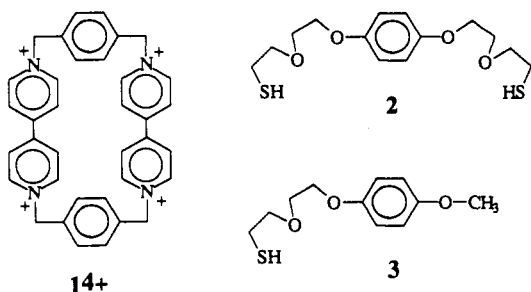tertwined macrocycles (see Scheme I). The second macrocyclic component is provided by cyclophane $\mathbf{1^{4+}}$, which is *indirectly, but irreversibly, attached to the electrode surface through its mechanical linkage to the hydroquinol ring.*

The confinement of $\mathbf{1^{4+}}$ to the electrode surface was verified using electrochemical methods. Clean gold bead electrodes were first exposed overnight to a deoxygenated MeCN solution[9] containing both **2** and $\mathbf{1^{4+}}$, rinsed extensively with MeCN and highly purified water, and immersed in deoxygenated aqueous 0.1 M Na_2SO_4 for voltammetric analysis. Figure 1 shows a typical cyclic voltammogram obtained with an electrode treated in this way. The voltammetric response confirmed the presence of surface-confined viologen groups. The set of waves centered around –0.46 V vs SSCE is consistent with the reversible monoelectronic reduction of the surface-confined viologen groups ($\Delta E_p \leq 40$ mV at scan rate ≤ 500 mV/s; linear i_{pc} vs scan rate plot). This voltammetric response was stable and did not exhibit significant changes after several hours of potential cycling. Furthermore, viologen reduction waves are observed only after the gold electrode is exposed to a solution containing both compounds (**2** and $\mathbf{1^{4+}}$).[9] No faradaic response in the potential window of interest was observed if either one of these compounds was absent in the monolayer-forming solution. Similarly, exposing the gold electrode first to a solution of **2** and then to a solution of $\mathbf{1^{4+}}$ does not result in the observation of reproducible surface-confined viologen waves. Experiments with monothiol hydroquinol **3** were particularly informative. This compound also forms an inclusion charge-transfer complex with $\mathbf{1^{4+}}$ although the binding constant in MeCN at 25 °C was found to be lower (73 ± 5 M^{-1}) than the corresponding value for **2**. However, no viologen waves were detected in the voltammetric response of gold electrodes which were first exposed overnight to MeCN solutions containing **3** and $\mathbf{1^{4+}}$, rinsed, and later transferred to the aqueous supporting electrolyte solution. The fact that one thiol group is not enough to afford surface-confined viologen groups clearly supports the formation of surface-attached catenanes in the case of the bis(thiol) **2**.

Assuming that the observed voltammetric waves correspond to a two-electron reduction per catenane species (monoelectronic reduction of each of the viologen groups),[10] the integration of the cathodic wave yields a value of $(7.1 \pm 1.6) \times 10^{-12}$ mol/cm^2 (average of five independent determinations) for the surface coverage. This represents about 8% of the maximum coverage value (8.5×10^{-11} mol/cm^2) that is calculated using the catenane's molecular area (1.9×10^2 Å^2) estimated from molecular modeling methods.[11] That only a small fraction of the electrode surface is covered by the catenane structure is not unexpected, considering the complexity of the surface attachment process for this species.[12]

In conclusion, we have shown that *it is possible to utilize noncovalent intermolecular interactions, such as stacking forces between aromatic π-donor and π-acceptor subunits, to build catenane-like structures supported on gold surfaces.* This approach represents a significant contribution to the ongoing efforts to control molecular organization at the electrode solution interface.

