8.04 (2H, t, $^3J_{HH} = 8$, H_c bipy), 7.96−7.92 (2H, m, H_{arom} $C_{10}H_7$), 7.67 (2H, td, $^3J_{HH} = 7$, $^4J_{HH} = 1$, H_b bipy), 7.53 (1H, d, $^4J_{HH} = 2$, H_{arom} $C_{10}H_7$), 7.37 (1H, t, $^3J_{HH} = 6$, H_{arom} $C_{10}H_7$), 7.25−7.13 (3H, m, H_{arom} $C_{10}H_7$), 7.02 (1H, s, =CH), 1.79 (3H, s, CH_3). ^{13}C NMR (100.7 MHz, CD_2Cl_2): δ 221.1, 213.6 (br, CO); 184.7 ($C_{carbene}$), 155.0 (C_1 bipy), 153.8 (C_2 bipy), 139.1 (C_3 bipy); 135.3, 133.7, 133.5, 130.3, 128.7, 128.4, 128.2, 127.2, 125.8 ($C_{10}H_7$); 127.7 (C_4 bipy), 123.6 (C_5 bipy), 118.1 (=CH), 10.3 (CH_3).

Synthesis of 4d·ClO$_4$. To a solution of **1d**·ClO_4 (0.1 g, 0.19 mmol) in thf (10 mL) was added propargylamine (0.487 mL, 7.60 mmol) at rt. After 24 h of stirring a second amount of propargylamine (0.244 mL, 3.81 mmol) was added. The resulting solution was stirred for another 3 days; after this period of time a yellow solid appeared. The solid was filtered off and dissolved in CH_2Cl_2 (5 mL). Addition of hexane (15 mL) and cooling (0 °C) gave a yellow solid, which was dried under vacuum. Yield: 0.080 g (72%). Anal. (%) Calcd for $C_{25}H_{22}N_4ClMnO_7$: C 51.69, H 3.82, N 9.65. Found: C 51.81, H 3.99, N 9.29. IR (CH_2Cl_2): ν 2029 (vs), 1945 (s), 1925 (s) cm^{-1} (CO). ^1H NMR (400 MHz, CD_2Cl_2): δ 9.60 (1H, s, NH), 8.81 (2H, d, $^3J_{HH} = 5$, H_a bipy), 8.30 (2H, d, $^3J_{HH} = 8$, H_d bipy), 8.13 (2H, t, $^3J_{HH} = 8$, H_c bipy), 7.58 (2H, t, $^3J_{HH} = 8$, H_b bipy), 7.38 (1H, t, $^3J_{HH} = 7$, H_{para} xylyl), 7.21 (2H, d, $^3J_{HH} = 7$, H_{meta} xylyl), 7.09 (1H, s, =CH), 1.76 (6H, s, CH_3 xylyl), 1.72 (3H, s, CH_3). ^{13}C NMR (100.7 MHz, CD_2Cl_2): δ 220.9, 213,8 (br, CO); 155.6 (C_1 bipy), 154.2 (C_2 bipy), 145.7 (C_{ipso} Xylyl), 139.8 (C_3 bipy); 135.3−125.8 (C_{arom} xylyl); 128.2 (C_4 bipy), 124.4 (C_5 bipy), 119.5 (=CH), 18.3 (CH_3 xylyl), 10.0 (CH_3).

