

Carbonyl complexes of manganese, rhenium and molybdenum with ethynyliminopyridine ligands

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Dedicated to Prof. Víctor Riera on the occasion of his 70th birthday.

Abstract

[MBr(CO)₅] reacts with *m*-ethynylphenylamine and pyridine-2-carboxaldehyde in refluxing tetrahydrofuran to give, *fac*-[MBr(CO)₃(py-2-CH=N-C₆H₄-*m*-(C≡CH))] (M = Mn, **1a**; Re, **2a**). The same method affords the tetracarbonyl [Mo(CO)₄{py-2-CH=N-C₆H₄-*m*-(C≡CH)}] (**3a**) starting from [Mo(CO)₄(piperidine)₂]; and the methallyl complex [MoCl(η³-C₃H₄Me-2)(CO)₂{py-2-CH=N-C₆H₄-*m*-(C≡CH)}] (**4a**) from [MoCl(η³-C₃H₄Me-2)(CO)₂(NCMe)₂]. The use of *p*-ethynylphenylamine gives the corresponding derivatives (**1b**, **2b**, **3b**, and **4b**) with the ethynyl substituent in the *para*-position at the phenyl ring of the iminopyridine. All complexes have been isolated as crystalline solids and characterized by analytical and spectroscopic methods. X-ray determinations, carried out on crystals of **1a**, **1b**, **2a**, **2b**, **3a**, **4a**, and **4b**, reveals the same structural type for all compounds with small variations due mainly to the different size of the metal atoms. The reaction of complexes **1a** or **2a** with dicobalt octacarbonyl affords the tetrahedrane complexes [MBr(CO)₃{py-2-CH=N-C₆H₄-*m*-(μ-C≡CH)Co₂(CO)₆}] (M = Mn, **5**; Re, **6**), the structures of which have been confirmed by an X-ray determination on a crystal of compound **5**.

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1. Introduction

Complexes with diimine ligands are object of current interest because of their potentially useful electrochemical, spectroscopic or photochemical properties [1]. Among these, iminopyridines derived from the condensation of pyridine-2-carboxaldehyde with a primary amine are attractive because of their electronic properties which are intermediate between those of the more classic, ubiquitous bipyridine or phenanthroline [2], and the more flexible diazabutadienes [3]. Imino pyridines have been employed recently as multidentate ligands [4], and to prepare polynuclear complexes [5]. There is also interest in the use of imi-

nopyridine ligands having additional functions such as ester [6] or hydroxo [7], capable to anchor them to polymers [8] or biological molecules [9]. On the other hand, more classic complexes of Mn(II), Ni(II) and Fe(II) and other cations with functionalized iminopyridines have been reported to exhibit very interesting properties such as spin crossover [10], second order non-linear optical properties [11], luminescence [12], or mesogenic behavior [13]. Complexes of ions having d⁶ configuration such as Mn(I), Re(I) or Mo(0); or d⁴, such as Mo(II) containing chelate N-donors such as bipy or phen have proved to undergo interesting reactivity in insertion of unsaturated molecules into metal alkoxy and metal-amido bonds [14]. We considered interesting to explore the chemistry of these metals with iminopyridines, and we have reported recently the preparation of molybdenum complexes with chelating iminopyridines bearing an additional carboxylate function

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capable to establish supramolecular interactions in the solid state [15]. The availability of commercial *meta*- and *para*-ethynylanilines prompted us to explore its use to introduce an additional ethynyl function. We report here the preparation of Mn, Re, and Mo complexes containing iminopyridine ligands functionalized with an additional ethynyl group, and their reactivity towards dicobalt octacarbonyl.

2. Results and discussion

Manganese and rhenium complexes containing *meta*-ethynyl-phenyliminopyridine ligands were obtained by one-pot reactions by heating $[M(CO)_5Br]$ ($M = Mn, Re$) with equimolar quantities of pyridine-2-carboxaldehyde and *m*-ethynylphenylamine in THF at reflux temperature (Scheme 1).

After workup, complexes *fac*- $[M(CO)_3\{py-2-CH=NC_6H_4-m-(C\equiv CH)\}]$ ($M = Mn$ (**1a**), Re (**2a**)) were isolated as red solids in good yields (see Section 3). Similarly, the tetracarbonyl complex $[Mo(CO)_4\{py-2-CH=NC_6H_4-m-(C\equiv CH)\}]$ (**3a** in Scheme 1) can be obtained from $[Mo(CO)_4(pip)_2]$ via replacement of two piperidine ligands; and the dicarbonyl complex $[Mo(CO)_2Cl(\eta^3-C_3H_4-Me-2)\{py-2-CH=NC_6H_4-m-(C\equiv CH)\}]$ (**4a** in Scheme 1) by substitution of two acetonitrile ligands from $[MoCl(\eta^3-C_3H_4-Me-2)(NCMe)_2]$. Starting from *p*-ethynylaniline, the same method afforded the corresponding compounds **1b**, **2b**, **3b** and **4b**, containing *p*-ethynyliminopyridine, as summarized in Scheme 1.

The new complexes were characterized by analytical and spectroscopic methods and their structures were determined by X-ray crystallography for **1a–b**, **2a–b**, **3b**, and **4a–b**. Crystal data and refinement details are collected in Table 1, and thermal ellipsoid plots are presented in Figs. 1–4.

Table 2 summarizes the relevant distances and angles for all complexes together for a better comparison. Bromotri-

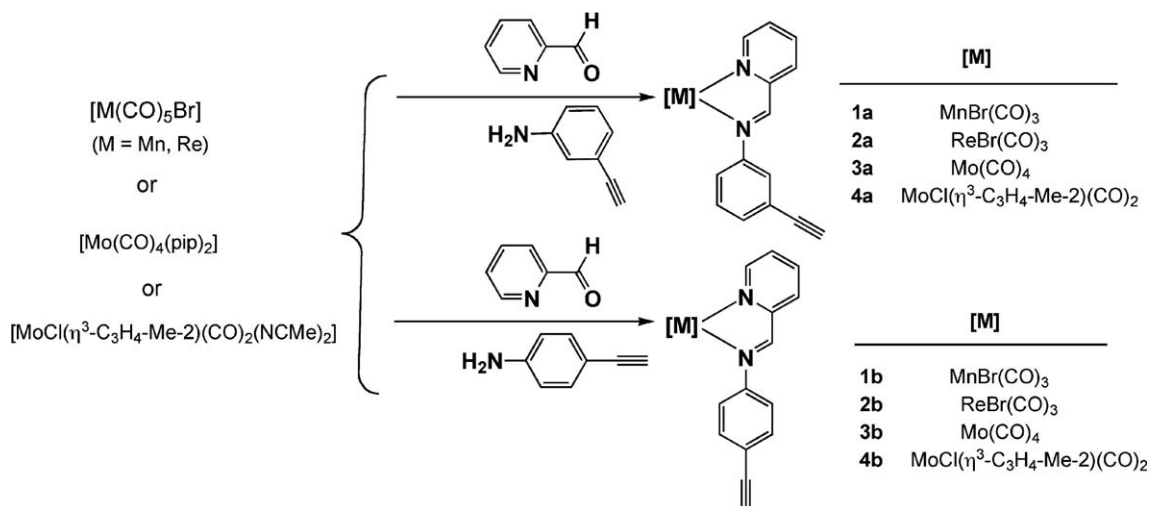
carbonyl compounds **1a** ($M = Mn$) and **2a** ($M = Re$) bearing 3-ethynylphenyliminopyridine are isostructural, as can be noticed from the plots in Fig. 1, and from the geometrical parameters in Table 2.