Novel Arene Complexes of Titanium(IV), Zirconium(IV), and Hafnium(IV)

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Although η^6-arene complexes of titanium, zirconium, and hafnium in lower oxidation states have been known for many years,[1] complexes of the d^0 tetravalent metals are extremely rare. To our knowledge, the only previously reported examples are cationic complexes of the type $[(\eta^6\text{-}C_6Me_6)MCl_3]^{+\,2a,b}$ and the zwitterionic compound $(\eta^6\text{-}C_6H_5BPh_3)Zr(CH_2Ph)_3$;[2c] a small number of analogous actinide complexes are also known.[2d–h] We now report the preparation of a novel homologous series of η^6-arene complexes of the type $[Cp^*MMe_2(\eta^6\text{-arene})][BMe(C_6F_5)_3]$ (M = Ti, Zr, Hf; Cp$^* = \eta^5\text{-}C_5Me_5$; arene = benzene, toluene, mesitylene, and even styrene).

Treatment of solutions of Cp*MMe$_3$[3a,b] (M = Zr, Hf) in toluene/hexanes (1:10) with equimolar amounts of B(C$_6$F$_5$)$_3$[4] results in the almost quantitative formation of yellow precipitates which, after being thoroughly washed and then dried in vacuo at 298 K, were identified on the basis of elemental analyses and spectroscopic properties as the cationic arene complexes $[Cp^*MMe_2(\eta^6\text{-PhMe})][BMe(C_6F_5)_3]$.[5] Apart from ^{1}H and

(1) (a) Bottrill, M.; Gavens, P. D.; McMeeking, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 3, p 282. (b) Cardin, D. J.; Lappert, M. F.; Raston, C. L.; Riley, P. I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 3, p 644.

(2) (a) Solari, E.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1747. (b) Floriani, C.; Berno, P.; Solari, E. *Chem. Scr.* **1989**, *29*, 423. (c) Bochmann, M.; Karger, G.; Jaggar, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1038. (d) Cesari, M.; Pedretti, U.; Zazzetta, A.; Lugli, G.; Marconi, W. *Inorg. Chim. Acta* **1970**, *5*, 439. (e) Cotton, F. A.; Schwotzer, W. *Organometallics* **1985**, *4*, 942. (f) Cotton, F. A.; Schwotzer, W.; Simpson, C. Q. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 637. (g) Cotton, F. A.; Schwotzer, W. *J. Am. Chem. Soc.* **1986**, *108*, 4657. (h) Baudry, D.; Bulot, E.; Charpin, P.; Ephritikhine, M.; Lance, M.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1989**, *371*, 155.

(3) (a) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793. (b) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701. (c) Mena, M.; Royo, P.; Serrano, R.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1989**, *8*, 476.

(4) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623.

(5) $[Cp^*ZrMe_2(\eta^6\text{-PhMe})][BMe(C_6F_5)_3]$: NMR (CD$_2Cl_2$ at 298 K) ^{1}H δ 7.78 (d, 2 H, *o*-H), 7.38 (t, 2 H, *m*-H), 7.04 (t, 1 H, *p*-H), 2.71 (s, 3 H, Ph*Me*), 1.96 (s, 15 H, Cp*), 0.48 (br s, 3 H, BMe), –0.11 (6 H, s, ZrMe); ^{13}C{^{1}H} δ 147.0 (toluene *ring C*), 134.8 (toluene *ring C*), 130.9 (toluene *ring C*), 129.2 (toluene *ring C*), 123.6 (Cp* *ring C*), 11.5 (Cp* *Me*), 45.5 (ZrMe), 22.4 (Ph*Me*), 10.2 (br s, BMe). Anal. Calcd for C$_{38}$H$_{32}$BF$_{15}$Zr: C, 52.12; H, 3.68. Found: C, 52.40; H, 3.75. $[Cp^*HfMe_2(\eta^6\text{-PhMe})][BMe(C_6F_5)_3]$: NMR (CD$_2Cl_2$ at 273 K) ^{1}H δ 7.55 (d, 2 H, *o*-H), 7.32 (t, 2 H, *m*-H), 7.28 (t, 1 H, *p*-H), 2.76 (s, 3 H, Ph*Me*), 2.10 (s, 15 H, Cp*), 0.56 (br s, 3 H, BMe), –0.28 (6 H, s, HfMe); ^{13}C{^{1}H} δ 146.8 (toluene *ring C*), 134.7 (toluene *ring C*), 130.5 (toluene *ring C*), 124.7 (toluene *ring C*), 121.7 (Cp* *ring C*), 46.5 (HfMe), 31.8 (Ph*Me*), 11.6 (Cp* *Me*), 10.2 (br s, BMe). Anal. Calcd for C$_{38}$H$_{32}$BF$_{15}$Hf: C, 47.38; H, 3.32. Found: C, 46.62; H, 3.41. Compare toluene: NMR (CD$_2$Cl$_2$ at 273 K) ^{1}H δ 7.23 (d, 2 H, *o*-H), 7.17 (t, 2 H, *m*-H), 7.13 (t, 1 H, *p*-H), 2.34 (s, 3 H, Me).

