

Figure 1. Molecular structure of *fac*-(CO)₃Mo(PhC₃H₆)₃ (**3**). Selected bond lengths (Å) and angles (deg): Mo–P(1), 2.507 (1); Mo–P(2), 2.455 (1); Mo–P(3), 2.465 (1); Mo–C(1), 1.983 (4); Mo–C(2), 1.987(3); Mo–C(3), 1.962(3); C(1)–O(1), 1.142 (5); C(2)–O(2), 1.162 (4); C(3)–O(3), 1.146(4); P–C range, 1.826 (4)–1.848 (4); C–C range, 1.510 (5)–1.525 (5); ∠P–Mo–P range, 88.18 (3)–89.27 (3); ∠C–Mo–P(cis) range, 87.7 (1)–92.8 (1); ∠C–Mo–C range, 90.45 (1)–93.5 (1).

gave identical ³¹P NMR and mass spectra. Recrystallization of **3** from CD₂Cl₂ yields only needles.⁹ Single-crystal X-ray analysis of these needles results in the structure¹⁰ shown in Figure 1. The complex consists of a [12]ane-P₃ ring, *facially* coordinated to the Mo(CO)₃ moiety. The molecule has approximate C₃ symmetry, with a mirror plane passing through Mo, P(1), O(2), C(2), and C(8). The macrocycle ring structure is such that two of the six-membered metallocycle rings, [MoP(1)C(4)C(5)C(6)P(2)] and MoP(3)C(10)C(11)C(12)P(1)], are in chair conformations while the third ring, [MoP(2)C(7)C(8)C(9)P(3)], is in a boat conformation. In contrast, in solution at 25 °C, a structure having either an all-boat or all-chain conformation or an "averaged" conformation arises, since only one ³¹P NMR resonance is observed.

Selected bond distances and angles are given in the figure legend. The Mo–P and M–C_{CO} distances are typical of those observed in other phosphine–molybdenum(0) carbonyl complexes.¹¹ The principal structural distortion involves the Mo–P(1) and Mo–C(2) distances, which are slightly longer than the other Mo–P and Mo–C distances, respectively. It is noted these bonds are from Mo to the atoms that share octahedral faces with the phosphorus atoms [P(2) and P(3)] of the boat-conformation metallocycle.

The formation of the triligated *sec*-phosphine macrocyclic ligand in **3** involves anti-Markovnikov P–H bond addition across the carbon–carbon double bonds of neighboring allyl groups, in a novel metal-templated process. The reaction exemplifies the kinetic template effect since uncoordinated allylphosphine when treated with AIBN yields entirely different products.¹² The reaction is

(9) Crystal data for (CO)₃Mo(PhC₃H₆)₃ (needles from CD₂Cl₂): space group P2₁/c, *a* = 12.606 (3) Å, *b* = 8.508 (2) Å, *c* = 15.420 (2) Å, β = 93.39 (2)°, *V* = 1652.5 (6) Å³, *D*_o = 1.61 g cm⁻³, *D*_c = 1.616 g cm⁻³, *Z* = 4. Data were collected on a Syntex P1 autodiffractometer using graphite-monochromatized Mo Kα radiation.

(10) The structure was solved by heavy-atom techniques and refined by full-matrix least-squares calculations to *R* = 0.026 and *R*_w = 0.032 for 2685 unique observed reflections. Hydrogen atoms were located, and their positions were refined; anisotropic thermal parameters were used for the non-hydrogen atoms. Details of the refinement and structure will be published later.

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clean, resulting in only slight molybdenum carbonyl complex degradation and no evidence for intramolecular ring closure to form coordinated phosphabutane rings or intermolecular P–H bond addition. The reaction is highly regioselective; no Markovnikov addition product has been detected.

Studies of the generality of this metal-templated cyclization approach, derivatization of the hydridomacrocycles complexes, and displacement of the macrocyclic phosphine from the metal are in progress currently.

