Electronic and Steric Factors for Elimination Reactions in Carbenium Ions Derived from (17β-ethynylestradiol)M_2L_6 Complexes (M_2L_6 = $Co_2(CO)_6$, $Mo_2Cp_2(CO)_4$). X-ray Structure of $[Mo_2Cp_2(CO)_4(\mu\text{-}CH{\equiv}CC_{19}H_{25}O)]^+BF_4^-$

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Carbenium ions of the type $[M_2L_6(\mu\text{-}CH{\equiv}CC_{18}H_{23}O]^+BF_4^-$ (M_2L_6 = $Co_2(CO)_6$ (**2a**) $Mo_2Cp_2(CO)_4$ (**2b**)), where $C_{18}H_{23}O$ represents 17α-ethynyl-3-hydroxyestradiol, and of the type $[M_2L_6(\mu\text{-}CH{\equiv}CC_{19}H_{25}O)]^+BF_4^-$ ($C_{19}H_{25}O$ = 17α-ethynyl-3-methoxyestradiol; M_2L_6 = $Co_2(CO)_6$ (**2a'**), $Mo_2Cp_2(CO)_4$ (**2b'**)) can be conveniently prepared by direct protonation of their corresponding parent 17β alcohols (**1a**,**b** and **1a'**,**b'**) with HBF_4 in ether solution. Further, the complexes **2a'** and **2b'** promote elimination of one molecule of HBF_4 in ether and methanol solution, respectively, affording the corresponding enyne complexes. At room temperature the dimolybdenum derivative **2b'** gave only the enyne complex **3'**, whereas the analogous dicobalt species under the same experimental conditions afforded **3a'**, **4a'**, and two other rearrangement isomers. This peculiar reactivity is attributable to the conjunction of the particular organometallic moiety (M_2L_6 = $Co_2(CO)_6$) complexing the 17α triple bond and to the steric factors induced by the estradiol skeleton. We describe the reactivity of the carbenium ions (**2a'**,**b'**) and propose a mechanism to explain the different enyne isomers obtained from complex **2a'**. In addition, the X-ray structure of complex **2b'** was determined; this compound crystallizes in the orthorhombic space group $P2_12_12_1$ with Z = 4 and cell dimensions a = 9.937 (2) Å, b = 17.912 (2) Å, and c = 19.177 (2) Å; the structure was refined to R and R° values of 4.35 and 4.89, respectively, with use of 2551 reflections.

Introduction

Several authors have reported the formation and the reactivity of carbenium ion complexes from primary, secondary, and tertiary propargylic alcohols stabilized by organometallic entities of general formula $[M_2L_6(\mu\text{-}RC{\equiv}CCH(OH)R_1R_2]$ (R_1 = R_2 = H; R_1 = H, R_2 = alkyl group; R_1 = R_2 = alkyl groups; M_2L_6 = $Co_2(CO)_6$, $Mo_2Cp_2(CO)_4$).[1-4] Analogous to this series of compounds are the 17α-alkynylestradiol derivatives of general formula $[M_2L_6(\mu\text{-}RC{\equiv}CC_{18}H_{24}O_2)]$ (M_2L_6 = $Co_2(CO)_6$ (**1a**), $Mo_2Cp_2(CO)_4$ (**1b**)) and $[M_2L_6(\mu\text{-}RC{\equiv}CC_{19}H_{26}O_2)]$ (M_2L_6 = $Co_2(CO)_6$ (**1a'**), $Mo_2Cp_2(CO)_4$ (**1b'**)).[5,6] These complexes **1a**,**b** recognize the estradiol receptor, displaying moderate relative binding affinities (RBA) in the range of 5–16% with respect to the value of estradiol, taken to be 100%.[5] A difference in the behavior of 17α-propynylestradiol)$Co_2(CO)_6$ and (17α-propynylestradiol)$Mo_2Cp_2(CO)_4$ estradiol has been reported.[7] The $Co_2(CO)_6$ hormone derivative binds irreversibly to the hormone receptor, presumably forming a covalent bond, while the corresponding $Mo_2Cp_2(CO)_4$ complex exhibits reversible binding.[7] We postulate that the difference in properties between these two systems **1a**,**b** may be related to the behavior of their corresponding carbenium ions **2a** and **2b** in solution. Hence, we have prepared the complexes **2a**,**b** and **2a'**,**b'** and investigated their reactivity.