^{13}C{^{1}H} resonances which may be assigned to Cp*, metal–Me, and coordinated toluene, the latter with significantly different chemical shifts than those of free toluene, the ^{1}H and ^{13}C{^{1}H} NMR spectra also exhibit relatively broad resonances at $\sim\delta$ 0.5 and δ 10.2, respectively, characteristic of the free BMe(C$_6$F$_5$)$_3^-$ ion.[4] Analogous zirconium complexes of mesitylene,[6] benzene, and styrene have also been made, but the latter two both decompose above 273 K and have to this point only been identified on the basis of their low-temperature ^{1}H and ^{13}C{^{1}H} NMR spectra. We find also that the more sterically hindered hexamethylbenzene does not form an arene–zirconium complex.

While the hapticity of the arene complexes has not yet been determined unambiguously, the ^{1}H and ^{13}C{^{1}H} spectra of [Cp*ZrMe$_2$(η^6-PhMe)][BMe(C$_6$F$_5$)$_3$] do not exhibit even incipient decoalescence of the aromatic resonances down to 193 K. Thus we tentatively suggest η^6- rather than, for instance, η^2- or η^4-arene coordination, noting that the compounds would then be 16-electron species, isoelectronic with the better-known, neutral metallocene compounds of the type Cp$_2$MMe$_2$.[7]

The ^{1}H NMR spectrum of the styrene complex in CD$_2$Cl$_2$ at 223 K shows clearly that coordination occurs via the arene ring rather than via the olefinic double bond. It has long been known that η^2-coordination of olefins in general[8a] and of styrene to iron(II)[8b] and platinum(II)[8c] in particular results in significant decreases in the *cis*- and *trans*-vinyl ^{1}H–^{1}H coupling constants, presumably because of changes in hybridization of the vinyl carbon atoms on coordination. While all of the styrene aromatic and vinyl ^{1}H NMR resonances of [Cp*ZrMe$_2$(PhCH=CH$_2$)][BMe-(C$_6$F$_5$)$_3$] shift significantly on coordination, the vinyl ^{1}H–^{1}H coupling constants change less than 0.1 Hz, indicating that the vinyl group does not coordinate directly.[9] Very similar results have been reported for the corresponding coupling constants of the analogous complexes (η^6-styrene)Cr(CO)$_3$[8d] and [Cp*Ru-(η^6-styrene)][OTf].[8e] Given the rarity of arene complexes of zirconium(0) and hafnium(0) and the ease with which these complexes catalyze olefin polymerization, presumably via olefin coordination (see below), it seems surprising to find that the zirconium(IV) and hafnium(IV) ions in the styrene complexes exhibit a higher proclivity for arene than for η^2-olefinic coordination.

In contrast to the zirconium and hafnium systems, a hexanes/toluene solution of Cp*TiMe$_3$ reacts smoothly and rapidly with B(C$_6$F$_5$)$_3$ at 223 K to form predominantly a yellow precipitate of the new compound Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$, in which the BMe group appears to coordinate to the titanium (cf. the analogous compound (η^5-C$_5$Me$_2$H$_3$)$_2$ZrMe(μ-Me)B(C$_6$F$_5$)$_3$[4]). Although this compound is too thermally unstable to isolate analytically pure, it is readily characterized spectroscopically; in addition to Cp* (δ 1.97) and TiMe (δ 1.53) resonances, the ^{1}H NMR spectrum (223 K, CD$_2$Cl$_2$) exhibits a broadened singlet at δ 1.19, very different from the above-mentioned resonance of the free borate anion and assigned to the bridging methyl group.[10]

