Supplementary Material Available: A brief outline of a representative experimental procedure for the synthesis of [Cp*ZrMe$_2$(η^6-PhMe)][BMe(C$_6$F$_5$)$_3$] and of a typical low-temperature NMR experiment on the unstable compound [Cp*ZrMe$_2$(η^6-PhCH=CH$_2$)][BMe(C$_6$F$_5$)$_3$] (1 page). Ordering information is given on any current masthead page.

Structure of the First Stable Ethene–Ethyne Metal Complex. Reaction of an Osmium(II) Dihydrogen Complex with Alkenes and Alkynes

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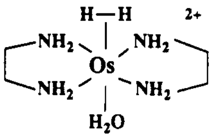
Since the discovery of the first η^2-dihydrogen complex in 1984,[2] the study of this class of compounds has become a very active area in the field of transition metal chemistry.[3] Recently, we have been interested in the η^2-dihydrogen osmium(II) complex, *trans*-[Os(en)$_2$(H$_2$)(H$_2$O)](CF$_3$SO$_3$)$_2$ (en = ethylenediamine), **1**,[4] which can conveniently be made by the reduction of *trans*-[Os(en)$_2$(O)$_2$](CF$_3$SO$_3$)$_2$ in water.[5] Herein, we report the synthesis



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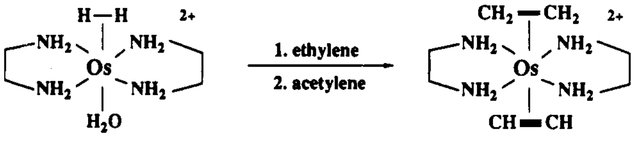
of a stable ethene–ethyne metal complex from this η^2-dihydrogen complex. The reaction of **1** with other alkene and alkyne molecules will also be described.

In a nitrogen atmosphere, ethylene was bubbled through a solution of **1** (0.088 mmol, 6.1 mM) in acetone.[6a,b] After 21 h, the solution was heated under N$_2$ at 50 °C for 20 h,[7] and then acetylene was bubbled through for 18 h. After removal of the solvent under vacuum, the residue was loaded onto an ion-exchange resin (Sephadex-SP, C-25) with water. Hydrochloric acid (0.2 M) was used to elute, and the first green band was collected. The chloride salt of **2** was isolated as a greenish solid in 85% yield after vacuum removal of the solvent and recrystallization from water/acetone. The ^{1}H NMR spectrum of **2** in deuterated water



1 **2**

demonstrates that upon coordination the proton signal of ethyne shifts downfield from δ ~2 to δ 7.30 (s, 2 H), whereas the proton signal of ethene shifts upfield from δ ~5 to δ 3.19 (s, 4 H). In the proton-coupled ^{13}C NMR spectrum of the compound, a doublet of doublets at δ 103.4 (J = 28, 241 Hz) is assigned to the ethyne ligand. A triplet is observed at δ 55.15 (J = 159 Hz) for the ethene ligand.

Although both stoichiometric and catalytic alkyne/alkene coupling reactions have attracted considerable interest and have increasingly found applications in organic chemistry,[8] very few compounds containing both alkene and alkyne ligands have been isolated.[9,10] Structural information of the parent type of this class of compounds is not available, though a *cis*-ethene–ethyne metal complex has been used as a model for theoretical calculations.[9a] To our knowledge, **2** is the first isolated stable metal ethene–ethyne complex.[10]

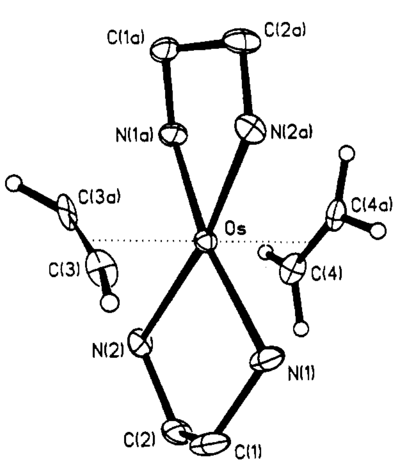
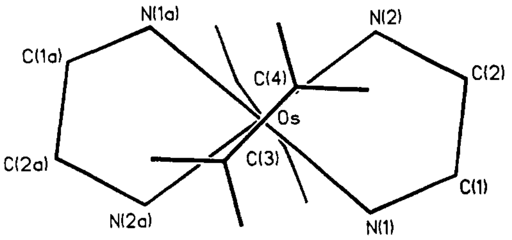


Figure 1. Molecular structure of **2**.