Experimental Section

Manipulations were carried out with use of a vacuum line under argon and by standard Schlenk techniques. Solvents were purified and dried prior to use by conventional distillation techniques under argon. IR spectra were recorded on a FT Bomem Michelson 100 spectrometer using both KBr disks and solution cells. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 250 instrument, and chemical shifts are relative to Me_4Si.[19] Data are presented as proton decoupled with downfield chemical shifts. The mass spectra were recorded on a Ribermag R10-10 spectrometer coupled to a PDP 11 digital computer. Elemental analyses were performed by the microanalysis service of CNRS-Vernaison, France. pK_{R^+} values were determined according to Deno's method adapted for our special use.[8] The organometallic clusters were first dissolved in an organic solvent (acetone or acetonitrile). Increasing quantities of aqueous sulfuric acid were then added to aliquots of the complex in solution, leading to a final percentage of solvent from 10% to 50% depending on the solubility of the product. Spectroscopic measurements were performed at a selected wavelength on a Kontron Uvikon 860 UV–visible spectrometer. Final calculations were done by using the Deno Co acidity function.

$[Co_2(CO)_6(\mu\text{-}CH{\equiv}CC_{18}H_{23}O_2H)]$ (1a). 17α-Ethynylestradiol (150 mg, 0.5×10^{-3} mol) in 10 mL of THF was added dropwise to a solution of $Co_2(CO)_8$ (190 mg, 0.55×10^{-3} mol) in 10 mL of THF. The reaction was followed by thin-layer chromatography on silica plates with an ether/pentane solution (50/50) as eluant. After 1 h the reaction was stopped, the mixture was filtered, and compound **1a** was separated by column chromatography with alumina as adsorbent and ether/pentane (40/60) mixture as eluant; yield 90%. ^1H NMR (in $CDCl_3$, δ): 7.16 (1 H1, d, 8.5 Hz), 6.64 (1 H2, dd, 8.5–2.8 Hz), 6.58 (1 H4, 2.8 Hz), 6.17 (1 H, acet,

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s), 4.77 (OH, s large), 2.83 (2 H6, m), 2.43–1.43 (m), 1.08 (3 H18, s). ^{13}C NMR (in $CDCl_3$ δ): C1, 126.4; C2, 112.7; C3, 159.0; C4, 115.2; C5, 138.0; C6, 29.5; C7, 27.3; C8, 39.7; C9, 43.3; C10, 132.2; C11, 26.3; C12, 32.7; C13, 48.7; C14, 50.0; C15, 22.9; C16, 44.0; C17, 85.2; C18, 15.7; C20–21, 73.4–103.6; CO, 199.5. IR (KBr disk, ν(CO), cm^{-1}): 2089, 2049, 2020.

$[Co_2(CO)_6(\mu\text{-}CH{\equiv}CC_{19}H_{25}O_2H)]$ (1a′). This complex was obtained by following the procedure described already for **1a**, yield 68%.[2] IR (KBr disk, ν(CO), cm^{-1}): 2081, 2050, 2021.

