

# Mono- and Dimetallic Cyano Complexes with {Mo( $\eta^3$ -allyl)(CO)<sub>2</sub>(N–N)} Fragments

Julio Pérez,<sup>\*[a]</sup> Eva Hevia,<sup>[a]</sup> Lucía Riera,<sup>[a]</sup> Víctor Riera,<sup>[a]</sup> Santiago García-Granda,<sup>[a]</sup> Esther García-Rodríguez,<sup>[b]</sup> and Daniel Miguel<sup>[c]</sup>

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Treatment of [MoCl( $\eta^3$ -allyl)(CO)<sub>2</sub>(phen)] with NaCN in CH<sub>2</sub>Cl<sub>2</sub>/MeOH afforded [Mo(CN)( $\eta^3$ -allyl)(CO)<sub>2</sub>(phen)] [allyl = C<sub>3</sub>H<sub>5</sub> (**1a**); 2-MeC<sub>3</sub>H<sub>4</sub> (**1b**)] as the sole products (no products of cyanide attack on the allyl group were detected). Treatment of **1a,b** with [Mo(OTf)( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(phen)] and NaBAR'<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> yielded the compounds {[Mo( $\eta^3$ -allyl)(CO)<sub>2</sub>(phen)]( $\mu$ -CN){Mo( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(phen)}}BAR'<sub>4</sub> (**2a,b**). Analogous treatment of **1a** with *fac*-[M(OTf)(CO)<sub>3</sub>(bipy)] (M = Mn, Re) and NaBAR'<sub>4</sub> resulted in the synthesis of {[Mo( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(phen)]( $\mu$ -CN){M(CO)<sub>3</sub>(bipy)}}BAR'<sub>4</sub> (**3**,

**4**), in which the C and N atoms of the cyano bridge are bonded to Mo and M (M = Mn, Re), respectively. The linkage isomer of **4** (C and N atoms of the cyano group bonded to Re and Mo, respectively) (**6**) was prepared by treatment of [Re(CN)(CO)<sub>3</sub>(bipy)] (**5**) with [Mo(OTf)( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(phen)] and NaBAR'<sub>4</sub>. Compounds **1a**, **2b**, **3**, and **6** were characterized by X-ray diffraction.

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## Introduction

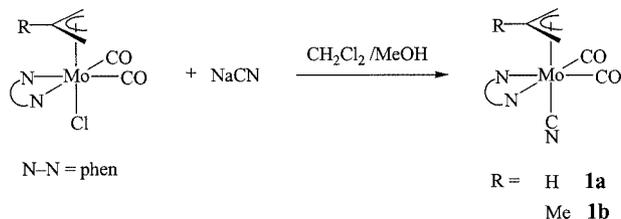
Monometallic complexes with terminal cyano ligands can act as metalloligands toward a second metal fragment through the uncoordinated nitrogen atom of the cyano group, affording dimetallic complexes with CN bridges,<sup>[1–6]</sup> simpler models of the supramolecular and solid-state entities in which cyano groups act as links between metal atoms.

We have recently found that pseudooctahedral [MoX( $\eta^3$ -allyl)(CO)<sub>2</sub>(N–N)] (N–N = 2,2'-bipyridine, bipy; 1,10-phenanthroline, phen) complexes react with organolithium or organomagnesium reagents and with sodium alkoxides to afford new alkyl,<sup>[7]</sup> alkynyl,<sup>[8]</sup> and alkoxo<sup>[9]</sup> complexes by selective halide substitution. A similar reactivity pattern would provide access to the previously unknown [Mo(CN)( $\eta^3$ -allyl)(CO)<sub>2</sub>(N–N)] complexes. Attractive features of the known [MoX( $\eta^3$ -allyl)(CO)<sub>2</sub>(N–N)] compounds are their ease of preparation<sup>[10]</sup> and the robustness of the {Mo( $\eta^3$ -allyl)(CO)<sub>2</sub>(N–N)} fragment<sup>[11]</sup> that directs the reactivity towards the remaining coordination position.<sup>[7–9]</sup> This paper summarizes the results of our

study on the reactivity of [MoX( $\eta^3$ -allyl)(CO)<sub>2</sub>(N–N)] complexes towards cyanide, as well as the behavior of the resulting cyano complexes as ligands.

## Results and Discussion

Treatment of [MoCl( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(phen)]<sup>[12]</sup> with excess sodium cyanide in CH<sub>2</sub>Cl<sub>2</sub>/MeOH resulted in the formation of [Mo(CN)( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(phen)] (**1a**) as the only product, as depicted in Scheme 1. Employment of methanol as co-solvent was needed to provide sufficient solubility for the sodium cyanide. The product **1a** was easily separated from the excess sodium cyanide and the sodium chloride by-product by extraction into pure CH<sub>2</sub>Cl<sub>2</sub>, followed by filtration and crystallization.



Scheme 1

The IR spectrum of **1a** shows, in addition to the two strong bands corresponding to the *cis*-Mo(CO)<sub>2</sub> fragment, a weak band indicative of the presence of a cyano group.<sup>[1,2]</sup> Its  $\nu_{\text{CN}}$  value (2113 cm<sup>-1</sup>) is higher than that of the free cyanide anion (2080 cm<sup>-1</sup>), as is typically found for C-

<sup>[a]</sup> Departamento de Química Orgánica e Inorgánica/I.U.Q.O.E.M., Facultad de Química, Universidad de Oviedo – C.S.I.C., Julián Clavería s/n, 33071 Oviedo, Spain

Fax: (internat.) + 34-985/103446

E-mail: japm@sauron.quimica.uniovi.es

<sup>[b]</sup> Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo – C.S.I.C., Julián Clavería s/n, 33071 Oviedo, Spain

<sup>[c]</sup> Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Spain

bound cyano ligands in transition metal complexes.<sup>[13]</sup> The <sup>1</sup>H NMR spectrum of **1a** reveals the presence of a molecular mirror plane (four signals for the phen ligand), and a symmetric, static η<sup>3</sup>-allyl group. The methallyl complex [Mo(CN)(η<sup>3</sup>-2-MeC<sub>3</sub>H<sub>4</sub>)(CO)<sub>2</sub>(phen)] (**1b**) was prepared in a similar manner. Its spectroscopic features are also indicative of a geometry like that of **1a**, and so the structures shown in Scheme 1 are assumed. The low solubility of **1a,b** in organic solvents precluded the observation of significant <sup>13</sup>C NMR spectroscopic data, but the structure of **1a** was determined by single-crystal X-ray diffraction. A view of the molecule is displayed in Figure 1, and selected distances and angles are given in Table 1.