A single-crystal X-ray analysis has been performed on **2**,[11] and the structure shows a distorted octahedral geometry about the osmium center with *trans*-en ligands and *trans*-ethene–ethyne ligands (Figure 1). The trans-coordinated ethene and ethyne molecules are almost orthogonal to each other, with an angle of 78.3°. The drawing below, in which the structure of **2** is viewed along the ethene–Os–ethyne axis, shows the relative conformation of the ethene and ethyne ligands.



This orthogonal arrangement can be understood as resulting from the competition of the two π acid ligands for π d electron density which is minimized when orthogonal orbitals are engaged. Prior

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(5) The procedure to prepare **1**: In a nitrogen box, to a water solution of *trans*-[Os(en)$_2$(O)$_2$](CF$_3$SO$_3$)$_2$ (625 mg, 0.99 mmol, 38 mM) was added Zn[Hg] (12 g). The light brown solution immediately turned black, gradually fading to form a white slurry. After the reaction mixture was stirred at room temperature for 2 days, water was removed under vacuum and acetone was added to extract the product. A light yellow green solution was obtained after filtration through Celite. Addition of ether produced **1** as a greenish solid (415 mg) in 66% yield.

(6) (a) The ^{1}H NMR spectrum of the reaction mixture shows the disappearance of the η^2-H$_2$ signal and formation of two compounds, A and B. Compound A is a monoethene coordinated compound which has NMR peaks at δ 3.11 (s, 4 H, CH$_2$=CH$_2$), 2.68 (m, 4 H, CH_2NH$_2$), and 2.40 (m, 4 H, CH_2NH$_2$). Compound B is a *trans*-bis(ethene) coordinated compound which has NMR peaks at δ 3.78 (s, 8 H, CH$_2$=CH$_2$) and 2.76 (br, 8 H, CH_2NH$_2$). (b) Prior to this work, Z. Li in this laboratory has shown that, at room temperature in acetone as solvent, treatment of *trans*-[Os(NH$_3$)$_4$(η^2-H$_2$)]$^{2+}$ with ethene produces *trans*-[Os(NH$_3$)$_4$(C$_2$H$_4$)$_2$]$^{2+}$ and of *trans*-[Os(en)$_2$(η^2-H$_2$)]$^{2+}$ produces *trans*-[Os(en)$_2$(C$_2$H$_4$)$_2$]$^{2+}$, each in recovered yield (triflate salt) exceeding 80%.

(7) ^{1}H NMR spectroscopy shows that the bis(ethene) complex B has been completely converted to the monoethene complex A.[6a]

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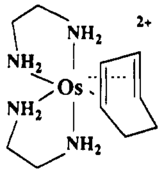
Table I. Selected Data for the Structure of **2** and of Other Alkene–Alkyne Metal Complexes[a]

	M–C(alkyne)	M–C(alkene)	Δ[b]	C≡C	C=C	∠C≡C–R, deg
trans-$[Os(en)_2(CH{\equiv}CH)(CH_2{=}CH_2)]^{2+}$, **2**	2.155(4)	2.175(4)	0.02	1.199(9)	1.352(9)	157.4(1)
cis-$W(ma)(PhC{\equiv}CH)(S_2CNEt)_2$[9a]	2.006(8)	2.233(9)	0.24	1.32(1)	1.41(1)	136.6(8)
ma = maleic anhydride	2.01(1)	2.261(8)				
$[CpMo(PPh_2C_6H_4CH{=}CH_2)(MeC{\equiv}CMe)]^{+}$[9b]	1.996(8)	2.266(7)	0.25	1.293(10)	1.425(11)	142.0(8)
	2.037(7)	2.265(8)				136.7(7)
cis-$W(PhC{\equiv}CPh)(CH_2{=}CH_2)(Cl)_2(PMe_3)_2$[9c]	2.033(5)	2.248(5)	0.22	1.330(10)	1.399(13)	135.7(5)
	2.033(5)	2.248(5)				128.0(5)

[a] The bond distances are in Å. [b] Δ is the average of M–C(alkene) – M–C(alkyne).