$[Mo_2Cp_2(CO)_4(\mu\text{-}CH{\equiv}CC_{19}H_{25}O_2H)]$ (1b′). A solution of 700 mg (2.26×10^{-3} mol) of mestranol in 10 mL THF was added to a solution of 1 g (2.30×10^{-3}) of $Mo_2Cp_2(CO)_4$[9] in 20 mL of THF, and the mixture was stirred for 4 h; at this stage the reaction was stopped and the reaction mixture was concentrated under vacuum followed by chromatography on thin-layer silica gel, with CH_2Cl_2 as eluant, to give **1b′** in 38% yield. ^1H NMR (in $CDCl_3$, δ): 7.18 (1 H1, d, 8.5 Hz), 6.70 (1 H2, dd, 8.5–2.8 Hz), 6.62 (1 H4, d, 2.8 Hz), 6.49 (1 H acet, s), 5.46 (5 H, Cp, s), 5.40 (5 H, Cp s), 3.76 (3 H, OCH_3, s), 2.85 (2 H6, m), 2.20–1.24, 0.96 (3 H18, s). ^{13}C NMR (in $CDCl_3$, δ): C1, 126.2; C2, 111.6; C3, 157.7; C4, 114.0; C5, 138.0; C6, 26.5; C7, 22.9; C8, 40.0; C9, 44.1; C10, 132.4; C11, 29.8; C12, 32.3; C13, 50.8; C14, 49.7; C15, 27.8; C16, 41.4; C17, 91.8; C18, 16.6; C20–21, 89.0–92.5; C_5H_5 92.5–93.2; OCH_3, 55.3. IR (KBr disk, ν(CO), cm^{-1}): 1977, 1907, 1888, 1825.

$[Mo_2Cp_2(CO)_4(\mu\text{-}CH{\equiv}CC_{19}H_{25}O)]^+BF_4^-$ (2b′). The alcohol complex **1b′** obtained in the previous preparation was treated with an excess of aqueous HBF_4 solution (34%) in 100 mL of ether. An orange-yellow precipitate was obtained. This compound was filtered, washed several times with ether, and recrystallized from CH_2Cl_2/diethyl ether; yield 90%. Anal. Calculated for $C_{35}H_{35}O_5BF_4Mo_2$: C, 48.6; H, 4.1; Mo, 21.2. Found: C, 50.8; H, 4.2; Mo, 23.3. ^1H NMR (in $CDCl_3$, δ): 7.18 (1 H1, d, 8.5 Hz), 6.73 (1 H2, dd, 8.5–2.75 Hz), 6.62 (1 H4, d, 2.75 Hz), 5.75 (10 H, Cp, s large), 2.85 (2 H6, m), 3.77 (3 H, OCH_3, s large), 0.97 (3 H18, s large). ^{13}C NMR (in $CDCl_3$, δ): C1, 126.2; C2, 111.6; C3, 157.2; C4, 113.9; C5, 137.4; C6, 26.5; C7, 23.4; C8, 40.2; C9, 43.3; C10, 131.5; C11, 29.7; C12, 29.7; C13, 52.5; C14, 54.2; C15, 27.1; C16, 36.1; C20–21, 75.5; Cp, 93.7–93.5; OCH_3, 55.3. IR (KBr disk, ν(CO), cm^{-1}): 2026, 1992, 1960, 1861.

Crystal Data for 2b′. The selected crystal was set up on an automatic four-circle diffractometer (Nonius CAD4). The accurate cell dimensions and orientation matrix were obtained from least-squares refinements of the setting angles of 25 well-defined reflections. Two standard reflections were monitored periodically; they showed no significant change during data collection. Crystal data and crystal data parameters are listed in the supplementary material. Corrections were applied for Lorentz and polarization effects. No absorption correction was made (flat 4-scan).

Computations were performed by using CRYSTALS[10] adapted to a Microvax II computer. Atomic form factors for neutral Mo, C, O, B, F, and H atoms were taken from ref 11. The structure was resolved by standard Patterson–Fourier techniques and refined by least squares with anisotropic thermal parameters for all non-hydrogen atoms except B and F atoms. Hydrogen atoms were calculated and included as fixed contributors after each refinement. The BF_4 anion is disordered; the resolution led to two sets of F atoms whose coordinates were refined with an overall refinable isotropic thermal parameter and a refineable factor of occupancy (final value 62%–38% occupancy) applying restraints on B–F bonds and F–B–F angles. Fractional atomic parameters for non-hydrogen atoms and main interatomic distances and bond angles are listed in the supplementary material.