The same occurs to the pair **1b** and **2b** containing *p*-ethynylphenyliminopyridine (see Fig. 2). In fact the coordination environments of the metals in the four complexes are quite similar. The main distortion from the ideal octahedral geometry arises from the small bite angle $N(1)–M–N(2)$ of the iminopyridine which falls in the range $74.5(2)–78.47(16)^\circ$. They all display the expected *facial*-tricarbonyl arrangement, with the chelate iminopyridine and bromo ligands in the opposite face of the octahedron. This geometry derives from the *cis*-labilization effect of Br directing the substitution of carbonyl ligands from $[MnBr(CO)_5]$ [16].

The structure of the tetracarbonyl molybdenum complex **3b** (Fig. 3) is very close to those of the tricarbonyls **1a–b** and **2a–b**, with the Mo atom in an octahedral environment in which the main distortion is again the small bite angle of the iminopyridine ligand [$72.48(7)^\circ$]. Methallyldicarbonyl molybdenum complexes **4a–b** display pseudooctahedral coordination geometry, with the distortions imposed by the diimine and the methallyl ligands (Fig. 4).

There is a consistent and significant variation of the $M–X$, $M–N$, and $M–C$ distances on passing from Mn to Re and (where applicable) to Mo complexes. This pattern has been observed for other families of complexes [17], and correlates well with the size of the metal center, estimated from their metallic radii (Mn 1.18 Å, Re 1.28 Å, Mo 1.30 Å [18]).

The spectroscopic properties of the complexes in solution correlate well with their solid state structures. IR spectra in dichloromethane display (see Table 3) the expected patterns of three active $\nu(CO)$ normal modes for the tricarbonyls **1a–b**, and **2a–b**; four active $\nu(CO)$ normal modes for the tetracarbonyls **3a–b**, and two active $\nu(CO)$ normal modes for the dicarbonyls **4a–b** [19].



Scheme 1.

Table 1
Crystal data and refinement details for **1a**, **1b**, **2a**, and **2b**; **3b**, **4a**, **4b** and **5**

| | 1a | 1b | 2a | 2b | 3b | 4a | 4b | 5 |
|---|--|---|--|--|---|--|---|--|
| Empirical formula | C ₁₇ H ₁₀ BrMnN ₂ O ₃ 0.5 CH ₂ Cl ₂ | C ₁₇ H ₁₀ BrMn N ₂ O ₃ | C ₁₇ H ₁₀ BrReN ₂ O ₃ · 0.5 CH ₂ Cl ₂ | C ₁₇ H ₁₀ BrN ₂ O ₃ Re | C ₁₈ H ₁₀ MoN ₂ O ₄ | C ₂₀ H ₁₇ ClMoN ₂ O ₂ · CH ₂ Cl ₂ | C ₂₀ H ₁₇ ClMoN ₂ O ₂ | C ₂₇ H ₁₈ BrMn Co ₂ N ₂ O ₁₀ |
| Formula weight | 467.58 | 425.12 | 598.84 | 556.38 | 414.22 | 533.67 | 448.75 | 783.14 |
| Crystal system | Triclinic | Triclinic | Triclinic | Triclinic | Monoclinic | Triclinic | Triclinic | Triclinic |
| Space group | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ | <i>P</i> 2(1)/ <i>c</i> | <i>P</i> 2(1)/ <i>n</i> | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ |
| <i>a</i> (Å) | 9.192(7) | 8.964(3) | 9.154(5) | 9.034(5) | 9.782(2) | 11.4078(17) | 8.011(4) | 11.253(7) |
| <i>b</i> (Å) | 9.388(7) | 9.120(4) | 9.461(5) | 9.050(5) | 10.657(2) | 14.508(2) | 11.384(5) | 12.026(8) |
| <i>c</i> (Å) | 12.477(10) | 10.883(4) | 12.556(6) | 10.800(6) | 17.011(3) | 14.154(2) | 12.254(6) | 12.243(8) |
| α (°) | 68.28(1) | 82.172(7) | 68.841(8) | 75.537(9) | 90 | 90 | 62.951(8) | 83.856(11) |
| β (°) | 73.35(1) | 74.695(6) | 72.998(9) | 83.16(1) | 103.023(4) | 102.665(3) | 82.117(9) | 89.404(12) |
| γ (°) | 81.80(2) | 86.211(7) | 83.020(9) | 86.21(1) | 90 | 90 | 77.247(8) | 71.855(13) |
| <i>V</i> Å ³ | 957.5(13) | 849.7(5) | 969.6(8) | 848.4(8) | 1727.8(6) | 2285.5(6) | 969.8(8) | 1565.0(17) |
| <i>Z</i> | 2 | 2 | 2 | 2 | 4 | 4 | 2 | 2 |
| <i>T</i> (K) | 296(2) | 296(2) | 293(2) | 293(2) | 296(2) | 296(2) | 293(2) | 296(2) |
| <i>D</i> _{calc} (g cm ⁻³) | 1.622 | 1.662 | 2.051 | 2.178 | 1.592 | 1.551 | 1.537 | 1.662 |
| <i>F</i> (000) | 462 | 420 | 562 | 520 | 824 | 1072 | 452 | 776 |
| λ (Mo K α) (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal size (mm); color | 0.07 × 0.11 × 0.23; orange-red | 0.14 × 0.06 × 0.05; red | 0.19 × 0.10 × 0.05; red | 0.16 × 0.09 × 0.05; red | 0.13 × 0.19 × 0.34; dark red | 0.23 × 0.19 × 0.09; black | 0.27 × 0.17 × 0.12; black | 0.45 × 0.14 × 0.07; dark red |
| μ (Mo K α) (mm ⁻¹) | 2.933 | 3.144 | 8.482 | 9.533 | 0.783 | 0.944 | 0.830 | 2.776 |
| Collection range (°) | 1.82 ≤ θ ≤ 23.33 | 1.96 ≤ θ ≤ 23.32 | 1.81 ≤ θ ≤ 23.35 | 1.96 ≤ θ ≤ 23.28 | 2.14 ≤ θ ≤ 23.26 | 2.04 ≤ θ ≤ 23.29 | 1.87 ≤ θ ≤ 23.37 | 1.79 ≤ θ ≤ 23.47 |
| Correction factors (SADABS) min/max | 0.5803 | 0.6940 | 0.6137 | 0.5662 | 0.7120 | 0.827023 | 0.7741 | 0.587066 |
| Reflections collected | 4275 | 3895 | 4415 | 3875 | 7208 | 9913 | 4352 | 7110 |
| Independent reflections [<i>R</i> _{int}] | 2696 [0.0237] | 2433 [0.0694] | 2793 [0.0233] | 2403 [0.0465] | 2460 [0.0196] | 3287 [0.0294] | 2755 [0.0152] | 4506 [0.0169] |
| Reflections observed, <i>I</i> > 2 σ (<i>I</i>) | 2007 | 1026 | 2406 | 1696 | 2235 | 2544 | 2496 | 3568 |
| GOF on <i>F</i> ² | 1.010 | 0.843 | 1.010 | 1.016 | 1.068 | 1.012 | 1.046 | 1.007 |
| Number of parameters | 241 | 217 | 226 | 217 | 227 | 263 | 236 | 388 |
| Residuals <i>R</i> , <i>wR</i> ₂ (all) | 0.0453, 0.1215 | 0.0583, 0.0786 | 0.0326, 0.0760 | 0.0516, 0.1004 | 0.0218, 0.0583 | 0.0369, 0.0937 | 0.0233, 0.0641 | 0.0334, 0.0933 |