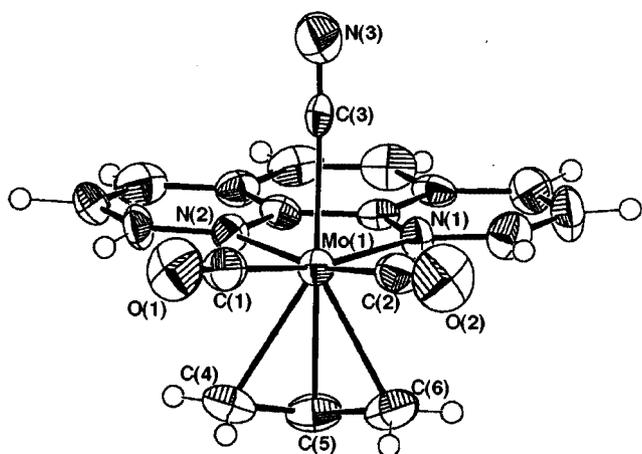


Figure 1. Molecular structure and numbering scheme of [Mo(CN)(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(phen)] (**1a**); thermal ellipsoids are drawn at the 30% probability level

Table 1. Selected bond lengths [Å] and angles [°] for [Mo(CN)(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(phen)] (**1a**)

Mo(1)–C(1)	1.966(7)	Mo(1)–N(1)	2.243(5)
Mo(1)–C(2)	1.959(9)	Mo(1)–N(2)	2.255(5)
Mo(1)–C(4)	2.329(7)	C(1)–O(1)	1.140(7)
Mo(1)–C(5)	2.229(7)	C(2)–O(2)	1.155(8)
Mo(1)–C(6)	2.325(7)	C(3)–N(3)	1.103(8)
Mo(1)–C(3)	2.188(8)		
C(1)–Mo(1)–C(2)	79.0(3)	C(2)–Mo(1)–C(3)	89.0(2)
N(1)–Mo(1)–N(2)	73.65(17)	C(3)–Mo(1)–N(1)	81.5(2)
C(1)–Mo(1)–N(1)	169.8(2)	C(3)–Mo(1)–N(2)	81.09(19)
C(2)–Mo(1)–N(2)	169.6(2)	N(3)–C(3)–Mo(1)	178.3(6)
C(1)–Mo(1)–C(3)	88.4(2)		

The molecule is isostructural with previously known [MoX(η<sup>3</sup>-allyl)(CO)<sub>2</sub>(N–N)] compounds.<sup>[14]</sup> It can thus be described, if the η<sup>3</sup>-allyl group is regarded as occupying one coordination position, as pseudooctahedral: the molybdenum atom is surrounded by the two carbonyl groups, the cyano group, the η<sup>3</sup>-allyl group, and the two nitrogen atoms of the phenanthroline ligand. The two CO groups are mutually *cis*, and each is *trans* to a phen nitrogen atom. The cyano and allyl groups are therefore mutually *trans*. The C(3)–N(3) [1.103(8) Å] and N(3)–C(3)–Mo(1) [178.3(6)

°] values are typical for M–C–N groupings,<sup>[1,2]</sup> and the Mo(1)–C(3) distance [2.188(8) Å] is similar to Mo–C(alkynyl) distances recently found in isostructural complexes.<sup>[8,15]</sup>

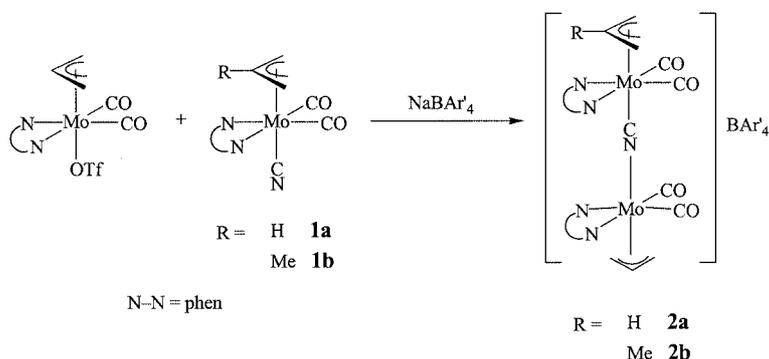
This structure concurs with the static structure in solution as deduced from the spectroscopic data (see above). In fact, X-ray diffraction does not allow clear differentiation between carbonyl and cyano groups, and so the spectroscopic data constitute the stronger evidence of their relative positions (two *cis*-carbonyl ligands related by a mirror plane). The cyano complexes **1a,b** are obtained in good yield, and no products resulting from cyanide anion attack on the allyl group could be detected. It is worth noting that, in general, attack on the allyl moiety is preferred for stabilized, soft nucleophiles, whereas hard ones preferentially attack the metal atom.<sup>[16,17]</sup> For [MoX(η<sup>3</sup>-allyl)(CO)<sub>2</sub>(L–L)] complexes in particular, stabilized carbanions – such as those resulting from deprotonation of dialkyl malonates – attack the allyl ligand.<sup>[18]</sup> In contrast, we have found here that the soft cyanide anion attacks the metal atom.

We aimed to explore the potential of the cyano complexes **1a,b** as ligands. We recently found that triflate abstraction from [Mo(OTf)(η<sup>3</sup>-allyl)(CO)<sub>2</sub>(phen)] can be smoothly effected by use of NaBAR'<sub>4</sub><sup>[19]</sup> [Ar' = 3,5-bis(trifluoromethyl)phenyl] in CH<sub>2</sub>Cl<sub>2</sub>.<sup>[20]</sup> We thus treated equimolar amounts of this triflate complex, **1a,b**, and NaBAR'<sub>4</sub>, in each case obtaining a single product, the IR ν<sub>CN</sub> band of which showed the shift to higher wavenumber values expected for a change in the coordination mode of the cyano group from terminal to bridge (ν<sub>CN</sub>: 2129 cm<sup>-1</sup> for **2a** and 2132 cm<sup>-1</sup> for **2b**) (Scheme 2).<sup>[1,2]</sup>

These compounds, partly due to the presence of the BAR'<sub>4</sub> anion, displayed high solubility in dichloromethane, allowing the acquisition of their <sup>13</sup>C NMR spectra. The most characteristic features are the weak signals at δ = 169.8 ppm (**2a**) and δ = 169.9 ppm (**2b**), attributable to the CN groups. Red crystals of **2a** could be obtained from CH<sub>2</sub>Cl<sub>2</sub>/hexane mixtures, but an attempt to determine its structure by X-ray diffraction was complicated by the severe disorder affecting one of the allyl groups. The analogous dimetallic compound **2b** did not suffer from this problem, and its structure could be determined with acceptable accuracy (see Figure 2 for a view of the cation, Tables 2 and 5 for selected geometrical data). The cation of **2b** consists of two {Mo(η<sup>3</sup>-allyl)(CO)<sub>2</sub>(N–N)} fragments, isostructural with that of **1a**, bridged by a CN group in linear fashion [Mo(1)–C(1)–N(1) = 176.2(8)°, C(1)–N(1)–Mo(2) = 179.4(8)°].

The bond between the cyano group and a second metal fragment is therefore formed without disruption of the Mo–CN bond. In contrast, the alkynyl group (for which similarities with CN as a ligand have been noted)<sup>[21]</sup> is transferred from {Mo(η<sup>3</sup>-allyl)(CO)<sub>2</sub>(N–N)} to other metal fragments.<sup>[15]</sup> Since the two metal fragments of **2b** are distinguishable, and only one species is present both in solution and in the crystal, the complex is stable with respect to CN ⇌ NC isomerization of the bridge.