$[Mo_2Cp_2(CO)_4(\mu\text{-}CH{\equiv}CC_{19}H_{23}O)]$ (3b′). Methanol (5 mL) was added to 62 mg (5×10^{-4} mol) of **2b′** to give an orange suspension. This mixture was stirred for 2 h, during which time the color of the solution became deeper and clearer. Later the reaction mixture was diluted with water and compound **3b′** was extracted by ether and dried over $MgSO_4$. The orange-red solution was filtered and concentrated under vacuum to give **3b′** in quantitative yield. ^1H NMR (in acetone-d_6, δ): 7.16 (1 H1, d, 8.5 Hz), 6.67 (1 H2, dd 8.5–2.8 Hz), 6.61 (1 H4, d, 2.8 Hz), 6.27 (1 H, acet, s), 5.85 (1 H16, m), 5.41 (5 H, Cp, s), 5.38 (5 H, Cp, s), 3.73 (3 H, OCH_3, s), 0.87 (3 H18, s). IR (KBr disk, ν(CO), cm^{-1}) 1981, 1908, 1826.

Reaction of 2b′ with $NaBH_4$. An excess of $NaBH_4$ was added at room temperature to a solution of **2b′** (100 mg) in a 10-mL mixture of CH_2Cl_2/THF (2/1), causing a color change from brown to deep red; later the excess amount of $NaBH_4$ was hydrolyzed by a cold aqueous solution of NH_4Cl. The organic phase was extracted with ether, and the extracts were dried and concentrated under vacuum to give an oily residue. Separation of products was performed by thin-layer chromatography with silica plates and CH_2Cl_2 as eluant, yielding the α-isomer (10%) **8b′**, β-isomer (80%) **7b′**, and compound **3b′** (10%). ^1H NMR (in CD_2Cl_2, δ): Cp α-isomer 5.33–5.49; Cp β-isomer, 5.52–5.30; **3b**, 5.40–5.42; 18-CH_3 α isomer, 0.94; 18-CH_3 β isomer, 0.65; **3b**, 0.87.

In order to verify that the β-isomer **7b′** is the major isomer in the previous preparation, 50 mg of the obtained product was decomplexed in the presence of 100 mg of $Fe(NO_3)_3{\cdot}9H_2O$ in 10 ml of ethanol and the free ligand was separated and dried under vacuum, yielding 15 mg of white solid product **9′**. The NMR spectrum recorded in $CDCl_3$ solution exhibits results similar to those reported in the literature for the β-isomer.[12] ^1H NMR (in $CDCl_3$, δ): 7.22 (1 H1, d, 9 Hz), 6.74 (1 H2, dd, 9–2.8 Hz), 6.64 (1 H4, d, 2.8 Hz), 3.78 (3 H, OCH_3 s), 2.11 (1 H, acet, d, 2.2 Hz), 0.85 (3 H18, s). Mass spectrum (with NH_3 as reactant gas): M^+, m/e 295.

$[Co_2(CO)_6(\mu\text{-}CH{\equiv}CC_{19}H_{23}O)]$ (3a′). An aqueous solution of HBF_4 (34%) (12 mL) was added at −40 °C to 358 mg (0.6×10^{-3} mol) of **1a′** in 10 mL of ether solution in the presence of 56.7 mL of acetic anhydride. The reaction mixture was stirred under argon for 6 h; at this stage the reaction was stopped and the mixture hydrolyzed with methanol and then at room temperature with a saturated solution of aqueous $NaHCO_3$. The organic phase was extracted with ether, and the extracts were dried over $MgSO_4$. The ether solution was evaporated to dryness to give a red-brown compound. **3a′** was further purified by column chromatography on silica gel with ether/pentane (3/7) as eluant; after recrystallization from pentane, 100 mg of **3a′** was obtained (yield 25%). This compound was the only product obtained from **1a′** when the reaction was carried out at low temperature. Anal. Calcd for $C_{27}H_{24}O_7Co_2$: C, 56.0; H, 4.2; Co, 20.4. Found: C, 56.9; H, 4.3; Co, 19.8. Mass spectrum (with NH_3 as reactant gas): M^+, m/e 579. IR (KBr disk, ν(CO), cm^{-1}): 2093, 2064, 2051, 2028, 2016. ^1H NMR (in $CDCl_3$, δ): 7.2 (H1, d, 9 Hz), 6.73 (H2, dd, 9–2.75 Hz), 6.65 (H4, d, 2.75 Hz), 6.21 (H16, m), 6.22 (H acet, s), 3.80 (OCH_3, s), 2.90 (H6, m), 0.95 (18-CH_3, s). ^{13}C NMR (in $CDCl_3$, δ): C1, 126.0; C2, 111.5; C3, 157.7; C4, 114.0; C5, 137.9; C6, 26.6; C7, 27.7; C8, 37.7; C9, 44.3; C10, 132.8; C11, 29.8; C12, 32.1; C13, 48.7; C14, 55.2; C15, 35.0; C16, 136.4; C17, 152.1; C18, 16.5; C≡CH, 82.1–72.7; CO, 200,0; OCH_3, 56.7.