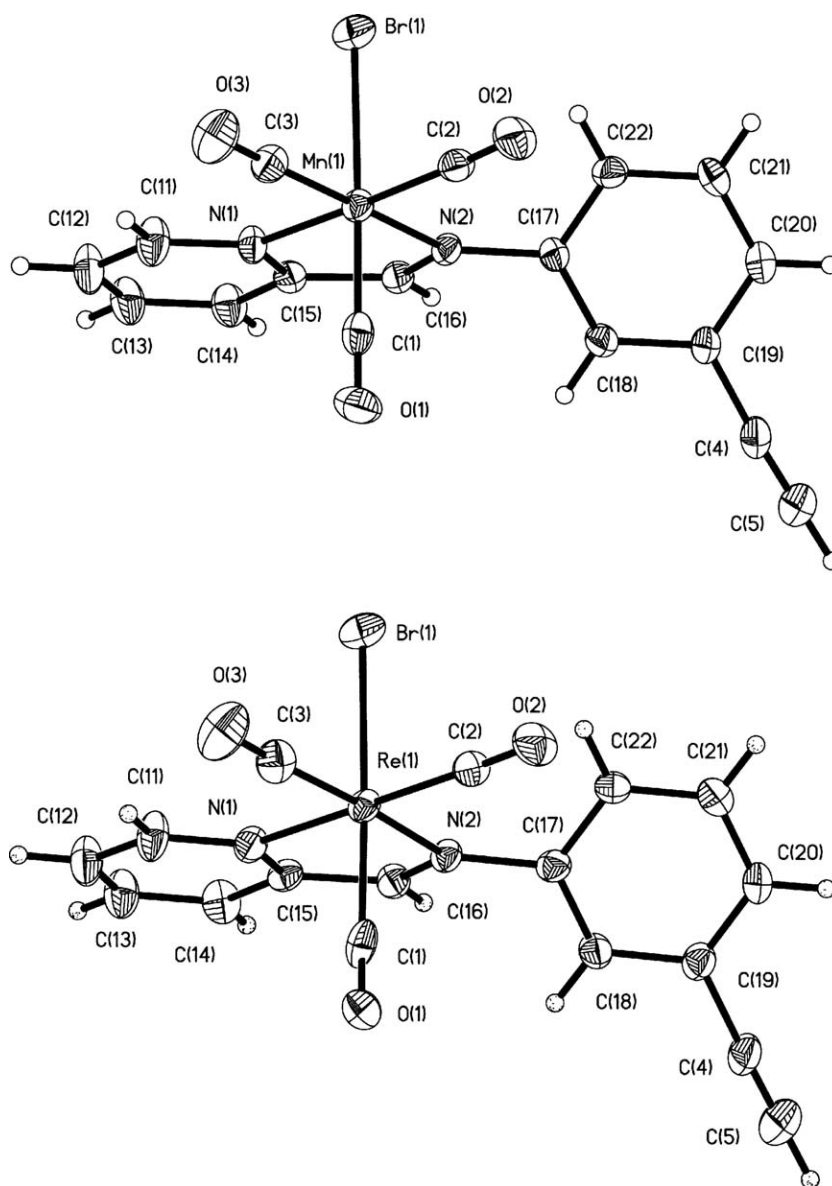


Fig. 1. ORTEP plot (30% ellipsoid probability) of compounds **1a** (above) and **2a** (below) showing the atom numbering.

As it can be seen in Table 3, the $\nu(\text{CO})$ bands appear very close (within 1 cm^{-1}) for each pair of complexes containing the ethynyl group in *meta*- or *para*-position. Moreover, there is a very small change when compared with the corresponding complexes such as $[\text{MBr}(\text{CO})_3(\text{pyCH}=\text{N}-\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)]$ containing a methyl group in *para*-. On the other hand, the position of the $\nu(\text{CO})$ bands is shifted slightly but consistently to higher energy on passing from bipy (or phen) [20] to iminopyridine complexes.

In the ^1H NMR spectra in acetone- d_6 , the signal of the imine proton appears for all complexes as an easily identifiable singlet in the range δ 9.34–8.55 ppm, shifted upfield from the signal of the starting aldehyde at δ 9.99 ppm, while the terminal acetylene proton appears as a singlet in the range δ 3.79–3.83 ppm.

The ^1H NMR spectra in solution of complexes **4a–b** in solution are consistent with the solid state structure depicted

for them in Fig. 4. The usual disposition of the allyl and chloride ligands on opposite sides of the equatorial plane defined by the two carbonyls and the two nitrogen atoms [21], with the open face of the allyl ligand directed towards the two carbonyls, is maintained in solution, and thus the *syn* protons of the allyl terminus exhibit two different signals coupled to each other. Two separate signals are also observed for the *anti* protons which are also inequivalent. This implies that the inequivalency of the two allyl *termini* is maintained in solution at room temperature. Nevertheless this would be compatible with the existence of a trigonal twist involving the “triangular” face formed by the η^3 -methallyl and the two carbonyls [22]. This concerted rotation would maintain the relative orientation of the allyl and carbonyl ligands, keeping the inequivalency of the two allyl halves.