We wanted to evaluate the ability of the new monometallic cyanomolybdenum complexes to act as ligands towards



Scheme 2

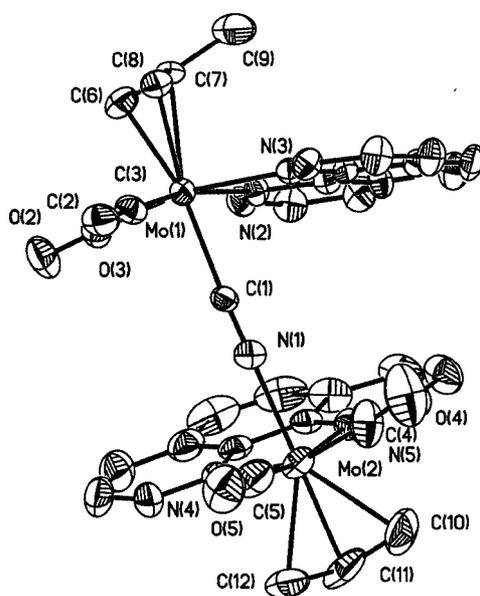


Figure 2. Thermal ellipsoid (30% probability) plot of the  $\{[\text{Mo}(\eta^3\text{-C}_3\text{H}_4\text{-Me-2})(\text{CO})_2(\text{phen})]\}(\mu\text{-CN})\{[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})]\}^+$  cation of **2b**, with hydrogen atoms omitted for clarity

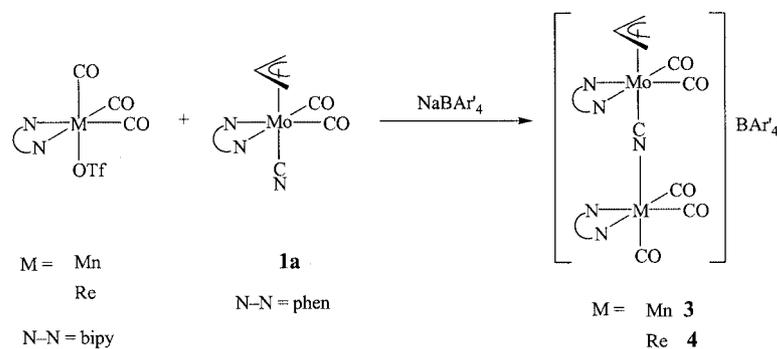
different metal centers. Treatment of the triflate complex  $[\text{Re}(\text{OTf})(\text{CO})_3(\text{bipy})]$  with the salt  $\text{NaBAR}'_4$  in the presence of neutral, two-electron ligands has recently been used to synthesize  $[\text{Re}(\text{L})(\text{CO})_3(\text{bipy})]\text{BAR}'_4$  compounds.<sup>[22]</sup> Similarly,  $[\text{Mo}(\text{CN})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})]$  (**1a**) reacted with  $[\text{M}(\text{OTf})(\text{CO})_3(\text{bipy})]$  ( $\text{M} = \text{Mn}, \text{Re}$ )<sup>[23]</sup> and  $\text{NaBAR}'_4$  to afford the dimetallic compounds **3** and **4**, respectively, as presented in Scheme 3.

The new compounds **3** and **4** could be isolated as solids by filtration, followed by crystallization (see Exp. Sect.). The simultaneous presence of the molybdenum and the manganese or rhenium fragments was indicated by the appearance of both the bipy and phen signals in a 1:1 ratio in the  $^1\text{H}$  NMR spectra. Accordingly, the IR spectra of **3** and **4**, in their  $\nu(\text{CO})$  regions, show two bands of similar intensity, attributed to the *cis*- $\text{Mo}(\text{CO})_2$  moiety, and bands similar to those of cationic *fac*- $[\text{M}(\text{CO})_3(\text{bipy})(\text{L})]^+$  ( $\text{M} = \text{Mn}, \text{Re}$ ) complexes. For the rhenium compound **4** the latter bands are some  $10\text{ cm}^{-1}$  lower than those of  $[\text{Re}(\text{CO})_3(\text{bi-}$

Table 2. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for the  $\{[\text{Mo}(\eta^3\text{-C}_3\text{H}_4\text{-Me-2})(\text{CO})_2(\text{phen})]\}(\mu\text{-CN})\{[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})]\}^+$  cation of **2b**

Mo(1)–C(2)	1.930(11)	Mo(2)–C(4)	1.966(12)
Mo(1)–C(3)	1.935(11)	Mo(2)–C(5)	1.904(13)
Mo(1)–C(6)	2.330(8)	Mo(2)–C(10)	2.325(11)
Mo(1)–C(7)	2.250(9)	Mo(2)–C(11)	2.226(12)
Mo(1)–C(8)	2.317(8)	Mo(2)–C(12)	2.258(11)
Mo(1)–C(1)	2.135(9)	Mo(2)–N(1)	2.195(8)
Mo(1)–N(2)	2.229(7)	Mo(2)–N(4)	2.250(8)
Mo(1)–N(3)	2.219(7)	Mo(2)–N(5)	2.249(8)
C(2)–O(2)	1.172(10)	C(4)–O(4)	1.173(11)
C(3)–O(3)	1.168(10)	C(5)–O(5)	1.193(12)
C(1)–N(1)	1.142(9)		
C(2)–Mo(1)–C(3)	82.0(4)	C(4)–Mo(2)–C(5)	76.3(5)
C(2)–Mo(1)–N(3)	167.1(3)	C(4)–Mo(2)–N(4)	164.3(4)
C(3)–Mo(1)–N(2)	167.7(3)	C(5)–Mo(2)–N(5)	170.1(4)
N(2)–Mo(1)–N(3)	74.3(3)	N(4)–Mo(2)–N(5)	73.4(3)
C(1)–Mo(1)–C(2)	87.7(4)	N(1)–Mo(2)–C(4)	86.2(4)
C(1)–Mo(1)–C(3)	89.7(4)	N(1)–Mo(2)–C(5)	87.9(4)
C(1)–Mo(1)–N(2)	78.8(3)	N(1)–Mo(2)–N(4)	79.0(3)
C(1)–Mo(1)–N(3)	79.5(3)	N(1)–Mo(2)–N(5)	82.8(3)
Mo(1)–C(1)–N(1)	176.2(8)	C(1)–N(1)–Mo(2)	179.4(8)

$\text{py})(\text{NCR})]\text{BAR}'_4$  ( $\text{R} = \text{Me}, \text{Ph}$ ),<sup>[22]</sup> indicating that the cyano complex is a stronger donor than nitriles. On the other hand, the frequencies corresponding to the *cis*- $\text{Mo}(\text{CO})_2$  fragment are little shifted with respect to those of the monometallic precursor. Thus, coordination of the cyano nitrogen atom to the rhenium atom modifies the electron density at the molybdenum center only a little. The presence of the bridging cyano group is shown by the weak C–N stretches in the IR spectra ( $2145\text{ cm}^{-1}$  for **3**,  $2140\text{ cm}^{-1}$  for **4**), and by the low-intensity signals in the  $^{13}\text{C}$  NMR spectra ( $\delta = 166.6$  and  $163.8$  ppm for **3** and **4**, respectively). The close similarity between these  $^{13}\text{C}$  NMR chemical shifts and those of the homodimetallic compounds **2a,b** is consistent with coordination of the cyano bridge to the molybdenum atom through the carbon atom in compounds **3** and **4** (see below for carbon coordination to a rhenium atom). Crystals of **3** suitable for structural determination by X-ray diffraction were obtained, and the results are presented in Figure 3, Tables 3 and 5. These results confirm the  $\{[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})]\}(\mu\text{-CN})\{[\text{Mn}(\text{CO})_3(\text{bipy})]\}\text{BAR}'_4$  formulation for **3**.



