The discovery of these three novel types of stannoxane structural entities, the drum,[1-3] the ladder,[2,3] and the oxygen-capped cluster, suggests that additional cluster arrangements remain to be discovered possessing interesting properties.

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Supplementary Material Available: Atomic coordinates (Table S1) and isotropic thermal parameters (Table S2) (5 pages). Ordering information is given on any current masthead page.

Preparation of the First Molecular η^2-Acetylene Complex of a 4f Transition Metal, $(Me_5C_5)_2Yb(\eta^2\text{-}MeC\equiv CMe)$

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Most d-block transition metals form well-defined complexes with acetylenes.[1] Even Cu(I) and its congeners yield isolable complexes.[2] No η^2-acetylene complexes of the f-block transition metals have been described, though lanthanide metal atoms react with acetylenes,[3a,b] and a black substance of unknown structure whose composition is $[(Me_5C_5)_2Sm]_2[PhC\equiv CPh]$ has been isolated.[3c] Monosubstituted acetylenes such as $PhC\equiv CH$ react with $(Me_5C_5)_2Yb(OEt_2)$ to give the mixed-valence phenylacetylide $(Me_5C_5)_4Yb_3(\mu\text{-}C\equiv CPh)_4$ presumably by way of prior acetylene coordination.[3d] The bonding in metal-acetylene complexes is similar to that in olefin complexes, viz., the filled orbitals of σ-symmetry act as donors and the empty π-symmetry orbitals on the acetylene act as acceptor orbitals.[4a-c] $(\eta^6\text{-}Me_6C_6)Sm(AlCl_4)_3$ has been isolated recently.[4d] Because lanthanide metallocenes can act as Lewis acids, though not as π-donors since the filled energy levels are too low in energy,[5] a reasonable strategy for synthesis of acetylene complexes is to use donor rather than acceptor substituents on the acetylene. The first vertical ionization energy of $MeC\equiv CMe$ and tetrahydrofuran are 9.59[6a] and 9.57 eV,[6b] respectively, so it is, perhaps, not unexpected that $MeC\equiv CMe$ will yield an isolable complex since the THF complex is known.[7]

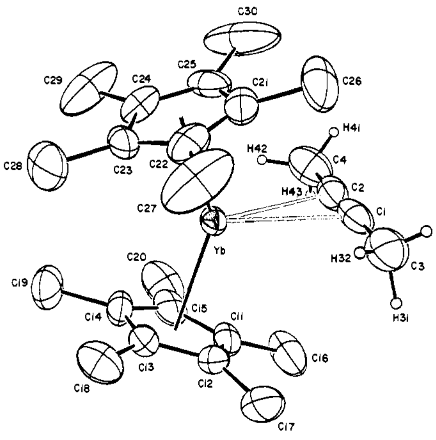

Figure 1. ORTEP diagram of $(Me_5C_5)_2Yb(\eta^2\text{-}MeC\equiv CMe)$. Thermal ellipsoids represent 50% probability surfaces except those of the hydrogen atoms which are arbitrary.

Addition of 2-butyne to base-free $(Me_5C_5)_2Yb$[5] in pentane results in a color change from orange to red from which dark purple-red needles, mp 170-173 °C, may be isolated in quantitative yield on cooling to -70 °C. The infrared spectrum of the complex as a Nujol mull shows no absorptions which may be attributed to $\nu(C\equiv C)$.[8] The ^1H NMR spectrum in C_6D_6 at 30 °C shows that the complex is diamagnetic and that the Me_5C_5 resonance in the complex is slightly deshielded relative to the base-free compound, δ 1.92 vs. 1.99, under identical conditions. The $^{13}\{^1H\}$ NMR chemical shifts of the Me_5C_5 rings in the complex are also slightly perturbed relative to the base-free complex; the ring carbons are unchanged at δ 113.4 and the methyl carbons are deshielded in the complex, δ 10.6 vs. 10.9. The greatest effect is on the resonances of the 2-butyne ligand. The free ligand at 30 °C in C_6D_6 shows a resonance in the ^1H NMR spectrum at δ 1.52 which shifts to δ 1.27 on coordination. In the $^{13}C\{^1H\}$ NMR spectrum the methyne and methyl carbons are deshielded on coordination, δ 74.6 to 76.9 and δ 3.08 to 3.76, respectively. The complexed 2-butyne is undergoing chemical exchange at 30 and -75 °C (200 MHz) since at 30 °C the ^1H NMR resonance of the acetylene in methylcyclohexane-d_{14} with a 10-fold molar excess of acetylene occurs as a sharp singlet at δ 1.63 (relative to the most intense resonance due to residual protons of the solvent at δ 0.82); free 2-butyne resonates at δ 1.64 in C_7D_{14}. Cooling to -75 °C changes the averaged chemical shift to δ 1.73 with no discernible change in line shape. Both the vibrational spectrum of the solid and solution NMR spectra show that $MeC\equiv CMe$ is only weakly perturbed on coordination to the lanthanide center. This contention is supported by the crystal structure at -80 °C.