All the complexes exhibit a common feature: the planarity of the pyridine ring is extended to the imine system but

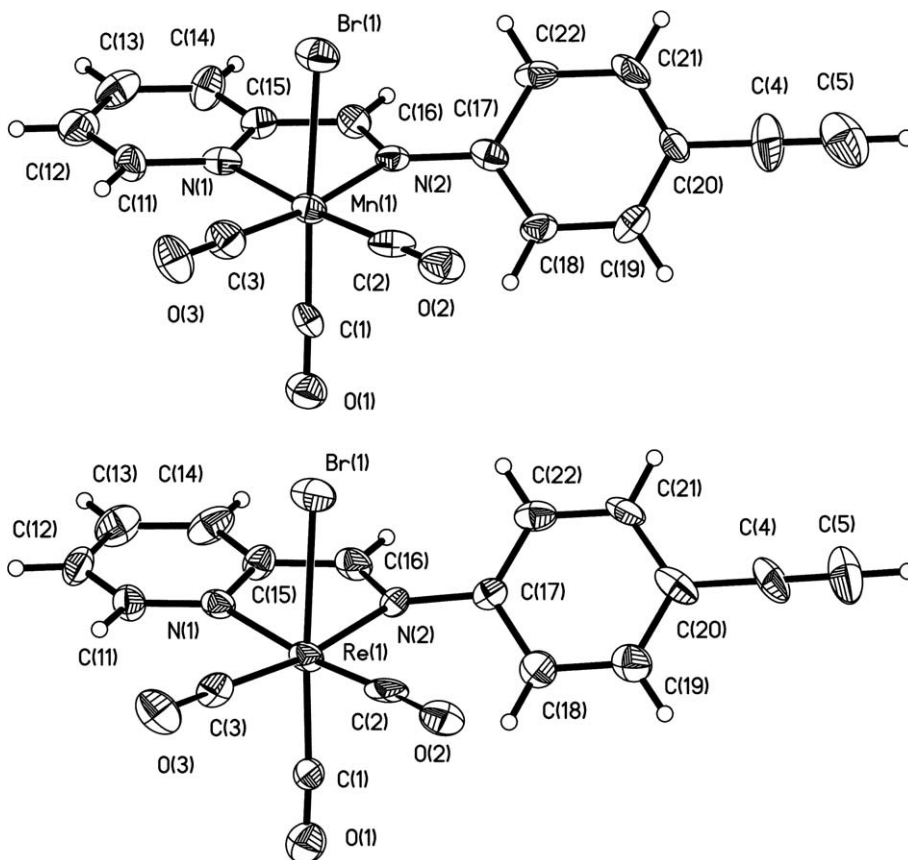


Fig. 2. ORTEP plot (30% ellipsoid probability) of compounds **1b** and **2b** showing the atom numbering.

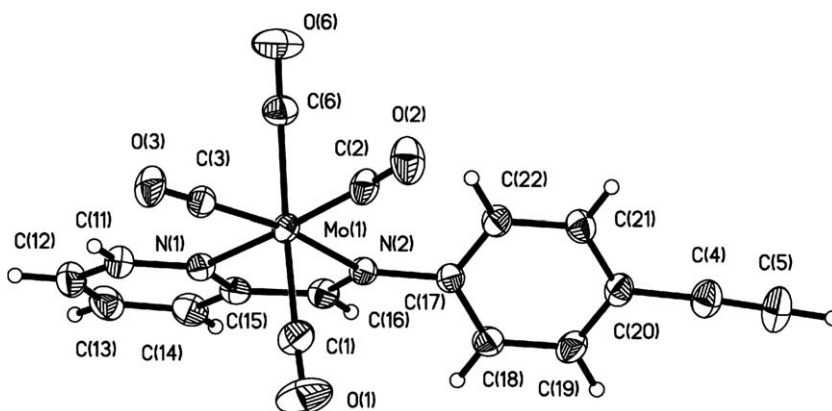


Fig. 3. ORTEP plot (30% ellipsoid probability) of compound **3b** showing the atom numbering.

this planarity does not extend to the phenyl ring which is rotated significantly with respect to the iminopyridine plane, the dihedral angles ranging from 35.7° (for **4b**) to 50.5° (for **1a**) as summarized in Table 4. The torsion is a common feature of the phenyliminopyridine ligands, and appears to correlate well with the steric hindrance around the metal [7], although electronic factors can not be ruled out. The results of DFT calculations led Heinze to conclude that the orientation of the phenyl ring is an intrinsic property of the molecules, not influenced by packing forces or hydrogen bonding [7a].

As a preliminary exploration of the alkynyl group reactivity, compounds **1a** and **2a** were made to react with dicobalt octacarbonyl in dichloromethane to afford the tetrahedrane complexes **5** and **6** which were isolated in good yield in crystalline form (Scheme 2). The presence of five bands in the ν_{CO} region of their IR spectra in THF (ν_{CO} for **5**: 2096m, 2059s, 2031vs, 1947s, 1926s, cm^{-1} ; ν_{CO} for **6**: 2096m, 2059s, 2028vs, 1931s, 1906s, cm^{-1}) clearly pointed to their polynuclear nature. All the bands can be assigned by comparison with those of the starting compounds and related tetrahedranes. Six ν_{CO}

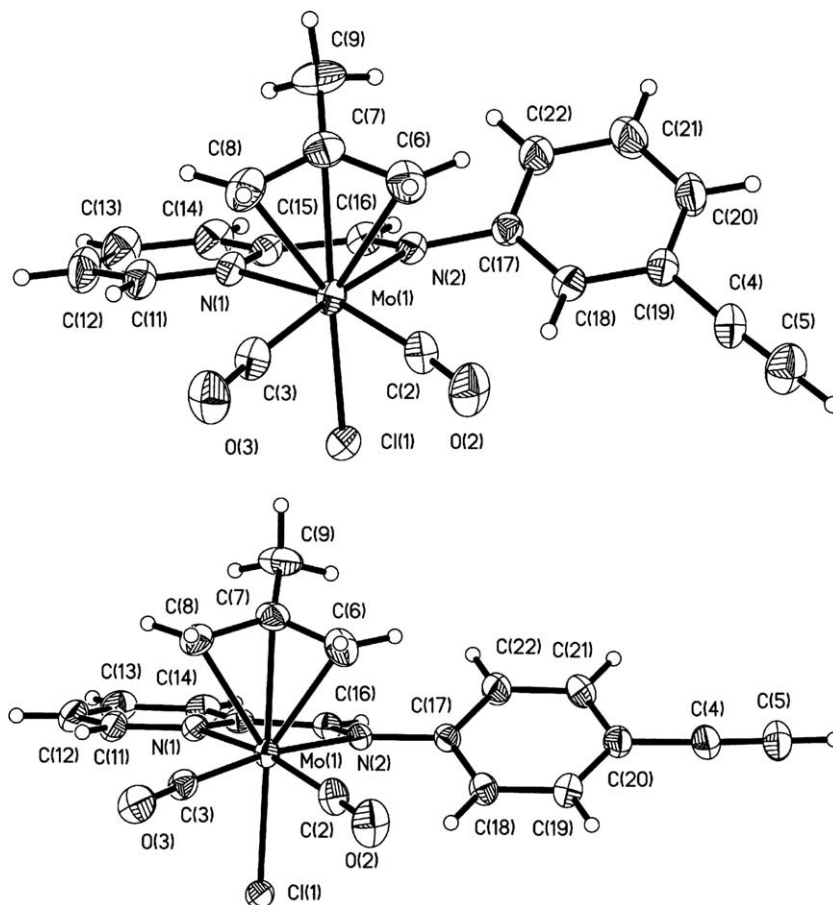


Fig. 4. ORTEP plot (30% ellipsoid probability) of compounds **4a** and **4b** showing the atom numbering.