Scheme 3

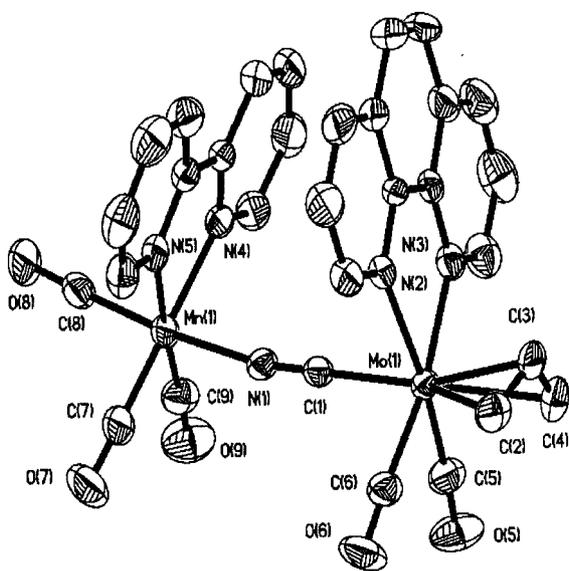


Figure 3. Thermal ellipsoid (30% probability) plot of the  $[\{\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})\}(\mu\text{-CN})\{\text{Mn}(\text{CO})_3(\text{bipy})\}]^+$  cation of **3**, with hydrogen atoms omitted for clarity

Table 3. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for the  $[\{\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})\}(\mu\text{-CN})\{\text{Mn}(\text{CO})_3(\text{bipy})\}]^+$  cation of **3**

Mn(1)–N(1)	2.008(4)	Mo(1)–C(6)	1.956(7)
Mo(1)–C(1)	2.161(5)	Mo(1)–C(5)	1.943(7)
C(1)–N(1)	1.148(6)	Mo(1)–N(2)	2.255(4)
Mn(1)–C(8)	1.812(6)	Mo(1)–N(3)	2.246(4)
Mn(1)–C(7)	1.809(7)	Mo(1)–C(2)	2.347(6)
Mn(1)–C(9)	1.797(8)	Mo(1)–C(3)	2.230(5)
Mn(1)–N(5)	2.051(5)	Mo(1)–C(4)	2.336(6)
Mn(1)–N(4)	2.051(4)		
N(1)–C(1)–Mo(1)	179.9(7)	C(6)–Mo(1)–C(1)	86.8(2)
C(1)–N(1)–Mn(1)	170.5(4)	C(5)–Mo(1)–C(1)	86.8(2)
C(8)–Mn(1)–N(1)	174.2(2)	C(1)–Mo(1)–N(3)	83.31(16)
C(7)–Mn(1)–N(1)	93.2(2)	C(1)–Mo(1)–N(2)	82.72(16)
C(9)–Mn(1)–N(1)	93.4(2)	N(3)–Mo(1)–N(2)	73.20(16)
N(5)–Mn(1)–N(4)	78.65(18)		

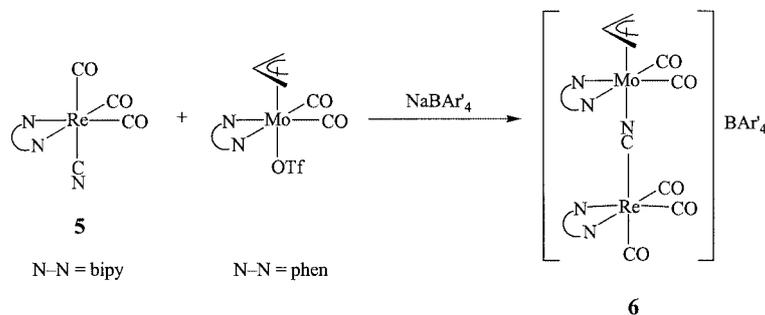
Given the asymmetric nature of the cyano bridge (i.e., one metal atom is bound to a carbon and the other to a nitrogen atom), heterodimetallic cyano-bridged complexes such as **3** and **4** have linkage isomers. For complexes **3** and

**4**, those isomers would feature Mo–N and M–C (M = Mn or Re) bonds. As recently pointed out, linkage isomers of cyano-bridged dimetallic complexes have been isolated in only a few instances.<sup>[24]</sup> This prompted us to attempt the synthesis of the linkage isomers of **3** and **4**. The Mo/Mn complex proved to be labile in solution, and attempts to isolate it by crystallization afforded crystals of the dimolybdenum compound **2a**. Therefore, only the Mo/Re complex is discussed.

The first step, just as in the synthesis of **3** and **4**, was to prepare the mononuclear cyano complexes.  $[\text{Re}(\text{CN})(\text{CO})_3(\text{bipy})]$  had previously been synthesized by heating  $[\text{ReCl}(\text{CO})_3(\text{bipy})]$  at reflux with a 100-fold molar excess of sodium cyanide in water or an ethanol/water mixture and subsequent extraction with dichloromethane.<sup>[25,26]</sup>

We have found that  $[\text{Re}(\text{CN})(\text{CO})_3(\text{bipy})]$  (**5**) can be conveniently prepared by treatment of the labile triflate complex  $[\text{Re}(\text{OTf})(\text{CO})_3(\text{bipy})]$  with tetraethylammonium cyanide. The reaction takes place in dichloromethane within 2 h at room temperature when 1.2 equiv. of  $[\text{Et}_4\text{N}]\text{CN}$  is used, and the IR spectrum of the resulting solution shows only the bands of  $[\text{Re}(\text{CN})(\text{CO})_3(\text{bipy})]$  (**5**). The coordinated cyano group appears as a weak signal at  $\delta = 156.1$  ppm in the  $^{13}\text{C}$  NMR spectrum. However, the isolated material (see Exp. Sect.) was contaminated with  $[\text{Et}_4\text{N}]\text{CN}$ , as indicated by the  $^1\text{H}$  NMR spectrum. Since purification of this mononuclear complex proved difficult, the crude material was employed for the synthesis of the targeted dimetallic compound. Thus, by the methodology used for the synthesis of **2**,  $[\text{Re}(\text{CN})(\text{CO})_3(\text{bipy})]$  (**5**) was added to the filtered solution obtained from the reaction between  $[\text{Mo}(\eta^3\text{-allyl})(\text{OTf})(\text{CO})_2(\text{phen})]$  and  $\text{NaBAR}'_4$  in  $\text{CH}_2\text{Cl}_2$ .