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Registry No. **2**, 82456-41-5; **3**, 82456-42-6; *fac*-(CO)₃Mo mesitylene, 12089-15-5; AIBN, 78-67-1.

Supplementary Material Available: Tables of positional and thermal parameters (2 pages). Ordering information is given on any current masthead page.

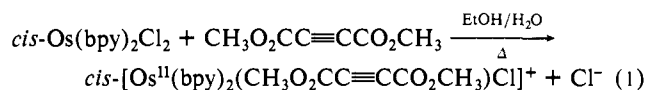
Cleavage of the Triple Bond in Phenylacetylene by Monomeric Ru(II) and Os(II) Complexes. Formation of Stable Ru(II) Alkyls from Terminal Alkynes

B. Patrick Sullivan,*^{1a} Robert S. Smythe,^{1b}
Edward M. Kober,^{1a} and Thomas J. Meyer*^{1a}

Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

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Complexes of ruthenium(II) containing "classical" ligands such as ammonia, pyridine, or polypyridine, or halide ions are known to bind with either alkenes or alkynes to form stable, isolable products such as [Ru^{II}(NH₃)₅(3-hexyne)]²⁺.^{2,3} We have extended this work to the synthesis and characterization of 2,2'-bipyridine (bpy) and 2,2',2''-terpyridine (trpy) complexes of both Os(II) and Ru(II) with unsaturated carbon ligands. Not surprisingly, quite stable complexes can be prepared containing internal alkynes, an example of which is shown in eq 1.⁴ Quite remarkably, under the



same reaction conditions but with phenylacetylene as the alkyne the carbonyl complex, *cis*-[Os(bpy)₂(CO)Cl]⁺, is obtained.⁵ The reaction is general for octahedral complexes of Ru(II) and Os(II) with one labile halide ligand in that the precursor complexes *cis*-Ru^{II}(bpy)₂Cl₂, *cis*-[Ru^{II}(trpy)(bpy)Cl](PF₆), and *cis*-Os^{II}(phen)[1,2 bis(diphenylphosphino)benzene]Cl₂ (phen = 1,10-phenanthroline) all give the corresponding monocarbonyl products in 70–91% yield.⁶ A somewhat related but less well-defined process has been observed as a competing reaction in the chlororuthenium(III)-catalyzed hydration of acetylenes.⁷

(1) (a) The University of North Carolina. (b) On leave from James Cook University, Townsville, Australia.

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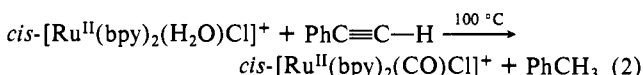
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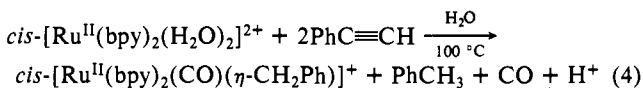
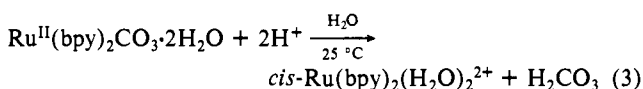
(6) All of the carbonyl complexes were characterized by cyclic voltammetry, elemental analysis, infrared spectroscopy, and in some cases by ¹H NMR spectroscopy.

We have studied in detail the particular reaction of $\text{PhC}\equiv\text{CH}$ with $\text{cis-Ru}^{\text{II}}(\text{bpy})_2\text{Cl}_2$, which is present as $\text{cis-}[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{H}_2\text{O})\text{Cl}]^+$ as the dominant form in aqueous solution. We find that the reaction involves a metal-promoted hydration/disproportionation of the alkyne (eq 2).