Table 2
Selected distances (Å) and angles (°) for ethynyliminopyridine compounds

| | 1a (X = Br, M = Mn) | 2a (X = Br, M = Re) | 1b (X = Br, M = Mn) | 2b (X = Br, M = Re) | 3b , (X = CO, M = Mo) | 4a (X = Cl, M = Mo) | 4b (X = Cl, M = Mo) |
|-------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|---------------------------------|-------------------------------|-------------------------------|
| M–X | 2.531(2) | 2.620(2) | 2.502(2) | 2.598(2) | 2.048(3) | 2.502(2) | 2.502(1) |
| M–N(1) | 2.062(5) | 2.188(6) | 2.030(8) | 2.14(1) | 2.247(2) | 2.235(3) | 2.234(2) |
| M–N(2) | 2.070(4) | 2.186(6) | 2.032(7) | 2.17(1) | 2.284(2) | 2.272(3) | 2.286(2) |
| M–C(1) | 1.860(7) | 2.00(1) | 1.809(9) | 1.90(2) | 2.023(3) | – | – |
| M–C(2) | 1.834(7) | 1.917(9) | 1.78(1) | 1.78(2) | 1.966(3) | 1.967(5) | 1.966(3) |
| M–C(3) | 1.807(6) | 1.92(1) | 1.78(1) | 1.91(2) | 1.948(3) | 1.956(5) | 1.952(3) |
| C(4)–C(5) | 1.123(8) | 1.10(1) | 1.15(2) | 1.10(2) | 1.168(4) | 1.111(7) | 1.167(5) |
| N(1)–M–N(2) | 78.5(2) | 74.5(2) | 77.9(4) | 75.3(4) | 72.48(7) | 73.1(1) | 73.11(8) |

bands can be observed for $[\text{Co}_2(\text{CO})_6(\text{PhC}\equiv\text{CH})]$ at 2095w, 2058s, 2032s, 2028(sh), 2016w, and 2001(sh) cm^{-1} [23]. The two at lower frequencies are very weak and often can not be observed in other tetrahedranes [24]. In the case of **5**, the two bands at upper frequencies (2095m and 2059s, cm^{-1}) can be assigned to $\nu(\text{CO})$ vibrations of the dicobalt hexacarbonyl moiety, only slightly shifted from those of the phenylacetylene analogue. Consistently with this assignment, the position of these two upper bands do not change in the rhenium complex **6**. The strongest band of **5**, at 2031 cm^{-1} , can be considered to be the envelope of the highest band of $\text{Mn}(\text{CO})_3$, overlapped with the two bands of the $\{\text{Co}_2(\text{CO})_6\}$ unit. The corresponding band

appears at 2028 cm^{-1} for the Re complex **6**. The bands of compound **5** at 1947s and 1926s cm^{-1} clearly correspond to the lower $\nu(\text{CO})$ vibrations of $\text{Mn}(\text{CO})_3$ shifted to 1931s and 1906s cm^{-1} for the rhenium complex **6**. It is worth to notice that while the bands of $\text{Co}_2(\text{CO})_6$ do not change significantly from those of $[\text{Co}_2(\text{CO})_6(\text{PhC}\equiv\text{CH})]$, the bands attributable to $\text{Mn}(\text{CO})_3$ and $\text{Re}(\text{CO})_3$ fragments are shifted to higher frequencies from those of the parent compounds **1a** and **2a**.

The most salient feature of the ^1H NMR spectra of **5** and **6** is the significant shift of the signal corresponding to the acetylenic proton, from ca δ 3.8 ppm in the starting **1a** and **2a** to about δ 6.9 ppm in **5** and **6**. This well preceded

Table 3
Carbonyl stretching frequencies (cm⁻¹, THF solution)^a for complexes **1a–b**, **2a–b**, **3a–b** and **4a–b**, and their analogues with bipy and phen

| | ν_1 (s) | ν_2 (s) | ν_3 (s) | |
|--|-------------|-------------|----------------|-------------|
| (N–N) in [Mn(CO) ₃ Br(N–N)] | | | | |
| (pyCH=NC ₆ H ₄ - <i>m</i> -C≡CH) (1a) | 2026 | 1944 | 1919 | |
| (pyCH=NC ₆ H ₄ - <i>p</i> -C≡CH) (1b) | 2026 | 1944 | 1919 | |
| (pyCH=NC ₆ H ₄ - <i>p</i> -CH ₃) | 2026 | 1942 | 1917 | |
| bipy | 2023 | 1935 | 1915 | |
| phen | 2024 | 1936 | 1915 | |
| (N–N) in [Re(CO) ₃ Br(N–N)] | | | | |
| (pyCH=NC ₆ H ₄ - <i>m</i> -C≡CH) (2a) | 2024 | 1927 | 1901 | |
| (pyCH=NC ₆ H ₄ - <i>p</i> -C≡CH) (2b) | 2024 | 1927 | 1900 | |
| (pyCH=NC ₆ H ₄ - <i>p</i> -CH ₃) | 2023 | 1925 | 1899 | |
| bipy | 2020 | 1920 | 1896 | |
| phen | 2021 | 1920 | 1897 | |
| | ν_1 (m) | ν_2 (s) | ν_3 (m,sh) | ν_4 (m) |
| (N–N) in [Mo(CO) ₄ (N–N)] | | | | |
| (pyCH=NC ₆ H ₄ - <i>m</i> -C≡CH) (3a) | 2013 | 1906 | 1892 | 1851 |
| (pyCH=NC ₆ H ₄ - <i>p</i> -C≡CH) (3b) | 2013 | 1905 | 1892 | 1851 |
| bipy | 2013 | 1901 | 1883 | 1842 |
| phen | 2012 | 1901 | 1884 | 1842 |
| | ν_1 (s) | ν_2 (s) | | |
| (N–N) in MoCl(methallyl)(CO) ₂ (N–N)] | | | | |
| (pyCH=NC ₆ H ₄ - <i>m</i> -C≡CH) (4a) | | 1952 | 1877 | |
| (pyCH=NC ₆ H ₄ - <i>p</i> -C≡CH) (4b) | | 1953 | 1877 | |
| bipy | | 1950 | 1871 | |
| phen | | 1950 | 1872 | |

^a For a more accurate comparison, the spectra of the complexes with bipy and phen have been taken in the same solvent and measured with the same instrument.