The formation of the dimetallic compound  $[\{\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2(\text{phen})\}(\mu\text{-NC})\{\text{Re}(\text{CO})_3(\text{bipy})\}]\text{BAR}'_4$  (**6**), depicted in Scheme 4, was instantaneous, as indicated by IR monitoring, and the product could be purified and isolated by crystallization and characterized by spectroscopy and single-crystal X-ray diffraction. The cyano ligand of **6** gives rise to a signal at  $\delta = 155.1$  ppm in the  $^{13}\text{C}$  NMR spectrum. This value, very close to that found for the mononuclear complex **5**, strongly supports C-coordination to Re in **6** (see above for the chemical shifts values found for the C–Mo isomer). The results of the structural determination of the



Scheme 4

cation are displayed in Figure 4, Tables 4 and 5. The cationic complex consists of a cyano bridge N-bonded to the molybdenum of an  $\{\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2(\text{phen})\}$  fragment, and C-bonded to the rhenium atom of a  $\{\text{Re}(\text{CO})_3(\text{bipy})\}$  fragment.

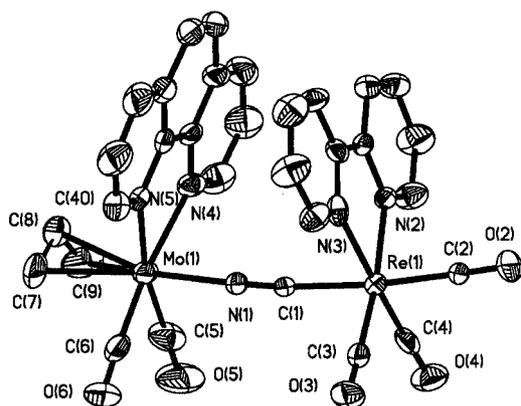


Figure 4. Thermal ellipsoid (30% probability) plot of the  $[\{\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})\}(\mu\text{-NC})\{\text{Re}(\text{CO})_3(\text{bipy})\}]^+$  cation of **6**, with hydrogen atoms omitted for clarity

Table 4. Selected bond lengths [Å] and angles [°] for the  $[\{\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})\}(\mu\text{-NC})\{\text{Re}(\text{CO})_3(\text{bipy})\}]^+$  cation of **6**

Mo(1)–N(1)	2.151(7)	Mo(1)–C(5)	1.916(13)
Re(1)–C(1)	2.123(8)	Mo(1)–C(6)	1.961(13)
C(1)–N(1)	1.143(9)	Mo(1)–N(4)	2.257(7)
Re(1)–C(2)	1.928(8)	Mo(1)–N(5)	2.228(8)
Re(1)–C(3)	1.948(9)	Mo(1)–C(7)	2.350(11)
Re(1)–C(4)	1.889(10)	Mo(1)–C(8)	2.227(9)
Re(1)–N(2)	2.162(6)	Mo(1)–C(9)	2.329(12)
Re(1)–N(3)	2.155(7)		
N(1)–C(1)–Re(1)	174.8(6)	C(5)–Mo(1)–N(1)	89.4(4)
C(1)–N(1)–Mo(1)	176.9(6)	C(6)–Mo(1)–N(1)	88.5(3)
C(2)–Re(1)–C(1)	174.5(3)	N(4)–Mo(1)–N(1)	82.0(2)
C(3)–Re(1)–C(1)	94.0(3)	N(5)–Mo(1)–N(1)	80.0(2)
C(4)–Re(1)–C(1)	91.1(3)	N(4)–Mo(1)–N(5)	73.9(3)
N(2)–Re(1)–N(3)	74.9(2)		

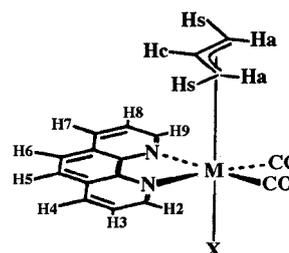
As in the isomer **4**, the IR spectrum of **6** shows sets of bands attributable to *cis*- $\{\text{Mo}(\text{CO})_2\}$  and *fac*- $\{\text{Re}(\text{CO})_3\}$ , together with a weak  $\nu_{\text{CN}}$  absorption at a higher frequency ( $2143\text{ cm}^{-1}$ ) than that of the starting monometallic cyano complex ( $2122\text{ cm}^{-1}$ ).

## Conclusion

In summary,  $[\text{Mo}(\text{CN})(\eta^3\text{-allyl})(\text{CO})_2(\text{phen})]$  complexes were easily synthesized and employed as building blocks for the preparation of cationic homo- and heterodimetallic cyano-bridged complexes by treatment with neutral triflate complexes in the presence of the salt  $\text{NaBAR}'_4$  as triflate abstractor. This strategy was extended to prepare the two linkage isomers of  $[\{\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2(\text{phen})\}(\mu\text{-NC})\{\text{Re}(\text{CO})_3(\text{bipy})\}]\text{BAR}'_4$ .

## Experimental Section

**General Remarks:** All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were distilled from freshly wired Na (hexanes) or  $\text{CaH}_2$  ( $\text{CH}_2\text{Cl}_2$  and MeOH) prior to use.  $\text{CD}_2\text{Cl}_2$  was degassed by three freeze-pump-thaw cycles, dried with molecular sieves (4 Å), and stored in the dark in a Young tube. Elemental analyses were obtained with a Perkin–Elmer 240-B microanalyzer. The IR and NMR spectra were recorded with Perkin–Elmer FT 1720-X and Bruker AC 200 or AC 300 spectrometers, respectively.  $[\text{MoCl}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})]$ ,<sup>[12]</sup>  $[\text{MoCl}(\eta^3\text{-C}_3\text{H}_4\text{-2-Me})(\text{CO})_2(\text{phen})]$ ,<sup>[27]</sup>  $[\text{Mo}(\text{OTf})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})]$ ,<sup>[20]</sup>  $[\text{M}(\text{OTf})(\text{CO})_3(\text{bipy})]$  (M = Mn, Re),<sup>[23]</sup> and  $\text{NaBAR}'_4$ <sup>[19]</sup> were prepared according to literature procedures. All other chemicals were used as received from commercial sources.  $\text{H}_s$  and  $\text{H}_a$  designate the *syn*- and *anti*-H atoms, respectively, of the allyl and methallyl ligands;  $\text{H}_c$  is the central H atom of the allyl ligand. The atom-labeling scheme for the allyl, 1,10-phenanthroline, and  $\text{BAR}'_4$  groups is shown below.



**$[\text{Mo}(\text{CN})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})]$  (1a):** NaCN (0.013 g, 0.294 mmol) was added to a solution of  $[\text{MoCl}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})]$  (0.100 g, 0.245 mmol) in a mixture of  $\text{CH}_2\text{Cl}_2$  (20 mL) and MeOH (3 mL), and the mixture was stirred for 2 h at room temperature. The red solution obtained was concentrated in vacuo, and the residue was

Table 5. Crystal data and refinement details for complexes **1a**, **2b**, **3**, and **6**