$[Co_2(CO)_6(\mu\text{-}CH{\equiv}CC_{19}H_{23}O)]$ (4a′). HBF_4 in ether (1.5 mL) was added at room temperature to **1a′** (179 mg, 0.3×10^{-3} mol) in 10 mL of ether, providing a deep red oily compound. The infrared spectrum of this compound suggests the formation of the compound **2a′**. Later the mixture was washed with a saturated aqueous solution of $NaHCO_3$, the organic phase was extracted with ether, and the extracts were dried over $MgSO_4$. Evaporation of solvent under vacuum afforded a deep brown residue (140 mg, yield 80%). Mass spectrum (with NH_3 as reactant gas): M^+, m/e 579. IR (KBr disk, ν(CO), cm^{-1}): 2087, 2047, 2030. ^1H NMR (in $CDCl_3$, δ): H1, 7.54, 7.20, 7.10 (d); H2, H4, 6.4–6.7 (d + dd); H16, H12, 6.2 (m); H acetylenic, 6.1 (4 s); OCH_3, 3.80 (s); 18-CH_3, 1.40, 1.30, 1.24, 0.94 (4 s). Compound **4a′** was separated by crystallization in ether/pentane (1/1); 20 mg (yield 14%) of **4a′** obtained. Mass spectrum (with NH_3 as reactant gas): M^+, m/e 579. ^1H NMR (in $CDCl_3$, δ): 7.54 (H1, d, 9 Hz), 6.71 (H2, dd, 9–2.9 Hz), 6.60 (H4, d, 2.9 Hz), 6.23 (H12, m), 6.09 (H acet, s), 3.78 (OCH_3,

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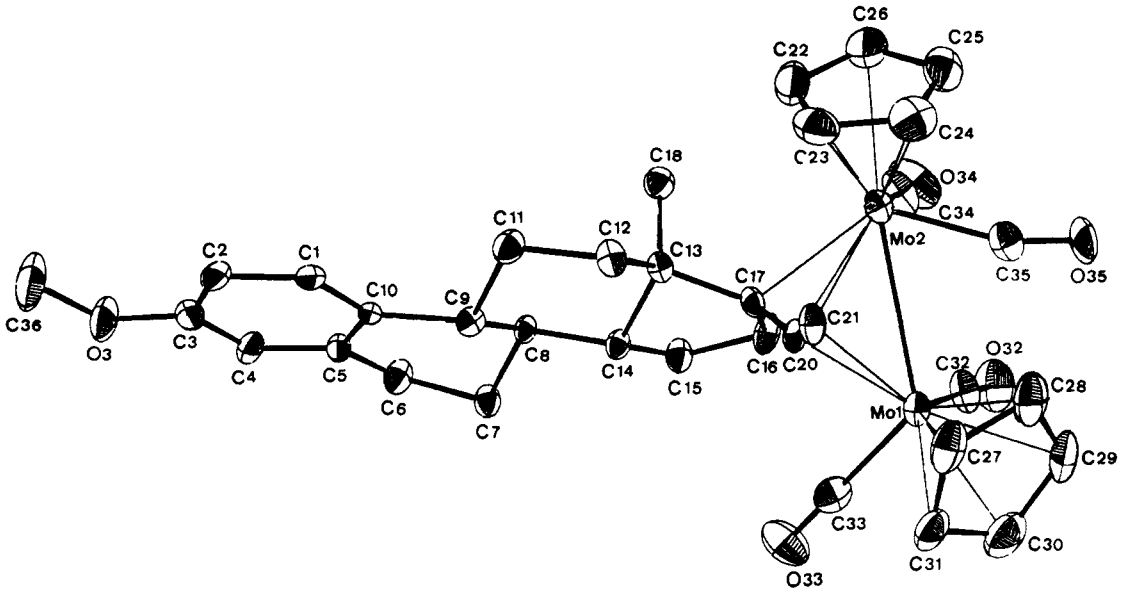
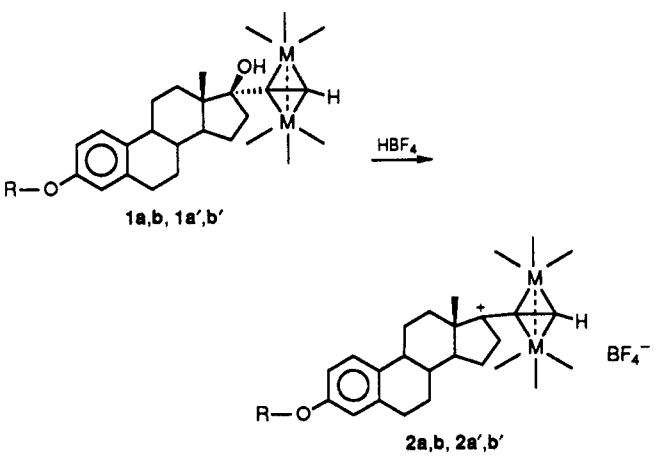