to our work only three alkene–alkyne metal compounds had been structurally characterized (see Table I).[9a–c] Comparison of the structure of **2** with the structures of these compounds reveals two striking differences. In contrast to their disposition in **2**, the alkene and alkyne ligands in the Mo or W complexes are cis and lie parallel. Moreover, in **2**, the metal–C(alkene) and –C(alkyne) bond distances are almost identical, but in the other compounds, the metal–C(alkene) bond distances are more than 0.2 Å longer than the metal–C(alkyne) bond distances. It is likely that the alkyne ligand in the W and Mo complexes acts as a 4e⁻ donor, while in **2** the ethyne ligand is a 2e⁻ donor, a change which leads to bond lengthening. Coordination of ethyne to the osmium center causes severe distortion of the molecule. The two C–H bonds bend away from the original linear configuration with a C–C–H angle of 153.4°, and the ligand loses planarity, the dihedral H–C–C–H angle being 60.5°.

When the dihydrogen complex **1** is treated with 1,3-cyclohexadiene or 1,4-cyclohexadiene, trans–cis isomerization occurs and both **3** and **4**, respectively, are isolated and characterized. To find out if a similar trans–cis isomerization occurs in the ethene–ethyne complex **2**, it was heated at 79 °C in D_2O. After 20 min, ^1H NMR spectroscopy showed decomposition of the compound with no indication of the formation of alkene–alkyne coupling products. **1** reacts with a conjugated dialkyne, 2,4-hexadiyne, to give a metallacyclopentatriene complex, **5**, an alkyne–alkyne coupling product analogous to that isolated from the reaction of **1** with 2-butyne.[4c,d] In contrast to the behavior of the internal alkynes just described, the reaction of **1** with ethyne leads to a *trans*-bis(ethyne) complex, **6**. *trans*-Bis(alkyne) complexes have not been observed as intermediates for the formation of metallacyclopentatrienes. Studies toward an understanding of the factors controlling alkene and alkyne coupling on the osmium center are under way.



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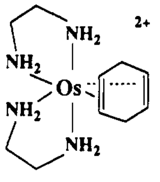

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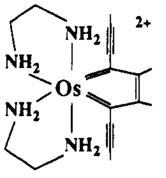

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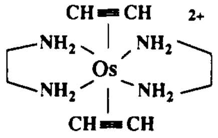

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Supplementary Material Available: Listings of analytical and spectroscopic data for compounds **2–6** and tables of atomic coordinates and equivalent isotropic displacement coefficients, bond lengths, bond angles, heavy atom anisotropic displacement coefficients, hydrogen atom coordinates, and isotropic displacement coefficients for **2** (5 pages); table of observed and calculated structure factors for **2** (5 pages). Ordering information is given on any current masthead page.

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(11) Crystal data for **2** (140 K): $C_8H_{22}N_4OsCl_2{\cdot}2H_2O$, monoclinic, $C2/c$, $a = 10.549(3)$ Å, $b = 10.885(3)$ Å, $c = 13.261(6)$ Å, $V = 1522.1(9)$ Å^3, $Z = 4$, $D_{calcd} = 2.057$ g cm^{-3}, $\mu = 8.742$ mm^{-1}. A colorless block (0.70 × 0.30 × 0.30 mm) was cut from a needle-shaped crystal and used for data collection (Siemens R3m/V, $0.0° < 2\theta < 50.0°$, Mo Kα). Of 2865 reflections collected, 1331 were independent ($R_{int} = 3.50\%$) and empirically corrected for absorption (XEMP and XABS programs were used). The atoms were located by Patterson and difference Fourier methods and refined by full-matrix least squares. Hydrogen atoms on ethylenediamines were placed in calculated positions, while hydrogens on ethene and ethyne were refined freely. All hydrogens had fixed isotropic U. $R = 2.09\%$, R_w $(=\sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1/2}) = 2.33\%$, all data $R = 2.09\%$, $wR = 3.20\%$, GOF $(=[\sum(w||F_o| - |F_c||^2)/(M - N)]^{1/2}) = 0.88$. All computer programs and sources of scattering factors are contained in SHELXTL PLUS (G. M. Sheldrick, A Program for Crystal Structure Determination, Version 4.0, 1989, Siemens Analytical X-ray Instruments, Madison, WI).

Enhanced Site-Specific Cleavage of the Tetracycline Repressor by Tetracycline Complexed with Iron

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The last several years have seen a serious increase in the emergence of bacterial infections resistant to previously effective antimicrobial agents.[1] Rational drug design based on a molecular

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