	<b>1a</b>	<b>2b</b>	<b>3</b>	<b>6</b>
Empirical formula	C <sub>18</sub> H <sub>13</sub> MoN <sub>3</sub> O <sub>2</sub> ·CH <sub>2</sub> Cl <sub>2</sub>	C <sub>68</sub> H <sub>40</sub> BF <sub>24</sub> Mo <sub>2</sub> N <sub>5</sub> O <sub>4</sub> ·0.25CH <sub>2</sub> Cl <sub>2</sub>	C <sub>64</sub> H <sub>35</sub> BF <sub>24</sub> MnMoN <sub>5</sub> O <sub>5</sub> ·CH <sub>2</sub> Cl <sub>2</sub>	C <sub>64</sub> H <sub>35</sub> BCl <sub>2</sub> F <sub>24</sub> MoN <sub>5</sub> O <sub>5</sub> Re·CH <sub>2</sub> Cl <sub>2</sub>
Molecular mass	484.18	1670.47	1642.56	1773.82
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	Pbca	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c
<i>a</i> [Å]	14.5230(10)	12.6202(19)	17.9066(12)	18.3397(18)
<i>b</i> [Å]	12.5750(10)	18241(3)	20.2195(14)	20.457(2)
<i>c</i> [Å]	21.0800(10)	31.537(5)	19.5450(13)	18.6142(18)
β [°]	90	100.241(3)	105.8300(10)	97.957(2)
<i>V</i> [Å <sup>3</sup> ]	3849.8(4)	7144.2(19)	6808.1(8)	6916.4(12)
<i>Z</i>	8	4	4	4
<i>T</i> [K]	293(2)	295(2)	297(2)	299(2)
<i>D</i> <sub>c</sub> [g cm <sup>-3</sup> ]	1.671	1.553	1.603	1.703
<i>F</i> (000)	1936	3320	3264	3464
λ(Mo- <i>K</i> <sub>α</sub> ) [Å]	1.54184	0.71073	0.71073	0.71073
Crystal size [mm]		0.19 × 0.13 × 0.06	0.14 × 0.20 × 0.34	0.09 × 0.14 × 0.24
μ [mm <sup>-1</sup> ]	8.297	0.483	0.566	2.123
Scan range [°]	5.10 to 68.17	1.29 to 23.33	1.18 to 23.29	1.12 to 23.33
No. of reflections measured	4259	31565	43929	30961
No. of ind. reflections	2782	10321	9791	9984
No. of data/restraints/parameters	2782/0/298	10321/0/960	9791/ 0/925	9984/ 0/298
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.002	1.013	1.028	1.019
<i>R</i> <sub>1</sub> / <i>R</i> <sub>w2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0533/0.1258	0.0686/0.1571	0.0602/0.1646	0.0489/0.1184
<i>R</i> <sub>1</sub> / <i>R</i> <sub>w2</sub> (all data)	0.0697/0.1312	0.1436/0.1780	0.0759/0.1840	0.0822/0.1353

redissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered through Celite. The volatiles were removed in vacuo, and the residue was washed with hexane (3 × 10 mL). Slow diffusion of hexane into a solution of [Mo(CN)(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(phen)] (**1a**) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) at room temperature produced red crystals of **1a**. A single crystal obtained in this way was used for the X-ray analysis. Yield: 0.088 g, 90%. C<sub>18</sub>H<sub>13</sub>MoN<sub>3</sub>O<sub>2</sub> (399.26): calcd. C 54.15, H 3.28, N 10.52; found C 54.11, H 3.07, N 10.15. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu}$  = 2113 (ν<sub>C≡N</sub>), 1952, 1868 (ν<sub>CO</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 9.06 (dd, *J*<sub>2,3-H</sub> = *J*<sub>9,8-H</sub> = 5.0, *J*<sub>2,4-H</sub> = *J*<sub>7,9-H</sub> = 1.5 Hz, 2 H, 2,9-H), 8.52 (dd, *J*<sub>H4,3</sub> = *J*<sub>H7,8</sub> = 8.3 Hz, 2 H, 4,7-H), 7.98 (s, 2 H, 5,6-H), 7.81 (dd, 2 H, 3,8-H), 3.35 (d, *J*<sub>H5,c</sub> = 6.5, 2 H, H<sub>s</sub>), 3.01 (m, 1 H, H<sub>c</sub>), 1.83 (d, *J*<sub>H<sub>a,c</sub></sub> = 9.8 Hz, 2 H, H<sub>a</sub>) ppm.

[Mo(CN)(η<sup>3</sup>-2-MeC<sub>3</sub>H<sub>4</sub>)(CO)<sub>2</sub>(phen)] (**1b**): The procedure was similar to that described above for the preparation of **1a**, starting from [MoCl(η<sup>3</sup>-2-MeC<sub>3</sub>H<sub>4</sub>)(CO)<sub>2</sub>(phen)] (0.100 g, 0.237 mmol) and NaCN (0.014 g, 0.284 mmol). Yield: 0.090 g, 92%. C<sub>19</sub>H<sub>15</sub>MoN<sub>3</sub>O<sub>2</sub> (413.28): calcd. C 55.22, H 3.66, N 10.17; found C 55.01, H 3.34, N 10.38. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu}$  = 2112 (ν<sub>C≡N</sub>), 1950, 1870 (ν<sub>CO</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 9.02 (dd, *J*<sub>2,3-H</sub> = *J*<sub>9,8-H</sub> = 5.0, *J*<sub>2,4-H</sub> = *J*<sub>7,9-H</sub> = 1.3, 2 H, 2,9-H), 8.53 (dd, *J*<sub>4,3-H</sub> = *J*<sub>7,8-H</sub> = 8.2 Hz, 2 H, 4,7-H), 8.00 (s, 2 H, 5,6-H), 7.83 (dd, 2 H, 3,8-H), 3.10 (s, 2 H, H<sub>s</sub>), 1.81 (s, 2 H, H<sub>a</sub>), 0.59 [s, 3 H, η<sup>3</sup>-C<sub>3</sub>H<sub>4</sub>(CH<sub>3</sub>)] ppm.

[{Mo(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(phen)}<sub>2</sub>(μ-CN)]BAR'<sub>4</sub> (**2a**): NaBAR'<sub>4</sub> (0.093 g, 0.105 mmol) was added to a solution of [Mo(OTf)(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(phen)] (0.055 g, 0.105 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL), and the resulting slurry was stirred for 15 min. The solution was filtered by cannula into a solution of [Mo(CN)(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(phen)] (**1a**, 0.038 g, 0.105 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) and the deep red solution obtained was stirred for 2 h. The solution was then concentrated in vacuo to a volume of 5 mL, and slow diffusion of hexane at room temperature gave red crystals of **2a**. Yield: 0.110 g, 71%. C<sub>67</sub>H<sub>38</sub>BF<sub>24</sub>Mo<sub>2</sub>N<sub>5</sub>O<sub>4</sub> (1635.73): calcd. C 49.20, H 2.34, N 4.28;

found C 48.93, H 2.38, N 4.34. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu}$  = 2129 (ν<sub>C≡N</sub>), 1958, 1878 (ν<sub>CO</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 8.75, 8.59, 8.46, 7.96, 7.95 and 7.68 (m, 16 H, 2 × phen), 7.78 (m, 8 H, C<sub>o</sub>-H), 7.58 (m, 4 H, C<sub>p</sub>-H), 3.27 (d, *J*<sub>H<sub>s,c</sub></sub> = 6.4 Hz, 2 H, H<sub>s</sub>), 3.19 (d, *J*<sub>H<sub>s,c</sub></sub> = 6.4 Hz, 2 H, H<sub>s</sub>), 2.87 (m, 2 H, H<sub>c</sub>), 1.75 (d, *J*<sub>H<sub>a,c</sub></sub> = 9.5 Hz, 2 H, H<sub>a</sub>), 1.45 (d, *J*<sub>H<sub>a,c</sub></sub> = 9.4 Hz, 2 H, H<sub>a</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 223.7 and 223.2 (CO), 169.8 (CN), 152.3, 152.1, 144.7, 138.6, 138.3 and 130.3 (phen), 162.1 (q, *J* = 49.8 Hz, C<sub>i</sub>), 135.2 (C<sub>o</sub>), 129.3 (q, *J* = 31.4 Hz, C<sub>m</sub>), 124.9 (q, *J* = 272.4 Hz, CF<sub>3</sub>), 117.9 (C<sub>p</sub>), 79.0 (C-2 of η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>), 60.2 (C-1 and C-3 of η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>), 57.8 (C-1 and C-3 of η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>) ppm.