Figure 1. X-ray molecular structure of $[Mo_2Cp_2(CO)_4(\mu\text{-}CH{\equiv}CC_{19}H_{25}O)]^+$ (**2b′**).

Scheme I



1a, 2a: R = H, $M_2L_6 = Co_2(CO)_6$
1a′, 2a′: R = CH_3, $M_2L_6 = Co_2(CO)_6$
1b, 2b: R = H, $M_2L_6 = Mo_2Cp_2(CO)_4$
1b′, 2b′: R = CH_3, $M_2L_6 = Mo_2Cp_2(CO)_4$

s), 2.89 (H6, m), 1.23 (18-CH_3, s). To confirm the position of the double bond in **4a′**, COSY 90 and ^1H–^{13}C chemical shift correlation spectra at 500 MHz were recorded in C_6D_6. Then the position of the double bond was confirmed by the ^1H–^1H connectivity pattern from the COSY 90 spectrum, H6α and H6β being the starting points for the determination of the position of the double bond in C_{11}–C_{12} (see the supplementary material). Attempts to separate other isomers were unsuccessful.

Results

The cationic species **2a′** and **2b′** were obtained in good yield by direct protonation of **1a′** and **1b′** with HBF_4 in ether solution (see Scheme I).

The dimolybdenum derivative $[Mo_2(CO)_4Cp_2(\mu\text{-}CH{\equiv}CC_{19}H_{25}O)]^+BF_4^-$ (**2b′**) was obtained as an orange powder and fully characterized by spectroscopic methods. In addition the X-ray structure was determined (see Figure 1).

The analogous dicobalt species **2a′**, however, formed a burgundy oil; attempts to isolate or crystallize the latter compound were unsuccessful due to the solution instability of the ion with respect to elimination. Spectroscopic data were accessible in acidic medium, however, and the IR spectrum in the ν(CO) region showed higher wavenumber absorptions at 2133, 2104, 2085, and 2060 cm^{-1} compared to those of the alcohol compound **1a′** (ν(CO) 2081, 2050, 2021 cm^{-1}). The pK_{R^+} values, a direct indication of carbenium ion thermodynamic stability, were measured for the complexes **2a′** and **2b′** and found to conform to those reported for the complexes $[Co_2(CO)_6(\mu\text{-}CH{\equiv}CCH_2)]^+BF_4^-$ and $[Mo_2Cp_2(CO)_4(\mu\text{-}CH{\equiv}CCH_2)]^+BF_4^-$ (see Table I).