In a typical stoichiometry experiment 0.64 mmol of $\text{cis-Ru}^{\text{II}}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ⁸ was heated at reflux with 0.78 mmol of $\text{PhC}\equiv\text{CH}$ in 20 mL of deoxygenated water for 3 h. Extraction of the reaction mixture with Et_2O and subsequent gas chromatographic analysis yielded 0.46 mmol of PhCH_3 as compared with 0.44 mmol of isolated $\text{cis-}[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$.⁹ The remaining ruthenium complexes in the reaction mixture were present as a mixture of cis- and $\text{trans-Ru}^{\text{II}}(\text{bpy})_2(\text{H}_2\text{O})_2^{2+10}$ and a small amount of a crystalline orange material, identified as shown below, as the air, water, and chromatographically stable ruthenium alkyl complex $\text{cis-}[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{CO})(\eta\text{-CH}_2\text{Ph})](\text{PF}_6)$. With H_2^{18}O (99.7%, Mound Laboratories) the Ru product was shown to be $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{C}^{18}\text{O})\text{Cl}]^+$ by the shift of $\nu(\text{CO})$ from $\nu(\text{C}^{16}\text{O})$ 1985 cm^{-1} to $\nu(\text{C}^{18}\text{O})$ 1943 cm^{-1} in CH_2Cl_2 solution ($\Delta\nu(\text{CO}) = 47 \text{ cm}^{-1}$, calculated on the basis of the change in reduced mass). In D_2O the product is $\text{C}_6\text{H}_5\text{CD}_3$ as shown by mass spectrometry.¹¹

Ruthenium carbonylbenzyl complexes are formed directly and in high yield as products of the reaction between phenylacetylene and the diaquo complexes $\text{cis-Ru}(\text{bpy})_2(\text{H}_2\text{O})_2^{2+}$ or $\text{cis-Ru}(\text{trpy})(\text{PPh}_3)(\text{H}_2\text{O})_2^{2+}$. The diaquo complexes were generated in situ by the stoichiometric addition of $\text{CF}_3\text{CO}_2\text{H}$ to the corresponding carbonato¹² complexes (eq 3) in water or by the thermal aquation of the Cl^- groups from $\text{cis-Ru}(\text{trpy})(\text{PPh}_3)\text{Cl}_2$.¹³



The stoichiometry of the reaction between $\text{cis-Ru}(\text{bpy})_2(\text{H}_2\text{O})_2^{2+}$ and $\text{PhC}\equiv\text{CH}$ as shown in eq 4 was determined by GC detection of toluene, as described above, and mass balance; no attempt was made to analyze for gaseous CO. The incorporation of H and O atoms from water in the carbonylbenzyl product was shown by infrared using H_2^{18}O where $\nu(\text{C}^{16}\text{O})$ 1944 cm^{-1} and $\nu(\text{C}^{18}\text{O}) = 1896 \text{ cm}^{-1}$ in the product and by $^1\text{H NMR}$ using D_2O where the disappearance of benzylic C-H resonances was observed (see Figure 1b).

Reasonably certain structural assignments for the benzyl



complexes $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{CO})(\eta\text{-CH}_2\text{Ph})]^+$ and $[\text{Ru}(\text{trpy})-$