[{Mo(η<sup>3</sup>-C<sub>3</sub>H<sub>4</sub>-Me-2)(CO)<sub>2</sub>(phen)}(μ-CN)]{Mo(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(phen)}]BAR'<sub>4</sub> (**2b**): The procedure was similar to that described above for the preparation of **2a**, starting from [Mo(CN)(η<sup>3</sup>-2-MeC<sub>3</sub>H<sub>4</sub>)(CO)<sub>2</sub>(phen)] (**1b**, 0.047 g, 0.115 mmol), [Mo(OTf)(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(phen)] (0.060 g, 0.115 mmol) and NaBAR'<sub>4</sub> (0.102 g, 0.115 mmol) to give complex **2b**. Yield: 0.143 g, 79%. C<sub>68</sub>H<sub>40</sub>BF<sub>24</sub>Mo<sub>2</sub>N<sub>5</sub>O<sub>4</sub> (1649.75): calcd. C 49.51, H 2.44, N 4.24; found C 49.17, H 2.38, N 4.01. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu}$  = 2132 (ν<sub>C≡N</sub>), 1959, 1878 (ν<sub>CO</sub>) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 8.73, 8.54, 8.47, 7.98 and 7.68 (m, 16 H, 2 × phen), 7.74 (m, 8 H, C<sub>o</sub>-H), 7.56 (m, 4 H, C<sub>p</sub>-H), 3.17 (d, *J*<sub>H<sub>s,c</sub></sub> = 6.5 Hz, 2 H, H<sub>s</sub>), 3.01 (s, 2 H, H<sub>s</sub>), 2.99 (d, *J*<sub>H<sub>s,c</sub></sub> = 6.7 Hz, 2 H, H<sub>s</sub>), 1.70 (s, 2 H, H<sub>a</sub>), 1.68 (d, *J*<sub>H<sub>a,c</sub></sub> = 9.2 Hz, 2 H, H<sub>a</sub>), 1.42 (d, *J*<sub>H<sub>a,c</sub></sub> = 9.3 Hz, 2 H, H<sub>a</sub>), 0.42 [s, 3 H, C<sub>3</sub>H<sub>4</sub>(CH<sub>3</sub>)] ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 223.7 and 223.6 (CO), 169.9 (CN), 152.1, 151.9, 144.8, 138.7, 138.1, 130.5, 127.8, 127.7, 125.4, 125.3, 125.2 and 119.5 (2 × phen), 162.1 (q, *J* = 49.4 Hz, C<sub>i</sub>), 135.1 (C<sub>o</sub>), 129.2 (q, *J* = 34.2 Hz, C<sub>m</sub>), 124.9 (q, *J* = 272.4 Hz, CF<sub>3</sub>), 117.8 (C<sub>p</sub>), 88.9, 73.6, 71.4, 58.3, 58.1 and 57.7 [C-1, C-2 and C-3 of η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub> and η<sup>3</sup>-C<sub>3</sub>H<sub>4</sub>(CH<sub>3</sub>)], 17.6 [η<sup>3</sup>-C<sub>3</sub>H<sub>4</sub>(CH<sub>3</sub>)] ppm.

[{Mo(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(phen)}(μ-CN)]{Mn(CO)<sub>3</sub>(bipy)}]BAR'<sub>4</sub> (**3**): NaBAR'<sub>4</sub> (0.099 g, 0.112 mmol) was added to a solution of [Mn(OTf)(CO)<sub>3</sub>(bipy)] (0.050 g, 0.112 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL)

and the resulting solution was stirred for 15 min at room temperature. The color of the solution turned from yellow to orange. The solution was filtered by cannula into a solution of  $[\text{Mo}(\text{CN})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})]$  (**1a**, 0.045 g, 0.112 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) and the color of the solution turned bright red. The resulting solution was concentrated in vacuo to a volume of 5 mL, and slow diffusion of hexane at  $-20^\circ\text{C}$  gave dark orange crystals of **3**. A single crystal obtained in this way was used for the X-ray analysis. Yield: 0.105 g, 62%.  $\text{C}_{63}\text{H}_{33}\text{BF}_{24}\text{MnMoN}_5\text{O}_5$  (1557.64): calcd. C 48.58, H 2.13, N 4.50; found C 48.78, H 1.98, N 4.85. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu} = 2145$  ( $\nu_{\text{C}=\text{N}}$ ), 2042, 1957, 1877 ( $\nu_{\text{CO}}$ )  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 8.77, 8.64, 8.45$  and  $7.94$  (m, 2 H each bipy and phen),  $7.76$  (m, 10 H,  $\text{C}_o\text{-H}$  and 4 H, bipy),  $7.57$  (m, 4 H  $\text{C}_p\text{-H}$ ),  $7.39$  (m, 2 H, phen),  $3.33$  (m, 2 H,  $\text{H}_c$ ),  $2.96$  (m, 1 H,  $\text{H}_c$ ),  $1.81$  (m, 2 H,  $\text{H}_a$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 223.9$  (2 CO, Mo-CO),  $219.4$  (2 CO, Mn-CO)  $217.1$  (1 CO, Mn-CO),  $166.6$  (CN),  $155.4, 153.3, 152.5, 144.9, 139.4, 138.94, 130.4, 127.8, 127.0, 125.3$  and  $122.6$  (bipy and phen),  $78.5$  (C-1 and C-3 of  $\eta^3\text{-C}_3\text{H}_5$ ),  $59.9$  (C-2 of  $\eta^3\text{-C}_3\text{H}_5$ ) ppm.