Synthesis of 4e·ClO$_4$. To a solution of **1e**·ClO_4 (0.1 g, 0.18 mmol) in thf (10 mL) was added propargylamine (0.502 mL, 7.32 mmol) and the resulting mixture stirred for 5 h. The solution was evaporated to dryness, affording a brown oil. CH_2Cl_2/toluene (1:3) (16 mL) was added and the mixture stirred for 10 min. The resulting suspension was filtered off and the solution concentrated to 5 mL. Addition of hexane (10 mL) gave a yellow solid, which was filtered off and dried under vacuum. Yield: 0.060 g (55%). Anal. (%) Calcd for $C_{24}H_{19}N_4Cl_2MnO_7$: C 47.94, H 3.19, N 9.32. Found: C 47.70, H 3.25, N 9.49. IR (CH_2Cl_2): ν 2029 (vs), 1946 (s), 1925 (s) cm^{-1} (CO). ^1H NMR (300 MHz, CD_2Cl_2): δ 9.54 (1H, s, NH), 9.01 (1H, d, $^3J_{HH} = 5$, H_a bipy), 8.74 (1H, d, $^3J_{HH} = 5$, H_a bipy), 8.35 (1H, d, $^3J_{HH} = 8$, H_d bipy), 8.31 (1H, d, $^3J_{HH} = 8$, H_d bipy), 8.19 (1H, td, $^3J_{HH} = 8$, $^4J_{HH} = 1$, H_c bipy), 8.10 (1H, td, $^3J_{HH} = 8$, $^4J_{HH} = 1$, H_c bipy), 7.70 (1H, t, $^3J_{HH} = 6$, H_b bipy), 7.54−7.39 (4H, m, H_b bipy, H_{arom} C_7H_6Cl), 7.08 (1H, d, $^4J_{HH} = 1$, =CH), 2.08 (3H, s, CH_3 C_7H_6Cl), 1.77 (3H, s, CH_3).

Synthesis of 4f·ClO$_4$. To a solution of **1f**·ClO_4 (0.1 g, 0.20 mmol) in thf (10 mL) was added propargylamine (0.501 mL, 7.82 mmol) and the mixture stirred for 24 h. After this period of time a new amount of propargylamine (0.250 mL, 3.90 mmol) was added and the mixture stirred for another 4 days. The solution was evaporated to dryness under vacuum and the resulting oil extracted with CH_2Cl_2/toluene (1:3) (16 mL), to afford an orange solution, which was filtered off and concentrated under reduced pressure (5 mL). Addition of hexane (10 mL) afforded an orange solid, which was filtered off and dried under vacuum. Yield: 0.080 g (72%). Anal. (%) Calcd for $C_{24}H_{20}N_4ClMnO_7$: C 50.85, H 3.56, N 9.88. Found: C 51.02, H 3.35, N 9.60. IR (CH_2Cl_2): ν 2031 (vs), 1949 (s), 1921 (s) cm^{-1} (CO). ^1H NMR (300 MHz, CD_2Cl_2): δ 9.70 (1H, s, NH), 9.07 (2H, d, $^3J_{HH} = 6$, H_a bipy), 8.35 (2H, d, $^3J_{HH} = 8$, H_d bipy), 8.12 (2H, t, $^3J_{HH} = 8$, H_c bipy), 7,63 (2H, t, $^3J_{HH} = 8$, H_b bipy), 7.26−7.24 (5H, m, H_{arom} Bz), 6,78 (1H, s, =CH), 4.89 (2H, s, CH_2 Bz), 1.88 (3H, s, CH_3).

Synthesis of 5b·ClO$_4$. To a solution of **1b**·ClO_4 (0.10 g, 0.19 mmol) in thf (10 mL) was added *N*-methylpropargylamine (0.624 mL, 7.49 mmol) and the mixture stirred for 24 h. The solution was evaporated to dryness, and the resulting brown oil extracted with CH_2Cl_2/toluene (1:3) (16 mL). The resulting yellow solution was filtered off and concentrated to 5 mL. Addition of hexane (10 mL) gave a yellow solid, which was filtered off and dried under vacuum. Yield: 0.060 g (53%). Anal. (%) Calcd for $C_{24}H_{18}N_4ClF_2MnO_7$: C 47.82, H 3.01, N 9.29. Found: C 47.98, H 3.09, N 9.33. IR (CH_2Cl_2): ν 2035 (vs), 1957 (s), 1928 (s) cm^{-1} (CO). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.77 (2H, d, $^3J_{HH} = 5$, H_a bipy), 8.11−8.08 (4H, m, H_d bipy, H_c bipy), 7.57 (2H, t, $^3J_{HH} = 5$, H_b bipy), 7.28 (1H, quint, $^3J_{HH} = {}^4J_{HF} = 7$, H_{para} $C_6H_3F_2$), 6.49 (2H, t, $^3J_{HH} = {}^3J_{HF} = 7$, H_{meta} $C_6H_3F_2$), 4.61 (2H, s, N−CH_2), 4.22 (1H, s, =CH_2), 3.66 (3H, s, N−CH_3), 3.41 (1H, s, =CH_2). ^{13}C NMR (100.7 MHz, CD_2Cl_2): δ 221.8, 212,3 (br, CO); 217.7 ($C_{carbene}$), 159.7 (d, $^1J_{FC} = 255$, CF), 156.1 (C_1 bipy), 154.5 (C_2 bipy), 145.7 (C_{ipso} $C_6H_3F_2$), 140.2 (C_3 bipy), 133,1 (C_{arom} $C_6H_3F_2$), 127.7 (C_4 bipy), 124.4 (C_5 bipy), 113.2 (d, $^2J_{FC} = 19$, C_{meta} $C_6H_3F_2$), 85,3 (=CH_2), 58.5 (N−CH_2), 40.4(N−CH_3).