An ORTEP diagram is shown in Figure 1. The geometry of the Me_5C_5 portion of the complex is not greatly perturbed from that of $(Me_5C_5)_2Yb(thf)$.[7] The averaged Yb-C and Yb-Me_5C_5 ring centroid distances and the Me_5C_5 ring centroid-Yb-Me_5C_5 ring centroid angle in the acetylene complex are 2.659 ± 0.009 Å, 2.38

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(8) We have isolated the unsymmetrical acetylene complexes $(Me_5C_5)_2Yb(L)$, L = $PhC\equiv CMe$ or $Me_3CC\equiv CMe$, though the $\nu(C\equiv C)$ is not observable in the infrared. As yet, we have not been able to observe the Raman spectrum of the $MeC\equiv CMe$ complex in the solid state nor in a methylcyclohexane solution.

(9) The compound crystallizes in the monoclinic crystal system in space group $P2_1/n$ with cell dimensions a = 15.738 (2) Å, b = 15.299 (2) Å, and c = 9.724 (1) Å, β = 103.90 (1)°, V = 2272.6 (8) $Å^3$ with Z = 4, and d(calcd) = 1.45 g cm^{-3}. The data were collected on a Nonius CAD4 automated diffractometer with Mo Kα X-rays (λ = 0.71073 Å) at -80 °C. The structure was solved from Patterson and electron density maps and refined by full-matrix least squares to a conventional R factor of 0.022 (R_W = 0.029 and GOF = 1.505) by using 2449 absorption corrected data, where $F_o^2 > 3\sigma(F_o^2)$ against 251 variables. The R value for all 2971 unique data was 0.044. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the 2-butyne ligand were located in a difference map and they were refined with isotropic thermal parameters. All other hydrogen atoms were located in a difference Fourier map and then placed in calculated positions included in the structure factor calculations, but were not refined.

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Å, and 143.3°, respectively. The equivalent distances and angle in the tetrahydrofuran complex are 2.663 ± 0.011 Å, 2.37 Å, and 143.5°, respectively. The C(1)C(2) and averaged C–C(Me) distances in the complex are 1.154 (6) and 1.468 ± 0.005 Å, respectively. The equivalent distances in free 2-butyne (−50 °C) are 1.21 (2) and 1.46 (1) Å, respectively.[10] The averaged C–C–C(Me) angle in the complex is 177.4 ± 0.7° and the equivalent angle in the free ligand is linear. Comparison of the C–C distance and the C–C–C(Me) angle in $(Me_5C_5)_2Yb(\eta^2\text{-MeC}{\equiv}\text{CMe})$ with the equivalent bond parameters in *trans*-$[MePt(PMe_2Ph)_2(\eta^2\text{-MeC}{\equiv}\text{CMe})]PF_6$[11a] and $(Ph_3P)_2Pt(\eta^2\text{-MeC}{\equiv}\text{CPh})$[11b] in which the C–C distance is 1.22 (3) and 1.28 (3) Å and the C–C–C(Me) angle is 168 ± 2° and 141.8(1.8)°, respectively, shows that little or no π-back-bonding is involved in the ytterbium–acetylene bond. The averaged Yb–C(1,2) distance is 2.850 ± 0.010 Å and the C(1)–Yb–C(2) angle is 23.4 (1)°. The dihedral angle formed by intersection of the plane defined by C(1,2,3,4) and Yb with the plane defined by the Me_5C_5 ring centroid–Yb–Me_5C_5 ring centroid is 91.5°. Clearly the 2-butyne to $(Me_5C_5)_2Yb$ interaction is weak as judged by spectroscopic and crystallographic data. The complex is best viewed as a Lewis acid–base adduct with little or no π-back-bonding.