$\{[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})](\mu\text{-CN})[\text{Re}(\text{CO})_3(\text{bipy})]\}$ BAR'<sub>4</sub> (**4**): The procedure was similar to that described above for the preparation of **3**, starting from  $[\text{Re}(\text{OTf})(\text{CO})_3(\text{bipy})]$  (0.050 g, 0.087 mmol),  $[\text{Mo}(\text{CN})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})]$  (**1a**, 0.034 g, 0.087 mmol), and NaBAR'<sub>4</sub> (0.077 g, 0.087 mmol), to give complex **4** as a microcrystalline red powder. Yield: 0.040 g, 69%.  $\text{C}_{60}\text{H}_{28}\text{BF}_{24}\text{MoN}_5\text{O}_5\text{Re}$  (1647.84): calcd. C 43.73, H 1.71, N 4.25; found C 43.44, H 1.89, N 4.57. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu} = 2140$  ( $\nu_{\text{C}=\text{N}}$ ), 2033, 1958, 1930, 1877 ( $\nu_{\text{CO}}$ )  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 8.76, 8.63$  and  $8.50$  (m, 2 H each bipy and phen),  $8.12$  (m, 4 H, bipy),  $7.99$  (m, 2 H, phen),  $7.76$  (m, 8 H,  $\text{C}_o\text{-H}$ , 2 H, phen and 2 H, bipy),  $7.57$  (m, 4 H  $\text{C}_p\text{-H}$ ),  $7.45$  (m, 2 H, phen),  $3.36$  (d,  $J_{\text{H}_{\text{sc}}} = 6.5$  Hz, 2 H,  $\text{H}_c$ ),  $2.98$  (m, 1 H,  $\text{H}_c$ ),  $1.83$  (d,  $J_{\text{H}_{\text{ac}}} = 9.2$  Hz, 2 H,  $\text{H}_a$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 225.3$  (2 CO, Mo-CO),  $196.1$  (2 CO, Re-CO),  $189.8$  (1 CO, Re-CO),  $163.8$  (CN),  $157.7, 155.2, 154.5, 146.9, 142.3, 140.6, 132.6, 129.9, 128.7, 127.4$  and  $119.9$  (bipy and phen),  $81.0$  (C-1 and C-3 of  $\eta^3\text{-C}_3\text{H}_5$ ),  $62.5$  (C-2 of  $\eta^3\text{-C}_3\text{H}_5$ ) ppm.

$[\text{Re}(\text{CN})(\text{CO})_3(\text{bipy})]$  (**5**):  $\text{NEt}_4\text{CN}$  (0.016 g, 0.104 mmol) was added to a solution of  $[\text{Re}(\text{OTf})(\text{CO})_3(\text{bipy})]$  (0.050 g, 0.087 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL), the mixture was stirred for 2 h at room temperature, and the color of the solution turned from yellow to orange. The volatiles were removed in vacuo and the residue was washed with  $\text{Et}_2\text{O}$  ( $3 \times 15$  mL). IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu} = 2122$  ( $\nu_{\text{C}=\text{N}}$ ), 2023, 1920 ( $\nu_{\text{CO}}$ )  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 9.02, 8.36, 8.14$  and  $7.56$  (2 H each, bipy),  $3.24$  (q,  $J = 7.1$  Hz,  $\text{CH}_2$ ,  $\text{Et}_4\text{N}$ ),  $1.31$  (t,  $J = 7.1$  Hz,  $\text{CH}_3$ ,  $\text{Et}_4\text{N}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 196.1$  and  $191.2$  (CO),  $156.1$  (CN),  $153.6, 143.1, 139.7, 127.7$  and  $124.1$  (bipy),  $53.86$  ( $\text{CH}_2$ ,  $\text{Et}_4\text{N}$ ),  $7.11$  ( $\text{CH}_3$ ,  $\text{Et}_4\text{N}$ ) ppm.

$\{[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})](\mu\text{-NC})[\text{Re}(\text{CO})_3(\text{bipy})]\}$ BAR'<sub>4</sub> (**6**): NaBAR'<sub>4</sub> (0.093 g, 0.105 mmol) was added to a solution of  $[\text{Mo}(\text{OTf})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})]$  (0.055 g, 0.105 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL), and the resulting slurry was stirred for 15 min. The solution was filtered by cannula into a solution of  $[\text{Re}(\text{CN})(\text{CO})_3(\text{bipy})]$  (**5**, 0.047 g, 0.105 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL), and the deep red solution obtained was stirred for 2 h. The solution was then concentrated in vacuo to a volume of 5 mL, and slow diffusion of hexane at room temperature gave red crystals of **6**. Yield: 0.151 g, 87%.  $\text{C}_{60}\text{H}_{28}\text{BF}_{24}\text{MoN}_5\text{O}_5\text{Re}$  (1647.84): calcd. C 43.73, H 1.71, N 4.25; found C 43.61, H 2.03, N 4.17. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu} = 2143$  ( $\nu_{\text{C}=\text{N}}$ ), 2030, 1947, 1926, 1875 ( $\nu_{\text{CO}}$ )  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 8.89, 8.49, 8.15, 8.06$  and  $7.37$  (m, 32 H, bipy, phen and BAR'<sub>4</sub>),  $3.26$  (d,  $J_{\text{H}_{\text{sc}}} = 6.0$  Hz, 2 H,  $\text{H}_c$ ),  $2.70$  (m, 1 H,  $\text{H}_c$ ),  $1.51$  (d,  $J_{\text{H}_{\text{ac}}} = 9.3$  Hz, 2 H,  $\text{H}_a$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 225.75$  and  $224.15$  (2

CO, Mo-CO),  $193.61$  (2 CO, Re-CO)  $191.78$  (1 CO, Re-CO),  $162.49$  (q,  $J = 49.9$  Hz,  $\text{C}_i$ ),  $155.67$  (CN),  $155.66, 153.35, 152.35, 139.95, 138.98$  (bipy and phen),  $135.20$  ( $\text{C}_o$ ),  $130.48, 130.40$  (bipy and phen),  $129.27$  (q,  $J = 31.9$  Hz,  $\text{C}_m$ ),  $127.92, 127.86, 126.79$  (bipy and phen),  $124.38$  (q,  $J = 272.3$  Hz,  $\text{CF}_3$ ),  $119.57$  (phen),  $117.91$  ( $\text{C}_p$ ),  $73.87$  (C-1 and C-3 of  $\eta^3\text{-C}_3\text{H}_5$ ),  $59.9$  (C-2 of  $\eta^3\text{-C}_3\text{H}_5$ ) ppm.

**X-ray Crystallographic Study:**<sup>[28]</sup> The crystal of **1a** was measured with a Nonius CAD4 diffractometer. Profile analysis was performed on all reflections.<sup>[29,30]</sup> Symmetry-equivalent and other redundant reflections were averaged, and drift, Lorentz, and polarization corrections were applied. The structure was solved by Patterson methods with DIRDIF-96.<sup>[31]</sup> Isotropic least-squares refinement was carried out on  $F^2$  by use of SHELXL-97.<sup>[32]</sup> An empirical absorption correction was applied at this stage, by use of XABS2.<sup>[33]</sup> All atoms were located by Fourier synthesis. During the final stages of the refinement, all positional parameters and the anisotropic temperature factors of all the non-H atoms were refined with SHELXL-97.<sup>[31]</sup> The atoms were isotropically refined. Plots were made with the EUCLID package.<sup>[34]</sup> Geometrical calculations were performed with PARST.<sup>[35]</sup> Data in common for compounds **2b**, **3**, and **6**: Bruker AXS SMART 1000 CCD diffractometer,  $\phi$  and  $\omega$  scans, Mo- $K_\alpha$  radiation ( $\lambda = 0.71073$  Å), graphite monochromator,  $T = 295$  K. Raw frame data integrated by use of the SAINT<sup>[36]</sup> program. Structures were solved by direct methods with SHELXTL,<sup>[37]</sup> semiempirical absorption correction with SADABS.<sup>[38]</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All calculations were performed with SHELXTL.

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