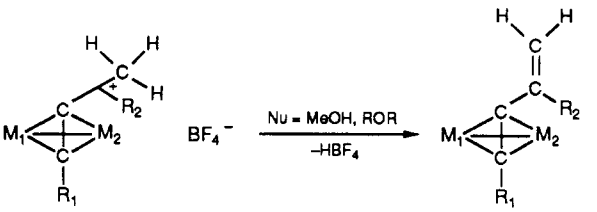
Table I

compd	pK_{R^+}	ref
$Co_2(CO)_6(\mu\text{-}CH{\equiv}CCH_2)^+$	−6.8	13
$Co_2(CO)_6(\mu\text{-}CH{\equiv}CCH_2)^+$	−5.5	this work
$Mo_2(CO)_4Cp_2(\mu\text{-}CH{\equiv}CCH_2)^+$	+3	14
$Mo_2(CO)_4Cp_2(\mu\text{-}CH{\equiv}CCH_2)^+$	+3.5	this work
2a′	−7.3	this work
2b′	+2.7	this work

In the presence of a nucleophile, both species **2a′** and **2b′** promoted elimination of HBF_4 in solution to give the corresponding enyne complexes. The dimolybdenum enyne complex **3b′** was obtained quantitatively in methanol; however, the analogous dicobalt enyne derivative **3a′** was formed only at low temperature. At room temperature, this reaction produced three further isomers, as shown by ^1H NMR spectroscopy. One of these isomers, **4a′**, was isolated and characterized, while attempts to separate the other two isomers by column chromatography with silver nitrate as adsorbate were unsuccessful. It is hypothesized that the noncharacterized compounds have the structures **5a′** and **6a′** shown in Scheme II.

Discussion

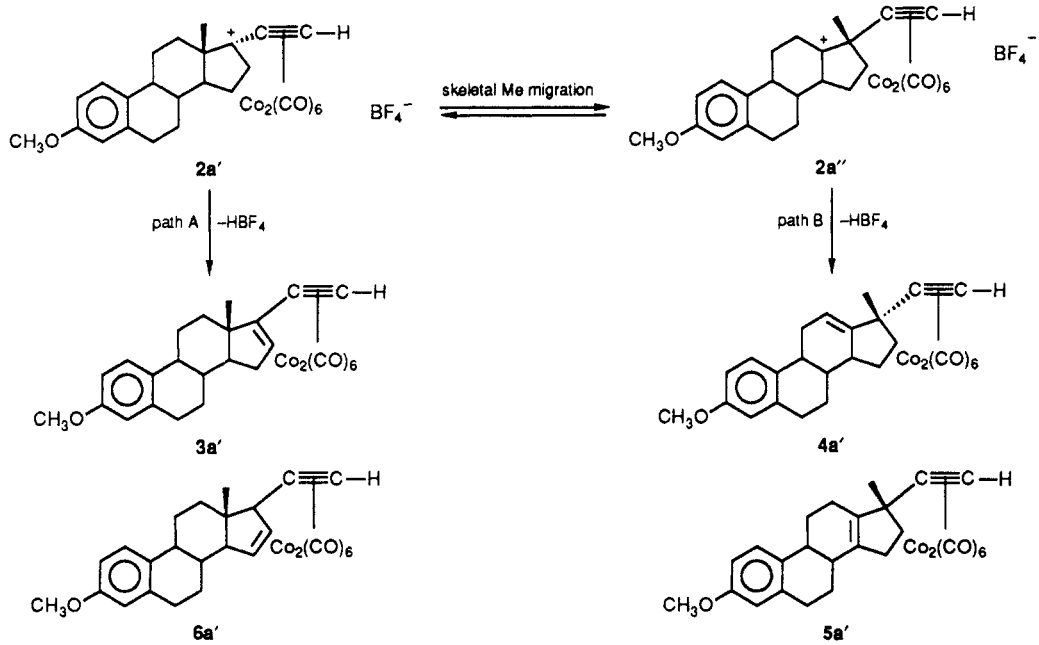
It has been shown that, in the presence of a nucleophile, secondary and tertiary carbenium ions possessing an α-hydrogen, relative to the carbenium ion center, can easily undergo elimination of HBF_4 to give the corresponding enyne compound (eq 1).[1]



(1)

These carbenium ion complexes can be regenerated by treating their corresponding enynes with electrophiles.[15]

Scheme II. Proposed Mechanism for the Formation of the Isomers 3a′ and 4a′



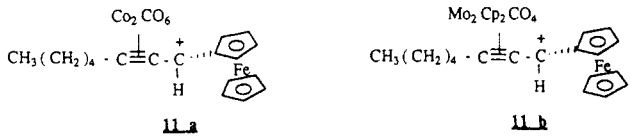


Figure 2.