Synthesis of 6a·ClO$_4$. To a solution of **4a**·ClO_4 (0.10 g, 0.18 mmol) in thf (10 mL) was added NaOtBu (0.018 g, 0.19 mmol). The mixture was stirred for 10 min, after which the color of the solution changed from yellow to red. Then the solution was filtered off and MeI (0.022 mL, 0.35 mL) added dropwise; the mixture was stirred for 3 h. The solution was concentrated to 3 mL and a

mixture of solvents hexane/ether (1:1) (15 mL) added dropwise, affording a yellow solid, which was filtered off and dried under reduced pressure. Yield: 0.080 g (78%). Anal. (%) Calcd for $C_{24}H_{20}N_4IMnO_3$: C 48.51, H 3.39, N 9.43. Found: C 48.27, H 3.61, N 9.65. IR (CH_2Cl_2): ν 2025 (vs), 1939 (s), 1917 (s) cm^{-1} (CO). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.82 (2H, d, $^3J_{HH} = 6$, H_a bipy), 8.19 (2H, d, $^3J_{HH} = 8$, H_d bipy), 8.09 (2H, t, $^3J_{HH} = 7$, H_c bipy), 7.64−6.91 (7H, m, H_b bipy, H_{arom} Ph), 6.35 (1H, s, =CH), 4.02 (3H, s, N−CH_3), 1.54 (3H, s, CH_3). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 221.6, 212,2 (br, CO); 181.9 ($C_{carbene}$), 155.1 (C_1 bipy), 153.1 (C_2 bipy), 139.3 (C_3 bipy), 136,4 (C_{ipso} Ph), 133.2 (=C(CH_3)); 129.6, 128.8, 126.8 (C_{arom} Ph); 127.0 (C_4 bipy), 124.2 (C_5 bipy), 122.1 (=CH), 39.6 (N−CH_3), 9.7 (CH_3).

Synthesis of 8a·ClO_4. To a suspension of **1a**·ClO_4 (0.10 g, 0.20 mmol) in propargylic alcohol (1 mL, 17.18 mmol) was added metallic sodium (0.04 g, 1.74 mmol). The mixture was stirred at room temperature for 3 h to give a dark red solution, and then some CH_2Cl_2 (15 mL) was added. The solution was washed with 6 × 15 mL of water; then the organic layer was dried over Na_2CO_3 and the solvent was reduced to 3 mL. Hexane (15 mL) was slowly added with continuous stirring to gave a yellow solid, which was filtered off and dried under vacuum. Yield: 0.080 g (72%). Anal. (%) Calcd for $C_{23}H_{17}N_3ClMnO_8$: C 49.88, H 3.09, N 7.59. Found: C 49.47, H 2.80, N 7.56. IR (CH_2Cl_2): ν 2040 (vs), 1964 (s), 1934 (s) cm^{-1} (CO). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.56 (2H, d, $^3J_{HH} = 5$, H_a bipy), 8.46 (2H, d, $^3J_{HH} = 8$, H_d bipy), 8.11 (2H, t, $^3J_{HH} = 7$, H_c bipy), 7.54−7.37 (5H, m, H_{arom} Ph, H_b bipy), 7.17 (2H, t, $^3J_{HH} = 7$, H_{arom} Ph), 5,14 (2H, t, $^4J_{HH} = 3$, O−CH_2), 4.51 (1H, q, $^2J_{HH} = {}^4J_{HH} = 3$, =$CH_2$), 3.99 (1H, q, $^2J_{HH} = {}^4J_{HH} = 3$, =$CH_2$). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 241.0 ($C_{carbene}$); 221.6, 212,2 (br, CO); 156.0 (C_1 bipy), 154.1 (C_2 bipy), 145.9 (C_{ipso} Ph), 140.1 (C_3 bipy), 134.2−129.2 (C_{arom} Ph), 127.7 (C_4 bipy), 124.2 (C_5 bipy), 90.8 (=CH_2), 75.5 (O−CH_2).