On warming of the solution to 273 K, the resonance at δ 1.19 broadens significantly (and reversibly), an observation which seems best interpreted in terms of a labile equilibrium between ion-paired and solvent-separated species:

$$Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3 \rightleftharpoons$$
$$[Cp^*TiMe_2]^+ + [BMe(C_6F_5)_3]^- \quad (1)$$
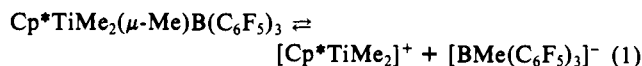
In a complementary experiment, it was found that addition of toluene to a CD$_2$Cl$_2$ solution of Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$ results in only partial conversion of the latter to [Cp*TiMe$_2$(η^6-PhMe)][BMe(C$_6$F$_5$)$_3$], identified by its ^{1}H NMR resonances.[11]

Although spin saturation transfer experiments show that free toluene does not exchange with the coordinated toluene of [Cp*ZrMe$_2$(η^6-PhMe)][BMe(C$_6$F$_5$)$_3$] at 298 K, the arene ligand is readily substituted by PMe$_3$ to form the cationic complex [Cp*ZrMe$_2$(PMe$_3$)$_2$][BMe(C$_6$F$_5$)$_3$],[12] analogous to the previously reported cationic complexes [Cp*ZrMe$_2$(THF)$_2$][BPh$_4$] and [Cp*ZrMe$_2$(dmpe)(THF)][BPh$_4$].[13] Addition of PMe$_3$ to solutions of [Cp*HfMe$_2$(η^6-PhMe)][BMe(C$_6$F$_5$)$_3$] or Cp*TiMe$_2$-(μ-Me)B(C$_6$F$_5$)$_3$ results in formation of the analogous complexes, [Cp*MMe$_2$(PMe$_3$)$_2$][BMe(C$_6$F$_5$)$_3$] (M = Ti, Hf), which have to this point only been identified spectroscopically.[14]

As anticipated, the ^{19}F NMR spectra of complexes such as [Cp*MMe$_2$(η^6-PhMe)][BMe(C$_6$F$_5$)$_3$] (M = Zr, Hf) and [Cp*MMe$_2$(PMe$_3$)$_2$][BMe(C$_6$F$_5$)$_3$] (M = Ti, Zr) at 223 and 273 K exhibit well-resolved, single resonances for each of the ortho, meta, and para fluorine sites, consistent with the proposed ionic formulations. Interestingly, however, the ^{19}F NMR spectrum of Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$ at 223 K exhibits pairs of broadened ortho, meta, and para resonances, each in 2:1 ratios, consistent with a staggered structure in which rotation of the triarylboron group relative to the Cp*TiMe$_2$ moiety is slow on the NMR time scale. Although a detailed variable temperature NMR study has not yet been carried out, the pairs of resonances are partially coalesced at 273 K, while the broadening of the resonances at 223 K may indicate restricted rotation about the aryl–B bonds.[15]

The properties of complexes of the types described here as olefin polymerization catalysts have been reported elsewhere while this work was in progress.[16] However, apparently neither the formation of arene complexes nor the directing and deactivating effects of arene coordination, to be reported elsewhere,[17] were realized.

(6) [Cp*ZrMe$_2$(η^6-1,3,5-C$_6$H$_3$Me$_3$)][BMe(C$_6$F$_5$)$_3$]: NMR (CD$_2$Cl$_2$ at 273 K) ^{1}H δ 7.29 (s, 3 H, C$_6$H$_3$Me$_3$), 2.47 (s, 9 H, C$_6$H$_3$Me$_3$), 1.96 (s, 15 H, Cp*), 0.50 (br s, 3 H, BMe), –0.15 (s, 6 H, ZrMe); ^{13}C{^{1}H} δ 141.1 (mesitylene *ring C*), 132.4 (mesitylene *ring C*), 122.4 (Cp* *ring C*), 40.7 (ZrMe), 21.3 (C$_6$H$_3$Me$_3$), 11.7 (Cp* *Me*), 10.2 (br s, BMe). Anal. Calcd for C$_{40}$H$_{36}$BF$_{15}$Zr: C, 53.16; H, 4.01. Found: C, 53.28; H, 4.12.