Table 4
Dihedral angles between the planes of the iminopyridine system and the phenyl ring

| Compound | Angle (°) |
|-----------|-----------|
| 1a | 50.5 (2) |
| 2a | 49.3(2) |
| 1b | 47.8(3) |
| 2b | 43.4(4) |
| 3b | 38.84(8) |
| 4a | 43.4(1) |
| 4b | 35.7(1) |
| 5 | 60.7(1) |

[25] effect of the change from a linear sp hybridisation of the acetylenic carbon in the starting complexes to a near-tetrahedral sp³ in **5** and **6** is in good agreement with the geometry of the molecule in solid state. An X-ray determination was carried out on a crystal of **5**, and the results are presented in Fig. 5 and Table 5. The coordination of the acetylene to the Co₂(CO)₆ fragment causes the expected elongation of the C(4)–C(5) distance from 1.123(8) Å in **1a** to 1.344(5) Å in **5**, and the loss of linearity of the C(Ph)–C(4)–C(5) sequence from 176.9° in **1a** to 141.4(3)° in **5**. This features are consistent with the C(4)–C(5) fragment acting as a 4e donor towards the cobalt atoms. A comparison between the geometric parameters of **1a** and **5** shows no significant change of the geometry around manganese. In contrast the torsion of the phenyl ring with respect to the plane of the iminopyri-

dine increases from 50.5(2)° in **1a** to 60.7° in **5** (see Table 4). As discussed above, this could be attributed to the steric bulk of the Co₂(CO)₆ moiety.

In conclusion, we have developed a facile “one-pot” method for the preparation of a variety of complexes of Mn(I), Re(I), Mo(0) and Mo(II), with phenyliminopyridine ligands bearing an ethynyl function at *meta*- or *para*-position. The structural determinations show little variations of the geometry of the metal-iminopyridine core which can be ascribed to the different size of the metals. The ethynyl functionality can be used for further reactivity, as illustrated by its reaction with octacarbonyl dicobalt, to afford tetrahedrane clusters.

3. Experimental

3.1. Materials and general methods

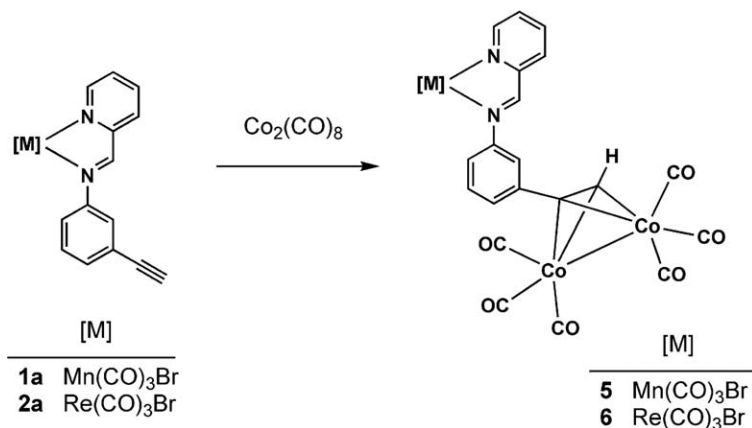
All operations were performed under an atmosphere of dry dinitrogen using Schlenk and vacuum techniques. Details of the instrumentation and experimental procedures have been given elsewhere [26]. IR spectra in solution were recorded with a Perkin Elmer Spectrum RX I FT-IR instrument, using cells with CaF₂ windows. Literature procedures for the preparation of starting materials are quoted in each case. Ligands and other reagents were purchased and used without purification unless otherwise stated.

3.2. [MnBr(CO)₃{py-2-CH=N-C₆H₄-*m*-(C≡CH)}] (**1a**)

[Mn(CO)₅Br] (0.1 g, 0.364 mmol), 2-pyridinecarboxaldehyde (0.039 g, 0.364 mmol) and 3-ethynylaniline (0.043 g, 0.364 mmol) were refluxed in THF (25 mL) for 3 h. The solvent was evaporated in vacuo, and the residue was taken up in CH₂Cl₂ and filtered through silica gel. The red band was collected and the solvent was evaporated in vacuo to obtain compound **1a** as a red, microcrystalline solid. Yield 0.130 g, 84%. Anal. Calc. for C₁₇H₁₀-BrMnN₂O₃: C 48.03, H 2.37, N 6.59. Found: C 48.18, H 2.44, N 6.79. ¹H NMR (acetone-*d*₆): δ = 9.33 [d(5), 1H, H⁶ py], 8.92 (s, 1H, -CH=N-), 8.30 (m, 2H, H^{3,4} py), 7.85 (m, 1H, H⁵ py), 7.74 (s, 1H, H² Ph), 7.72 (m, 1H, H⁴ Ph), 7.59 (m, 2H, H^{5,6} Ph), 3.81 (s, 1H, -C≡CH).

3.3. [MnBr(CO)₃{py-2-CH=N-C₆H₄-*p*-(C≡CH)}] (**1b**)

Compound **1b** was prepared as described above for compound **1a**, starting from [Mn(CO)₅Br] (0.275 g, 1 mmol), 2-pyridinecarboxaldehyde (0.107 g, 1 mmol) and 4-ethynylaniline (0.117 g, 1 mmol). The workup was as described for **1a** to afford compound **1b**. Yield 0.361 g, 84.9%. Anal. Calc. for C₁₇H₁₀BrMnN₂O₃: C 48.03, H 2.37, N 6.59. Found: C 48.12, H 2.42, N 6.70. ¹H NMR (acetone-*d*₆): δ = 9.32 [d(5), 1H, H⁶ py], 8.90 (s, 1H, -CH=N-), 8.30 (m, 2H, H^{3,4} py), 7.84 (m, 1H, H⁵ py), 7.68 (m, 4H, H^{2,3,5,6} Ph), 3.80 (s, 1H, -C≡CH).



Scheme 2.

3.4. [ReBr(CO)₃{py-2-CH=N-C₆H₄-m-(C≡CH)}] (**2a**)

[Re(CO)₅Br] (0.1 g, 0.246 mmol), 2-pyridinecarboxaldehyde (0.026 g, 0.246 mmol) and 3-ethynylaniline (0.029 g, 0.246 mmol) were refluxed in THF (25 mL) for 9 h. The workup was as described for **1a** to afford compound **2a**. Yield 0.109 g, 79.6%. Anal. Calc. for C₁₇H₁₀BrReN₂O₃: C 36.70, H 1.81, N 5.03. Found: C 36.85, H 1.89, N 5.03. ¹H NMR (acetone-*d*₆): δ = 9.34 (s, 1H, -CH=N-), 9.19 [d(6), 1H, *H*⁶ py], 8.45 [d(8), 1H, *H*³ py], 8.39 [pseudo-t(8), 1H, *H*⁴ py], 7.90 (m, 1H, *H*⁵ py), 7.75 (s, 1H, *H*² Ph), 7.70 (m, 1H, *H*⁴ Ph), 7.60 (m, 2H, *H*^{5,6} Ph), 3.82 (s, 1H, -C≡CH).