Synthesis of 8b·ClO_4. The procedure was completely analogous to that described above, using **1b**·ClO_4 (0.10 g, 0.19 mmol), propargylic alcohol (1 mL, 17.18 mmol), and Na (0.04 g, 1.74 mmol). Reaction time: 30 min. Yield: 0.060 g (54%). Anal. (%) Calcd for $C_{23}H_{15}N_3ClF_2MnO_8$: C 46.84, H 2.56, N 7.12. Found: C 46.43, H 2.72, N 7.41. IR (CH_2Cl_2): ν 2043 (vs), 1969 (s), 1936 (s) cm^{-1} (CO). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.67 (2H, d, $^3J_{HH} = 5$, H_a bipy), 8.33 (2H, d, $^3J_{HH} = 8$, H_d bipy), 8.12 (2H, dd, $^3J_{HH} = 6$, $^3J_{HH} = 7$, H_c bipy), 7.66−7.56 (1H, m, H_{para} $C_6H_3F_2$), 7.49 (2H, dd, $^3J_{HH} = 5$, $^3J_{HH} = 6$, H_b bipy), 7.11 (2H, m, H_{meta} $C_6H_3F_2$), 5.05 (2H, t, $^4J_{HH} = 3$, O−CH_2), 4.51 (1H, q, $^2J_{HH} = {}^4J_{HH} = 3$, =$CH_2$), 4.07 (1H, q, $^2J_{HH} = {}^4J_{HH} = 3$, =$CH_2$). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 245.9 ($C_{carbene}$); 218.8, 212.4 (br, CO); 159.2 (d, $^1J_{FC} = 256$, CF), 155.9 (C_1 bipy), 153.7 (C_2 bipy), 142.4 (C_{ipso} $C_6H_3F_2$), 140.2 (C_3 bipy), 134,3 (C_{arom} $C_6H_3F_2$), 127.6 (C_4 bipy), 124.0 (C_5 bipy), 113.8 (d, $^2J_{FC} = 19$, C_{meta} $C_6H_3F_2$), 89,5 (=CH_2), 75.7 (O−CH_2).