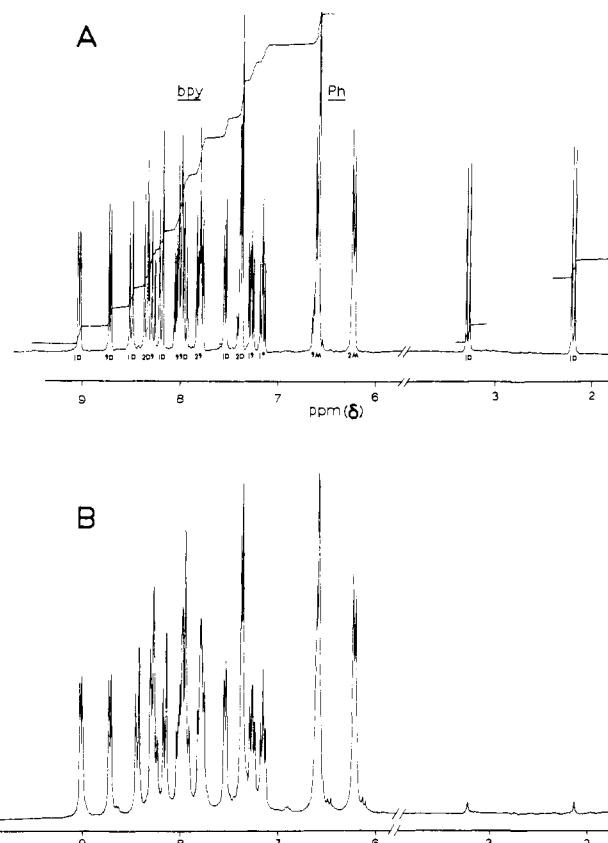


Figure 1. $^1\text{H NMR}$ spectrum in CD_2Cl_2 of (a) $[\text{cis-Ru}(\text{bpy})_2(\text{CO})(\eta\text{-CH}_2\text{Ph})](\text{PF}_6)$ and (b) $[\text{cis-Ru}(\text{bpy})_2\text{CO}(\eta\text{-CD}_2\text{Ph})](\text{PF}_6)$ isolated as the product of the reaction in D_2O (99.5%); see text. Me_4Si and methylene chloride peaks are deleted.

$(\text{PPh}_3)(\text{CO})(\eta\text{-CH}_2\text{Ph})]^+$ (note structure I above) are available based on elemental analyses¹⁴ and ^1H , ^{13}C , and ^{31}P NMR spectroscopy and for the bpy complex, field desorption mass spectrometry. In the latter experiment, a parent ion peak appeared at m/e 533 (^{102}Ru) as the most intense peak in the isotopic manifold.

Figure 1a shows the $^1\text{H NMR}$ spectrum of $\text{cis-}[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{CO})(\eta\text{-CH}_2\text{Ph})]^+$ taken in CD_2Cl_2 . In the spectrum there are eight doublets and eight triplets in first order in the bpy region, two multiplets of area 3 (ortho and para) and 2 (meta) for the phenyl protons, and two magnetically nonequivalent benzylic protons at δ 2.15 and 3.27 with a geminal coupling constant of 10.3 Hz. For $[\text{Ru}(\text{trpy})(\text{PPh}_3)(\text{CO})(\eta\text{-CH}_2\text{Ph})]^+$ a trpy + PPh_3 proton region of 26 protons occurs from δ 8.5 to 6.9 in addition to the 3:2 phenyl multiplet region centered at δ 6.54 and 5.88, respectively. The benzylic protons in the complex are both symmetrically and magnetically equivalent, appearing as a sharp doublet ($^3J_{\text{PH}} = 5.3 \text{ Hz}$) of area 2 at δ 2.26.

The $^{13}\text{C NMR}$ spectra of both complexes (see Figure 2b) show the carbonyl resonance at ca. +200–205 ppm (CD_3CN as internal standard) and a phenyl and polypyridyl region extending from +120 to +150 ppm. Both complexes show a benzylic carbon resonance at ca. 24 ppm with coupling to chemically equivalent protons; for $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{CO})(\eta\text{-CH}_2\text{Ph})]^+$ a triplet ($^1J_{\text{CH}} = 128 \text{ Hz}$) and for $[\text{Ru}(\text{trpy})\text{PPh}_3(\text{CO})(\eta\text{-CH}_2\text{Ph})]^+$ a doublet of triplets ($^1J_{\text{CH}} = 132.3 \text{ Hz}$, $^2J_{\text{PC}} = 45.8 \text{ Hz}$). That phosphorus-carbon ($-\text{CH}_2-$) coupling, $J_{\text{PRuCH}_2} = 45.8 \text{ Hz}$, is greater than phosphorus-carbon ($-\text{CO}$) coupling, $J_{\text{PRuCO}} = 12.7 \text{ Hz}$, suggests that the benzyl group is trans to phosphorus. The assignment is supported by the profound upfield chemical shift for PPh_3 in the $^{31}\text{P NMR}$ spectrum in CH_3CN . In our case, the $^{31}\text{P NMR}$ resonance for $\text{Ru}(\text{trpy})(\text{PPh}_3)(\text{CO})(\eta\text{-CH}_2\text{Ph})^+$ occurred at +28.3 ppm (vs.