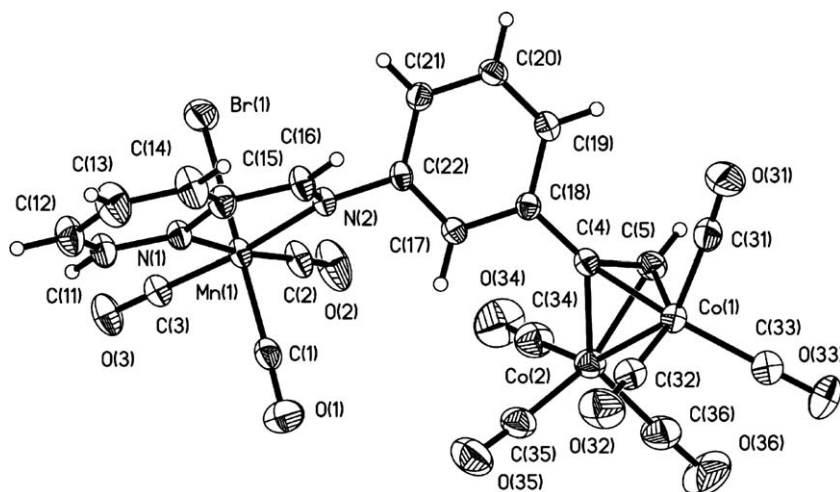
3.5. [ReBr(CO)₃{py-2-CH=N-C₆H₄-p-(C≡CH)}] (**2b**)

Compound **2b** was prepared as described above for compound **2a**, starting from [Re(CO)₅Br] (0.1 g, 0.246 mmol), 2-pyridinecarboxaldehyde (0.026 g, 0.246 mmol) and 4-ethynylaniline (0.029 g, 0.246 mmol). The workup was as described for **1a** to afford compound **2b**. Yield 0.115 g,

Table 5

Selected bond lengths (Å) and angles (°) for compound **5**

| | |
|------------------|------------|
| Mn(1)–Br(1) | 2.5146(14) |
| Mn(1)–N(1) | 2.071(3) |
| Mn(1)–N(2) | 2.054(3) |
| Mn(1)–C(1) | 1.828(5) |
| Mn(1)–C(2) | 1.818(5) |
| Mn(1)–C(3) | 1.808(4) |
| Co(1)–Co(2) | 2.4851(13) |
| Co(1)–C(4) | 1.987(4) |
| Co(1)–C(5) | 1.949(4) |
| Co(2)–C(4) | 1.971(4) |
| Co(2)–C(5) | 1.975(4) |
| C(4)–C(5) | 1.344(5) |
| | |
| N(1)–Mn(1)–N(2) | 78.23(11) |
| C(1)–Mn(1)–Br(1) | 178.88(12) |
| C(2)–Mn(1)–N(1) | 174.11(15) |
| C(3)–Mn(1)–N(2) | 173.11(14) |
| C(5)–Co(1)–Co(2) | 51.17(11) |
| C(4)–Co(1)–Co(2) | 50.81(10) |
| C(4)–Co(1)–C(5) | 39.92(14) |
| C(4)–Co(2)–C(5) | 39.84(14) |
| C(5)–Co(2)–Co(1) | 50.24(11) |
| C(18)–C(4)–C(5) | 141.4(3) |

Fig. 5. ORTEP plot (30% ellipsoid probability) of compound **5** showing the atom numbering.

84%. Anal. Calc. for $C_{17}H_{10}BrReN_2O_3$: C 36.70, H 1.81, N 5.03. Found: C 36.80, H 1.87, N 5.08. 1H NMR (acetone- d_6): δ = 9.33 (s, 1H, $-CH=N-$), 9.18 [d(6), 1H, H^6 py], 8.46 [d(8), 1H, H^3 py], 8.39 [*pseudo-t*(8), 1H, H^4 py], 7.90 (m, 1H, H^5 py), 7.72–7.65 (m, 4H, $H^{2,3,5,6}$ Ph), 3.83 (s, 1H, $-C\equiv CH$).

3.6. $[Mo(CO)_4\{py-2-CH=N-C_6H_4-m-(C\equiv CH)\}]$ (**3a**)

$[Mo(CO)_4(pip)_2]$ [27] (0.1 g, 0.264 mmol), 2-pyridinecarboxaldehyde (0.028 g, 0.264 mmol) and 3-ethynylaniline (0.031 g, 0.264 mmol) were made to react in THF (25 mL) for 2 h. The solvent was evaporated in vacuo, and the residue was taken up in CH_2Cl_2 and filtered through silica gel. The purple band was collected and the solvent was evaporated in vacuo to obtain compound **3a** as a dark purple, microcrystalline solid. Yield 0.071 g, 64.9%. Anal. Calc. for $C_{18}H_{10}MoN_2O_4$: C 52.19, H 2.43, N 6.76. Found: C 52.37, H 2.53, N 6.87. 1H NMR (acetone- d_6): δ = 9.17 [d(5), 1H, H^6 py], 9.01 (s, 1H, $-CH=N-$), 8.30 [d(7), 1H, H^3 py], 8.23 [*pseudo-t*(8), 1H, H^4 py], 7.78–7.67 (m, 3H, H^5 py and $H^{2,4}$ Ph), 7.56 (m, 2H, $H^{5,6}$ Ph), 3.80 (s, 1H, $-C\equiv CH$).

3.7. $[Mo(CO)_4\{py-2-CH=N-C_6H_4-p-(C\equiv CH)\}]$ (**3b**)

Compound **3b** was prepared as described above for compound **3a**, starting from $[Mo(CO)_4(pip)_2]$ (0.1 g, 0.264 mmol), 2-pyridinecarboxaldehyde (0.028 g, 0.264 mmol) and 4-ethynylaniline (0.031 g, 0.264 mmol). The workup was as described for **3a** to afford compound **3b**. Yield 0.080 g, 73.2%. Anal. Calc. for $C_{18}H_{10}MoN_2O_4$: C 52.19, H 2.43, N 6.76. Found: C 52.34, H 2.50, N 6.84. 1H NMR (acetone- d_6): δ = 9.18 [d(5), 1H, H^6 py], 9.00 (s, 1H, $-CH=N-$), 8.29 [d(7), 1H, H^3 py], 8.23 [*pseudo-t*(7), 1H, H^4 py], 7.75 (m, 1H, H^5 py), 7.66 (m, 4H, $H^{2,3,5,6}$ Ph), 3.79 (s, 1H, $-C\equiv CH$).