Synthesis of 8c·ClO_4. To 1 mL of propargylic alcohol (17.18 mmol) at 0 °C was slowly added butyl lithium (1.141 mL, 6.85 mmol, 6 M in hexane). The mixture was stirred for 5 min at room temperature. Then **1c**·ClO_4 (0.10 g, 0.18 mmol) was added and the suspension stirred for 1 h. Afterward, CH_2Cl_2 (15 mL) was added and the resulting solution washed with 6 × 15 mL of water. The organic layer was dried over Na_2CO_3 and the solution concentrated to 2 mL. Finally, some hexane (10 mL) was added to give a yellow solid, which was filtered off and dried under reduced pressure. Yield: 0.073 g (66%). Anal. (%) Calcd for $C_{27}H_{19}N_3ClMnO_8$: C 53.76, H 3.17, N 6.96. Found: C 53.83, H 3.37, N 7.07. IR (CH_2Cl_2): ν 2040 (vs), 1964 (s), 1934 (s) cm^{-1} (CO). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.57 (1H, d, $^3J_{HH} = 5$, H_a bipy), 8.51 (1H, d, $^3J_{HH} = 5$, H_a bipy), 8.34 (2H, d, $^3J_{HH} = 8$, H_d bipy), 8.11 (1H, td, $^3J_{HH} = 7$, $^4J_{HH} = 1$, H_{arom} $C_{10}H_7$), 8.03−7.95 (3H, m, H_c bipy, H_{arom} $C_{10}H_7$), 7.82 (1H, d, $^3J_{HH} = 9$, H_{arom} $C_{10}H_7$), 7.73−7.63 (2H, m, H_b bipy), 7.59 (1H, d, $^4J_{HH} = 2$, H_{arom} $C_{10}H_7$), 7.33 (1H, t, $^3J_{HH} = 6$, H_{arom} $C_{10}H_7$), 7.19−7.11 (2H, m, H_{arom} $C_{10}H_7$), 5.18 (2H, t, $^4J_{HH} = 3$, O−CH_2), 4.55 (1H, q, $^2J_{HH} = {}^4J_{HH} = 3$, =$CH_2$), 4.06 (1H, q, $^2J_{HH} = {}^4J_{HH} = 3$, =$CH_2$). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 241.2 ($C_{carbene}$), 220.2, 213,1 (br, CO); 155.9 (C_1 bipy), 154.0 (C_2 bipy), 146.0 (C_{ipso} $C_{10}H_7$), 140.0 (C_3 bipy), 134.3 (C_{quater} $C_{10}H_7$), 134.1 (C_{quater} $C_{10}H_7$), 131.5−125.5 (m, C_4 bipy, $C_{10}H_7$), 124.1 (C_5 bipy), 90.9 (=CH_2), 75,6 (O−CH_2).

Synthesis of 9a·ClO_4. The procedure was completely analogous to that for the synthesis of **8a**·ClO_4, using **1a**·ClO_4 (0.10 g, 0.20 mmol), propargylic alcohol (1 mL, 17.18 mmol), and Na (0.04 g, 1.74 mmol), but with a longer reaction time (5 h). Yield: 0.078 g (70%). Anal. (%) Calcd for $C_{23}H_{17}N_3ClMnO_8$: C 49.88, H 3.09, N 7.59. Found: C 49.62, H 2.98, N 7.92. IR (CH_2Cl_2): ν 2038 (vs), 1960 (s), 1933 (s) cm^{-1} (CO). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.71 (2H, d, $^3J_{HH} = 5$, H_a bipy), 8.37 (2H, d, $^3J_{HH} = 7$, H_d bipy), 8.13 (2H, t, $^3J_{HH} = 7$, H_c bipy), 7.64−7.32 (6H, m, H_b bipy, H_{arom} Ph, =CH), 7.11 (2H, d, $^3J_{HH} = 7$, H_{orto} Ph), 1.77 (3H, s, CH_3). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 219.8, 212,4 (br, CO), 215.9 ($C_{carbene}$), 155.2 (C_1 bipy), 153.2 (C_2 bipy), 145.2 (C_{ipso} Ph), 139.3 (C_3 bipy), 133.7−130.7 (C_{arom} Ph, =CH, *C*CH_3), 127.0 (C_4 bipy), 123.5 (C_5 bipy), 7.6 (CH_3).

Synthesis of 9b·ClO_4. The procedure was analogous to the synthesis of **8b**·ClO_4 using **1b**·ClO_4 (0.10 g, 0.19 mmol), propargylic alcohol (1 mL, 17.18 mmol), and Na (0.04 g, 1.74 mmol), but with a longer reaction time (3 h). Yield: 0.070 g (63%). Anal. (%) Calcd for $C_{23}H_{15}N_3ClF_2MnO_8$: C 46.84, H 2.56, N 7.12. Found: C 46.51, H 2.51, N 6.98. IR (CH_2Cl_2): ν 2041 (vs), 1965 (s), 1935 (s) cm^{-1} (CO). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.80 (2H, d, $^3J_{HH} = 5$, H_a bipy), 8.40 (2H, d, $^3J_{HH} = 8$, H_d bipy), 8.19 (2H, t, $^3J_{HH} = 7$, H_c bipy), 7.76−7.70 (1H, m, H_{para} $C_6H_3F_2$), 7.65 (1H, s, =CH), 7.56 (2H, t, $^3J_{HH} = 7$, H_b bipy), 7.23 (2H, t, $^3J_{HH} = {}^3J_{HF} = 8$, H_{meta} $C_6H_3F_2$), 1.84 (3H, s, CH_3). ^{13}C NMR (100.7 MHz, CD_2Cl_2): δ 220.7, 212.6 (br, CO), 219.0 ($C_{carbene}$), 158.4 (d, $^1J_{FC} = 255$, CF), 155.5 (C_1 bipy), 153.3 (C_2 bipy), 141.6 (C_{ipso} $C_6H_3F_2$), 139.8 (C_3 bipy), 134.1 (=CH), 131.2 (*C*CH_3), 127.2 (C_4 bipy), 123.7 (C_5 bipy), 113.3 (d, $^2J_{FC} = 19$, C_{meta} $C_6H_3F_2$), 6.9 (CH_3).