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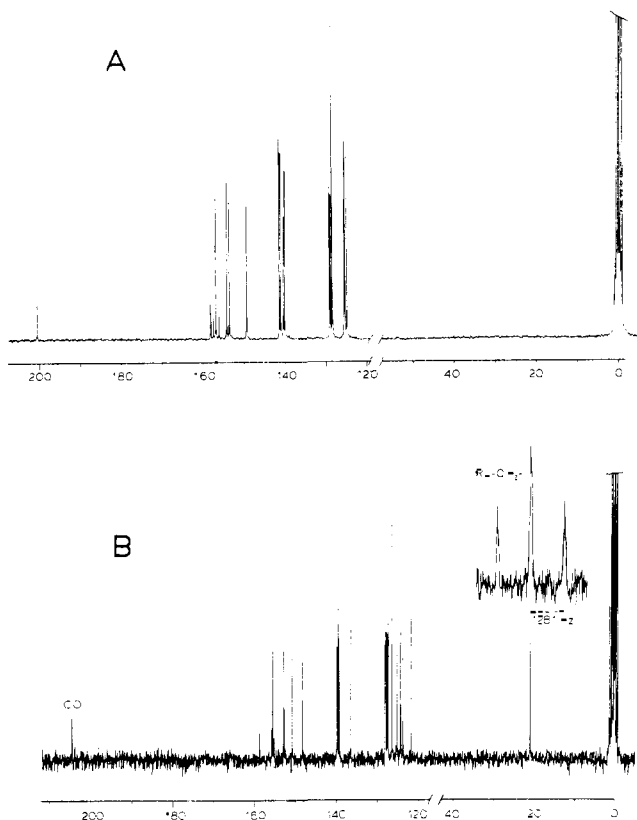


Figure 2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in CD_3CN of (a) $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$ produced by the reaction between $\text{PhC}\equiv\text{CH}$ and $\text{cis-}[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ and (b) $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{CO})(\eta\text{-CH}_2\text{Ph})]^+$ produced by the reaction between $\text{PhC}\equiv\text{CH}$ and $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$. The nitrile carbon resonance of CD_3CN has been deleted for clarity.

H_3PO_4) compared with -6.0 and -20.1 ppm for PPh_3 and $\text{trans-}[\text{Ru}(\text{trpy})(\text{PPh}_3)_2\text{Cl}]^+$, respectively.¹² It can be inferred from the chemical shift data that PPh_3 is trans to a powerful electron-donating substituent.

Further indication that the benzyl group is a powerful σ donor at Ru^{II} comes from cyclic voltammetry and electronic spectral data. In acetonitrile, oxidation of $\text{Ru}(\text{II})$ to $\text{Ru}(\text{III})$ for $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{CO})(\eta\text{-CH}_2\text{Ph})]^+$ is shifted negatively by ca. 0.7 V ($E_{\text{pa}} = 0.76$ V vs. SCE) compared to $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$ ($E_{1/2} = 1.50$ V). The λ_{max} for the lowest $\pi^*(\text{bpy}) \leftarrow d\pi(\text{Ru})$ CT transition in CH_3CN , which is also a measure of electron density⁸ at Ru^{II} , is at 476 nm for $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{CO})(\eta\text{-CH}_2\text{Ph})]^+$ and at 400 nm (sh) for $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$.