(7) Cardin, D. J.; Lappert, M. F.; Raston, C. L.; Riley, P. I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 3, p 580.

(8) (a) Herberhold, M. *Metal π-Complexes*; Elsevier: Amsterdam, 1974; Vol. 2, Part 2, p 50. (b) Laycock, D. E.; Hartgerink, J.; Baird, M. C. *J. Org. Chem.* **1980**, *45*, 291. (c) Albinati, A.; Caseri, W. R.; Pregosin, P. S. *Organometallics* **1987**, *6*, 788. (d) Knox, G. R.; Leppard, D. G.; Pauson, P. L.; Watt, W. E. *J. Organomet. Chem.* **1972**, *34*, 347. (e) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

(9) The *cis*- and *trans*-vinyl H–H coupling constants at [Cp*ZrMe$_2$(η^6-PhCHCH$_2$)][BMe(C$_6$F$_5$)$_3$] in CD$_2$Cl$_2$ at 223 K are 10.9 and 17.2 Hz, respectively, identical within experimental error to the coupling constants of free styrene under the same conditions; the geminal couplings of $\approx$1 Hz cannot be resolved at this temperature because of line broadening.

(10) The ^{13}C{^{1}H} NMR spectrum of Cp*TiMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$ at 223 K exhibits resonances at δ 131.0 (Cp* *ring C*), 79.9 (TiMe), 30.2 (br, μ-Me), and 12.5 (Cp* *Me*).

(11) [Cp*TiMe$_2$(η^6-PhMe)][BMe(C$_6$F$_5$)$_3$]: NMR (CD$_2$Cl$_2$ at 223 K) ^{1}H δ 7.74 (2 H, d, *o*-H), $\sim$7.2 (*m*-H, obscured by resonance of free toluene), 6.70 (t, 1 H, *p*-H), 2.78 (s, 3 H, Ph*Me*), 1.90 (s, 15 H, Cp*), 0.38 (br s, 3 H, BMe), 0.11 (6 H, s, TiMe).

(12) [Cp*ZrMe$_2$(PMe$_3$)$_2$][BMe(C$_6$F$_5$)$_3$]: NMR (CD$_2$Cl$_2$ at 273 K) ^{1}H δ 2.02 (s, 15 H, Cp*), 1.38 (deceptively simple t, 18 H, PMe), 0.41 (br s, 3 H, BMe), 0.07 (t, 6 H, ZrMe, J_{PH} 5.4); ^{13}C{^{1}H} δ 123.9 (Cp* *ring C*), 54.5 (t, ZrMe, J_{PC} 10.4), 12.6 (d, PMe, J_{PC} 10.2), 11.9 (br s, BMe), 11.2 (Cp* *Me*). Anal. Calcd for C$_{37}$H$_{42}$BF$_{15}$P$_2$Zr: C, 47.49; H, 4.52. Found: C, 47.94; H, 4.56.

(13) Crowther, D. J.; Jordan, R. F.; Baenziger, N. C.; Verma, A. *Organometallics* **1990**, *9*, 2574.

(14) [Cp*TiMe$_2$(PMe$_3$)$_2$][BMe(C$_6$F$_5$)$_3$]: NMR (CD$_2$Cl$_2$ at 273 K) ^{1}H δ 2.04 (s, 15 H, Cp*), 1.38 (deceptively simple t, 18 H, PMe), 0.66 (t, 6 H, TiMe, J_{PH} 9.1), 0.45 (br s, 3 H, BMe); ^{13}C{^{1}H} δ 128.5 (Cp* *ring C*), 71.0 (t, TiMe, J_{PC} 11.9), 15.6 (d, PMe, P_{PC} 10.1), 12.9 (Cp* *Me*), 9.8 (br s, BMe). [Cp*HfMe$_2$(PMe$_3$)$_2$][BMe(C$_6$F$_5$)$_3$]: NMR (CD$_2$Cl$_2$ at 273 K) ^{1}H δ 2.14 (s, 15 H, Cp*), 1.44 (deceptively simple t, 18 H, PMe), 0.50 (br s, 3 H, BMe), –0.04 (t, 6 H, HfMe, J_{PH} 6.4); ^{13}C{^{1}H} δ 122.3 (Cp* *ring C*), 11.4 (Cp* *Me*), 59.9 (t, HfMe, J_{PC} 10.5), 12.8 (d, PMe, J_{PC} 10.6), 10.9 (br s, BMe).