Synthesis of 10b·ClO_4. To a cold (0 °C) suspension of **1b**·ClO_4 (0.10 g, 0.19 mmol) in D,L-3-butyn-2-ol (1 mL, 12.76 mmol) was added some Na (0.04 g, 1.74 mmol). The resulting mixture was stirred at 0 °C for 30 min and then warmed to room temperature. CH_2Cl_2 (20 mL) was added and the solution washed with 6 × 10 mL of water. The organic layer was dried over Na_2CO_3 and the solvent reduced to 3 mL. Finally hexane (15 mL) was added to gave a brown solid, which was filtered off and dried under vacuum. Yield: 0.060 g (53%). Anal. (%) Calcd for $C_{24}H_{17}N_3ClF_2MnO_8$: C 47.74, H 2.84, N 6.96. Found: C 47.50, H 2.78, N 6.85. IR (CH_2Cl_2): ν 2039 (vs), 1962 (s), 1934 (s) cm^{-1} (CO). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.78 (1H, d, $^3J_{HH} = 5$, H_a bipy), 8.72 (1H, d, $^3J_{HH} = 5$, H_a bipy), 8.42 (2H, d, $^3J_{HH} = 8$, H_d bipy), 8.20 (2H, t, $^3J_{HH} = 8$, H_c bipy), 7.73−7.54 (3H, m, $^3J_{HH} = 5$, H_{arom} $C_6H_3F_2$, H_b bipy), 7.23−7.13 (2H, m, H_{meta} $C_6H_3F_2$), 4.48−4.46 (1H, m, =CH_2), 4.15−4.13 (1H, m, =CH_2), 1.21 (3H, d, $^3J_{HH} = 7$, CH_3). ^{13}C NMR (100.7 MHz, CD_2Cl_2): δ 243.2 ($C_{carbene}$), 218.3, 212.8 (br, CO), 158.5 (d, $^1J_{FC} = 257$, CF), 155.3 (C_1 bipy), 152.9 (C_2 bipy), 146.6 (C_{ipso} $C_6H_3F_2$), 139.5 (C_3 bipy), 133.6 (C_{arom} $C_6H_3F_2$), 126.9 (C_4 bipy), 123.3 (C_5 bipy), 113.1 (d, $^2J_{FC} = 19$, C_{meta} $C_6H_3F_2$),111.1 (s, *C*=CH_2), 89.1 (=CH_2), 83.4 (O−CH), 21.0 (CH_3).

Synthesis of 11a·ClO_4. To a suspension of **1a**·ClO_4 (0.10 g, 0.20 mmol) in D,L-3-butyn-2-ol (1 mL, 12.76 mmol) was added some Na (0.04 g, 1.74 mmol). The mixture was stirred for 3 days. Then CH_2Cl_2 (15 mL) was added, and the resulting solution was washed with 3 × 10 mL of water. The organic layer was dried over Na_2CO_3 and reduced to 5 mL under vacuum. Addition of hexane/diethyl ether (1:1) (20 mL) under vigorous stirring afforded an orange solid, which was filtered off and dried under reduced pressure. Yield: 0.070 g (61%). Anal. (%) Calcd for $C_{24}H_{19}N_3$-