The mechanism(s) for the conversion of phenylacetylene to CO and toluene or to CO and the benzyl complex are not known in detail but are currently under investigation. Reasonable intermediates that can be anticipated are acetylene, vinylidene, acetylidene, hydroxycarbene, and acyl complexes, all of which have chemical precedents in the chemistries of Re^{I} , Pt^{II} , Ru^{II} , or Fe^{II} .¹⁵ The chemistry appears to be general for terminal alkynes in that we have also observed reactions with acetylene and 1-hexyne, and it seems clear that we will be able to study the mechanisms of the reactions in some detail.

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tional Science Foundation under Grant No. CHE-8008922 for support of this research.

Registry No. $\text{PhC}\equiv\text{CH}$, 536-74-3; $\text{cis-}[\text{Ru}^{\text{II}}(\text{bpy})_2\text{Cl}_2]$, 19542-80-4; $\text{cis-}[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{H}_2\text{O})\text{Cl}]^+$, 76739-35-0; PhCH_3 , 108-88-3; $\text{cis-}[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$, 79850-20-7; $\text{cis-}[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$, 72174-09-5; $\text{trans-}[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$, 72174-10-8; $\text{cis-}[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{CO})(\eta\text{-CH}_2\text{Ph})](\text{PF}_6)$, 82482-60-8; $\text{cis-}[\text{Ru}^{\text{II}}(\text{trpy})(\text{PPh}_3)(\text{H}_2\text{O})_2]^{2+}$, 82482-61-9; $\text{cis-}[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{CO})(\eta\text{-CH}_2\text{Ph})]^+$, 82482-59-5; $[\text{Ru}^{\text{II}}(\text{trpy})(\text{PPh}_3)(\text{CO})(\eta\text{-CH}_2\text{Ph})]^+$, 82482-62-0; $\text{Ru}^{\text{II}}(\text{bpy})_2\text{CO}_3$, 59460-48-9.

Iron EXAFS of the Iron-Molybdenum Cofactor of Nitrogenase

Mark R. Antonio,^{1a} Boon-Keng Teo,^{*1b}
W. H. Orme-Johnson,^{1c*} Mark J. Nelson,^{1c} Susan E. Groh,^{1c}
Paul A. Lindahl,^{1c} Susan M. Kauzlarich,^{1a} and
Bruce A. Averill^{*1b}

Department of Chemistry, Michigan State University
East Lansing, Michigan 48824
Bell Laboratories, Murray Hill, New Jersey 07974
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
Received February 1, 1982

Chemical and physical analyses indicate that the iron-molybdenum cofactor ($\text{FeMo}(\text{co})$) of nitrogenase contains 6–8 mol of iron and 4–6 mol of sulfur per mol of molybdenum.^{2–5} The physical properties of this cofactor suggest that it contains a novel Mo-Fe-S cluster.⁴ The complementation of inactive molybdenum-iron protein by isolated cofactor^{2,3} indicates that it is an important functional component of the enzyme. Thus, determination of the structure of the cofactor is of significance and interest.

Extended X-ray absorption fine structure (EXAFS) data taken at the Mo edge indicate that the molybdenum has two or three iron atoms and four or five sulfur atoms as nearest neighbors.^{6–8} Several models are consistent with these data, including those with (1) a MoFe_3S_4 cluster with one molybdenum and three iron atoms at alternate corners of a distorted cube,^{9,10} (2) two Fe atoms bridged by a MoS_4 group,⁶ (3) two Fe_4S_4 cubes bridged by a MoS_4 unit,⁸ (4) two Fe_3S_3 units bridged by a molybdenum atom,¹¹ and (5) a $[\text{L}_3\text{MoFe}_7\text{S}_6(\text{SR})_7]^{2-}$ cluster containing a MoFe_5S_6 core with the metal atoms situated at corners of a cube and the quadruply bridging sulfurs occupying the six faces of the cube.¹² More information concerning the iron environment is needed to define the structure of the $\text{FeMo}(\text{co})$. We report here the successful measurement and analysis of the iron edge EXAFS of the FeMoco from *Azotobacter vinelandii* and relate initial structural information about the iron sites in that cluster.

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