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Supplementary Material Available: Tables of atomic positional parameters, thermal parameters, bond lengths, and bond angles (7 pages). Ordering information is given on any current masthead page.

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Activation of C–H Bonds with Intermediates Produced by Mild Thermal and Photochemical Decomposition of the Metallacycle $(\eta^5\text{-}C_5Me_5)\overline{Ir[C(p\text{-}ClC_6H_4){=}NOC}({=}O)](CO)$ in Hydrocarbon Solvents

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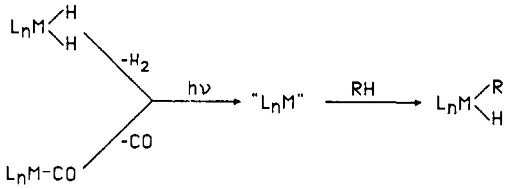
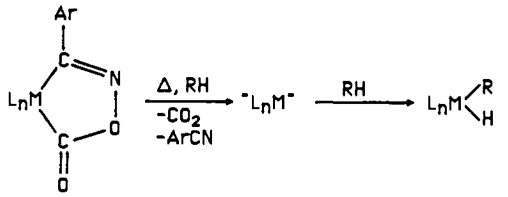
In recent years a number of transition-metal complexes have been found to undergo photochemically induced intermolecular C–H bond activation of their hydrocarbon solvents.[1-6] The aryl and alkyl metal hydride products of these reactions are believed to result from the oxidative addition of the 16-electron coordinatively unsaturated metal fragments, "ML_n", generated by the photolytically induced loss of H_2 or CO, into the C–H bonds of hydrocarbons (Scheme I). Insertion into C–H bonds also occurs with thermal activation, suggesting that these reactions do not specifically require the reactive metal fragment to be in a photoexcited state.[1a,4,7-18] A preponderance of the previously reported examples of thermal C–H bond activation, in which the products of direct oxidative addition are observed, involve the reductive elimination of the reactive species, ML_n, from an alkyl or aryl metal hydride followed by its oxidative addition into the C–H bond of another hydrocarbon.[1b,4,7-9,15-18] In effect, these reactions require as a reactant a metal center which has already undergone C–H activation into a C–H bond and constitute hydrocarbon exchange reactions.

Scheme I



Scheme II



We now wish to report the thermal activation of C–H bonds of hydrocarbons using the precursor metallacycle $(\eta^5\text{-}C_5Me_5)\overline{Ir[C(p\text{-}ClC_6H_4){=}NOC}({=}O)](CO)$ (**1**).[19,20] Thermolysis of **1** would be expected to generate the 16-electron four-coordinate species "$(\eta^5\text{-}C_5Me_5)Ir(CO)$" (Scheme II) which is presumed to be responsible for the activation of a number of hydrocarbons when generated photolytically from $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$.[2] When the metallacycle **1** was maintained in the dark at 50 °C in benzene solution for 5 weeks, a hydride resonance at −15.07 ppm was observed and attributed to the product $(\eta^5\text{-}C_5Me_5)Ir(CO)(H)(C_6H_5)$[2a] (**2**), formed by the oxidative addition of $(\eta^5\text{-}$

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(19) We have synthesized a number of metallacycles by cycloaddition of aryl nitrile *N*-oxides with low-valent metal carbonyl complexes. A preliminary paper has been published (Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1983**, *105*, 3370) and a complete report will be submitted shortly.

(20) Selected data for **1** (full details will be reported elsewhere[19]). **1**: Anal. Calcd for $C_{19}H_{19}ClIrNO_3$: C, 42.57; H, 3.58; Ir, 35.85; N, 2.61. Found: C, 42.12; H, 3.64; Ir, 35.88; N, 2.40. ^1H NMR (C_6D_6) δ 7.39 (d, 2 H, *J* = 8.5 Hz), 7.10 (d, 2 H, *J* = 8.4 Hz), 1.23 (s, 15 H).

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