$ClMnO_8$: C 50.77, H 3.37, N 7.40. Found: C 51.01, H 3.50, N 7.32. IR (CH_2Cl_2): ν 2036 (vs), 1958 (s), 1932 (s) cm^{-1} (CO). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.71 (2H, d, $^3J_{HH} = 5$, H_a bipy), 8.34 (2H, d, $^3J_{HH} = 7$, H_d bipy), 8.12 (2H, t, $^3J_{HH} = 7$, H_c bipy), 7.61−7.34 (5H, m, H_b bipy, Ph), 7.03 (2H, d, $^3J_{HH} = 7$, Ph), 2.08 (3H, s, OC*CH*$_3$), 1.64 (3H, s, NCCH$_3$). ^{13}C NMR (75,5 MHz, CD_2Cl_2): δ 220.8, 213.7 (br, CO), 213.3 ($C_{carbene}$), 155.9 (C_1 bipy), 153.9 (C_2 bipy), 150.3 (C_{ipso} Ph), 140.0 (C_3 bipy), 135.1−124.2 (Ph,C_4,C_5 bipy), 10.6 (CH_3), 8.2 (CH_3).

Synthesis of 11b·ClO_4. To a cold (0 °C) suspension of **1b**·ClO_4 (0.10 g, 0.19 mmol) in d,L-3-butyn-1-ol (1 mL, 12.76 mmol) was added some Na (0.04 g, 1.74 mmol). The resulting mixture was stirred at 0 °C for 30 min and then at room temperature for 1 day. Then CH_2Cl_2 (10 mL) was added and the solution was washed with 3 × 10 mL of water. The organic layer was dried over Na_2CO_3 and the solvent reduced to 3 mL. Addition of hexane (15 mL) gave an orange solid, which was filtered off and dried under vacuum. Yield: 0.080 g (72%). Anal. (%) Calcd for $C_{25}H_{19}N_3Cl_3F_2MnO_8$ (**11b**·CH_2Cl_2): C 43.60, H 2.78, N 6.10. Found: C 43.67, H 2.89, N 6.01. IR (CH_2Cl_2): ν 2043 (vs), 1969 (s), 1937 (s) cm^{-1} (CO). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.77 (2H, d, $^3J_{HH} = 5$, H_a bipy), 8.40 (2H, d, $^3J_{HH} = 8$, H_d bipy), 8.18 (2H, td, $^3J_{HH} = 8$, $^4J_{HH} = 1$, H_c bipy), 7.56 (2H, td, $^3J_{HH} = 5$, $^4J_{HH} = 1$, H_b bipy), 7.46 (1H, t, $^3J_{HH} = 8$, H_{para} $C_6H_3F_2$), 7.26 (2H, d, $^3J_{HH} = {}^3J_{HF} = 8$, H_{meta} $C_6H_3F_2$), 1.78 (3H, s, CH_3), 1.73 (3H, s, CH_3).

Synthesis of 12a·ClO_4. To 1 mL of 2-butyn-1-ol (13.37 mmol) at 0 °C was slowly added butyl lithium (0.628 mL, 6 M in hexane). The resulting mixture was stirred for 5 min at room temperature. Then **1a**·ClO_4 (0.10 g, 0.20 mmol) was added and the suspension stirred for 20 h. CH_2Cl_2 (15 mL) was added and the solution washed with 6 × 15 mL of water. The organic layer was dried over Na_2CO_3, and then the solvent reduced to 2 mL. Addition of hexane (10 mL) afforded a yellow solid, which was filtered off and dried under reduced pressure. Yield: 0.060 g (53%). Anal. (%) Calcd for $C_{24}H_{19}N_3ClMnO_8$: C 50.77, H 3.37, N 7.40. Found: C 50.39, H 3.23, N 7.89. IR (CH_2Cl_2): ν 2039 (vs), 1962 (s), 1934 (s) cm^{-1} (CO). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.64 (2H, d, $^3J_{HH} = 5$, H_a bipy), 8.38 (2H, d, $^3J_{HH} = 8$, H_d bipy), 8.14 (2H, t, $^3J_{HH} = 8$, H_c bipy), 7.59 (1H, d, $^3J_{HH} = 7$, H_{para} Ph), 7.51−7.45 (4H, m, H_b bipy, H_{arom} Ph), 7.23 (2H, t, $^3J_{HH} = 8$, H_{arom} Ph), 4.96 (2H, q, $^4J_{HH} = {}^5J_{HH} = 3$, O−$CH_2$), 4.80 (1H, qt, $^3J_{HH} = 8$, $^4J_{HH} = 3$, =CH), 0.77 (3H, dt, $^3J_{HH} = 8$, $^5J_{HH} = 3$, CH_3). ^{13}C NMR (75,5 MHz, CD_2Cl_2): δ 241.3 ($C_{carbene}$); 220.1, 213.2 (br, CO), 155.9 (C_1 bipy), 154.0 (C_2 bipy), 140.0 (C_3 bipy), 136.7 (C_{ipso} Ph), 135.4 (=C_{oxaz}), 131.1−129.4 (C_{arom} Ph), 127.4 (C_4 bipy), 123.9 (C_5 bipy), 101.3 (=CH), 76.3 (O−CH_2), 10.3 (CH_3).