(15) Willem, R.; Gielen, M.; Hoogzand, C.; Pepermans, H. *Adv. Dyn. Stereochem.* **1985**, *1*, 207 and references therein.

(16) (a) Pellechia, C.; Proto, A.; Longo, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 265. (b) Pellechia, C.; Proto, A.; Longo, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 277.

(17) Gillis, D. J.; Tudoret, M.-J.; Baird, M. C. To be published.

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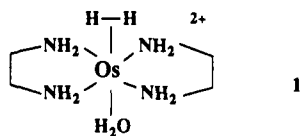
of a stable ethene–ethyne metal complex from this η^2-dihydrogen complex. The reaction of 1 with other alkene and alkyne molecules will also be described.

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
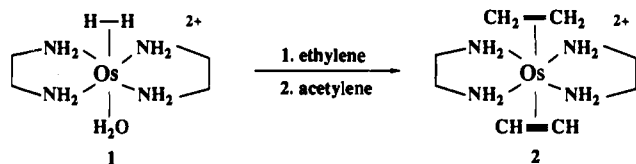
demonstrates that upon coordination the proton signal of ethyne shifts downfield from $\delta \sim 2$ to δ 7.30 (s, 2 H), whereas the proton signal of ethene shifts upfield from $\delta \sim 5$ to δ 3.19 (s, 4 H). In the proton-coupled ^{13}C NMR spectrum of the compound, a doublet of doublets at δ 103.4 (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
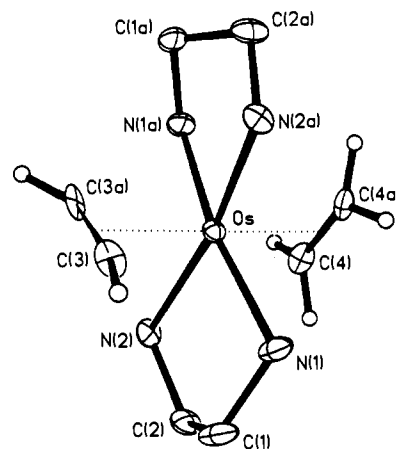

Figure 1. Molecular structure of **2**.

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]

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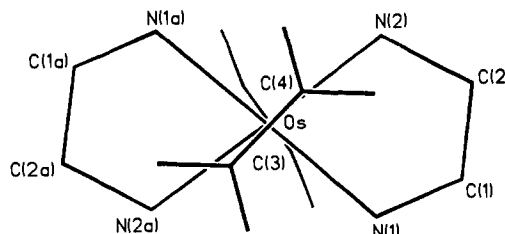
This orthogonal arrangement can be understood as resulting from the competition of the two π acid ligands for π d electron density which is minimized when orthogonal orbitals are engaged. Prior

(1) (a) Stanford University. (b) University of California at Davis.

(2) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.

(3) Reviews: (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95.

(4) (a) Li, Z.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946. (b) Li, Z.; Taube, H. *Science* **1992**, *256*, 210. (c) Pu, L.; Hasegawa, T.; Parkin, S.; Taube, H. *J. Am. Chem. Soc.* **1992**, *114*, 2712. (d) Pu, L.; Hasegawa, T.; Parkin, S.; Taube, H. *J. Am. Chem. Soc.* **1992**, *114*, 7609.

(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$_2$NH$_2$), and 2.40 (m, 4 H, CH$_2$NH$_2$). 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$_2$NH$_2$). (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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