3.8. $[MoCl(\eta^3-C_3H_4Me-2)(CO)_2\{py-2-CH=N-C_6H_4-m-(C\equiv CH)\}]$ (**4a**)

$[MoCl(\eta^3-C_3H_4Me-2)(CO)_2(NCMe)_2]$ [28] (0.1 g, 0.308 mmol), 2-pyridinecarboxaldehyde (0.033 g, 0.308 mmol) and 3-ethynylaniline (0.036 g, 0.308 mmol) were made to react in THF (25 mL) for 15 min. The solvent was evaporated in vacuo, and the residue was washed with hexane (3×10 mL). The resulting solid residue was dissolved in CH_2Cl_2 and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compound **4a** as dark blue microcrystals. Yield: 0.114 g, 82.5%. Anal. Calc. for $C_{20}H_{17}ClMoN_2O_2$: C 53.53, H 3.81, N 6.24. Found: C 53.70, H 3.90, N 6.34. 1H NMR (acetone- d_6): δ = 8.89 (m, 2H, H^6 py and $-CH=N-$), 8.24 (m, 2H, $H^{3,4}$ py), 7.74 (m, 3H, H^5 py and $H^{2,4}$ Ph), 7.55 (m, 2H, $H^{5,6}$ Ph), 3.80 (s, 1H, $-C\equiv CH$), 2.90 [d(4), 1H, H_{syn} allyl], 2.26 [d(4), 1H, H_{syn} allyl], 1.41 (s, 3H, $-CH_3$), 1.27 (s, 1H, H_{anti} allyl), 1.05 (s, 1H, H_{anti} allyl).

3.9. $[MoCl(\eta^3-C_3H_4Me-2)(CO)_2\{py-2-CH=N-C_6H_4-p-(C\equiv CH)\}]$ (**4b**)

Compound **4b** was prepared as described above for compound **4a**, starting from $[MoCl(\eta^3-C_3H_4Me-2)(CO)_2(NCMe)_2]$ (0.1 g, 0.308 mmol), 2-pyridinecarboxaldehyde (0.033 g, 0.308 mmol) and 4-ethynylaniline (0.036 g, 0.308 mmol). The workup was as described for **4a** to afford compound **4b**. Yield: 0.120 g, 86.8%. Anal. Calc. for $C_{20}H_{17}ClMoN_2O_2$: C 53.53, H 3.81, N 6.24. Found: C 53.71, H 3.90, N 6.30. 1H NMR (acetone- d_6): δ = 8.88 (m, 2H, H^6 py and $-CH=N-$), 8.23 (m, 2H, $H^{3,4}$ py), 7.76 (m, 1H, H^5 py), 7.65 (m, 4H, $H^{2,3,5,6}$ Ph), 3.82 (s, 1H, $-C\equiv CH$), 2.89 [d(3), 1H, H_{syn} allyl], 2.23 [d(3), 1H, H_{syn} allyl], 1.39 (s, 3H, $-CH_3$), 1.26 (s, 1H, H_{anti} allyl), 1.04 (s, 1H, H_{anti} allyl).

3.10. $[MnBr(CO)_3\{py-2-CH=N-C_6H_4-m-(\mu-C\equiv CH)Co_2(CO)_6\}]$ (**5**)

To a solution of compound **1a** (0.155 g, 0.364 mmol) in CH_2Cl_2 (25 mL) was added $Co_2(CO)_8$ (0.124 g, 0.364 mmol), and the mixture was stirred for 30 min. The solvent was evaporated in vacuo, and the residue was washed with hexane (3×10 mL). The residue was taken up in toluene and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compound **5** as red microcrystals. Yield: 0.246 g, 95%. Anal. Calc. for $C_{23}H_{10}BrMnCo_2N_2O_9$: C 38.85, H 1.42, N 3.94. Found: C 39.01, H 1.46, N 3.99. IR (THF), $\nu(CO)$: 2096m, 2059s, 2031vs, 1947s, 1926s, cm^{-1} . 1H NMR (acetone- d_6): δ = 9.31 (m, 1H, H^6 py), 8.93 (s, 1H, $-CH=N-$), 8.31 (m, 2H, $H^{3,4}$ py), 8.00 (s, 1H, H^2 Ph), 7.84 (m, 1H, H^5 py), 7.70 (m, 1H, H^4 Ph), 7.54 (m, 2H, $H^{5,6}$ Ph), 6.92 (s, 1H, $\mu-C-CH$).

3.11. $[ReBr(CO)_3\{py-2-CH=N-C_6H_4-m-(\mu-C\equiv CH)Co_2(CO)_6\}]$ (**6**)

Compound **6** was prepared as described above for compound **5**, from a solution of **2a** (0.137 g, 0.246 mmol) and $Co_2(CO)_8$ (0.084 g, 0.246 mmol). The workup was as described for **5** to afford compound **6**. Yield: 0.200 g, 96.5%. Anal. Calc. for $C_{23}H_{10}BrReCo_2N_2O_9$: C 32.80, H 1.20, N 3.33. Found: C 32.91, H 1.25, N 3.39. IR (THF), $\nu(CO)$: 2096m, 2059s, 2028vs, 1931s, 1906s, cm^{-1} . 1H NMR (acetone- d_6): δ = 9.35 (s, 1H, $-CH=N-$), 9.19 [d(5), 1H, H^6 py], 8.44 [d(7), 1H, H^3 py], 8.38 [*pseudo-t*(7), 1H, H^4 py], 8.00 (s, 1H, H^2 Ph), 7.89 (m, 1H, H^5 py), 7.73 [d(8), 1H, H^4 Ph], 7.56 (m, 2H, $H^{5,6}$ Ph), 6.91 (s, 1H, $\mu-C-CH$).

3.12. X-ray crystallography

Crystals suitable for diffraction studies were grown by slow diffusion of hexane into dichloromethane solutions (for **1a**, **1b**, **2a**, **2b**, **3b**, **4a** and **4b**) or toluene (for **5**) at

–20 °C. Data were collected on a Bruker Smart 1000 CCD diffractometer (graphite-monochromatized Mo K α radiation, $\lambda = 0.71073$ Å). Crystallographic data and experimental details for the structures are summarized in Table 1. Raw frame data were integrated with SAINT [29]. A semi-empirical absorption correction was applied with SADABS [30]. The structures were solved by direct methods with SIR 2002 [31] under WINGX [32] and refined against F^2 with SHELXTL [33]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. Graphics were made with SHELXTL. Additional calculations were made with PARST [34].

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Appendix A. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 292598 (compound **1a**), 292599 (**1b**), 292600 (**2a**), 292601 (**2b**), 292602 (**3b**), 292603 (**4a**), 292604 (**4b**) and 292605 (**5**). Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.04.024.

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