Synthesis of 12b·ClO_4. The procedure was analogous to that described above, using **1b**·ClO_4 (0.10 g, 0.19 mmol), 2-butyn-1-ol (1 mL, 13.18 mmol), and butyl lithium (0.586 mL, 6 M in hexane). Yield: 0.075 g (66%). Anal. (%) Calcd for $C_{24}H_{17}N_3ClF_2MnO_8$: C 47.74, H 2.84, N 6.96. Found: C 47.85, H 2.79, N 6.80. IR (CH_2Cl_2): ν 2042 (vs), 1968 (s), 1935 (s) cm^{-1} (CO). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.73 (2H, d, $^3J_{HH} = 5$, H_a bipy), 8.41 (2H, d, $^3J_{HH} = 8$, H_d bipy), 8.18 (2H, t, $^3J_{HH} = 7$, H_c bipy), 7.69−7.53 (3H, m, H_{arom} $C_6H_3F_2$, H_b bipy), 7.15 (2H, m, $^3J_{HH} = 8$, H_{meta} $C_6H_3F_2$), 4.99 (2H, t, $^4J_{HH} = 2$, O−CH_2), 4.84 (1H, q, $^3J_{HH} = 7$, =CH), 0.97 (3H, d, $^3J_{HH} = 7$, CH_3). ^{13}C NMR (75,5 MHz, CD_2Cl_2): δ 246.4 ($C_{carbene}$), 219.0, 212.6 (br, CO), 159.9 (d, $^1J_{FC} = 255$, CF), 155.9 (C_1 bipy), 153.7 (C_2 bipy), 140.2 (C_3 bipy), 134.4 (C_{ipso} $C_6H_3F_2$), 133.0 (C_{arom} $C_6H_3F_2$), 127.6 (C_4 bipy), 124.0 (C_5 bipy), 113.5 (d, $^2J_{FC} = 20$, C_{meta} $C_6H_3F_2$), 101.5 (s, =CH), 76.5 (O−CH_2), 10.5 (CH_3).

Single-Crystal X-ray Structure Determination of Compounds 3b, 4b, and 8a. Suitable yellow single crystals of **3b**, **4b**, and **8a** for the X-ray diffraction study were selected. For compound **8a** data collection was carried out at 293 K, whereas data collection for **3b** and **4b** was performed at 200(2) K, the crystals being covered with perfluorinated ether for **3b** and **4b**. The crystals were mounted on a Bruker-Nonius Kappa CCD single-crystal diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Multiscan[21] absorption correction procedures were applied to the data. The structures were solved, using the WINGX package,[22] by direct methods (SHELXS-97) and refined by using full-matrix least-squares against F^2 (SHELXL-97).[23] 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 C6 in compound **3b**, N1 in compound **4b**, and C4 in compound **8a**. 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 and stopped at shift/err < 0.001. The final residual electron density maps showed no remarkable features.

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Supporting Information Available: Crystallographic data in CIF format of complexes **3b**, **4b**, and **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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