Despite the difference between the pK_{R^+} values, both **2a′** and **2b′** promote elimination of HBF_4 in solution to form the expected enyne complexes **3a′** and **3b′**. The cobalt derivative, however, also undergoes an unexpected 1,2-methyl shift to give the isomer **4a′**.

A reasonable mechanism would lead to the formation of **4a′** starting from **2a′**. In this mechanism the first step involves the formation of the intermediate ion **2a″** by skeletal migration of the methyl group (C_{18}) from C_{13} to the position 17β. This species would then undergo loss of an HBF_4 molecule to give the complex **4a′** (see Scheme II). It is noteworthy that thermal factors are responsible for the observed methyl migration, since at low temperature (T = −40 °C) only isomer **3a′** is isolated. Hence, enthalpic factors would appear to displace the equilibrium toward path A (Scheme II), providing compound **3a′**, while entropic factors would favor the formation of complex **4a′** (path B, Scheme II).

It has been reported that the differences in reactivity and stability of the propargylic carbenium ions $[M_2L_6(\mu\text{-}CH{\equiv}CCH_2)]^+BF_4^-$ (M_2L_6 = $Co_2(CO)_6$, $Mo_2Cp_2(CO)_4$) can be correlated with the extent of interaction between the metal center and the positively charged carbon in the α-position. A notable example is the complex $[Mo_2Cp'_2(CO)_4(\mu\text{-}CH{\equiv}CCH_2)]^+BF_4^-$ (Cp′ = C_5H_4Me), where X-ray diffraction data suggest a direct interaction between the molybdenum and methylene group (d(Mo–C) = 2.47 Å).[3] This kind of stabilization is expected to be stronger in **2a′** relative to that in **2a″** (Chart I), where the metal and carbenium interaction are closer in space. A further contribution to the stability of these carbenium ions **2a′** and **2a″** is the methoxyestradiol bioligand, which may exert a positive or negative effect depending upon its conformation relative to the organometallic moiety. Similar ligand effects have been invoked to explain the stability of the compounds **11a** and **11b** (Figure 2).

Table II

compd	pK_{R^+}	ref
$Co_2(CO)_6(\mu\text{-}CH{\equiv}CCH_2)^+$	−5.5	this work
$Mo_2(CO)_4Cp_2(\mu\text{-}CH{\equiv}CCH_2)^+$	+3.0	this work
$FcCH_2^+$	−1.14	17
$FcCHCH_3^+$	−0.4	this work
11a	−1.4	this work
11b	−1.0	this work

Spectroscopic results indicate that the stability of these compounds is governed by a M–C_α interaction (C_α = carbenium ion in the α-position), which in the case of **11a** is dominated by Fe–C_α and in **11b** by Mo–C_α.[16] However, the pK_{R^+} values for the carbenium ions are similar and close to that of the ferrocene ion (see Table II). This unexpected equivalence is attributed to the dominant effect of the ferrocenyl ligand and the adjacent long-chain alkyl ligand.

In order to obtain further information on the structure and factors governing the stability of these intermediates **2a′** and **2a″**, structural data are necessary. Structural analogies between propargylic cationic complexes of $[Mo_2Cp_2(CO)_4(\mu\text{-}CH{\equiv}CCH_2)]^+BF_4^-$ and $[Co_2(CO)_6(\mu\text{-}CH{\equiv}CCH_2)]^+BF_4^-$ have been reported.[1,2,3,18] In the absence of crystals of **2a′**, therefore, we have investigated the X-ray structure of the isolobal carbenium ion **2b′**.

Molecular Structure of 2b′. The X-ray structure of compound **2b′** consists of four discrete molecules $[Mo_2Cp_2(CO)_4(C_{21}H_{26}O)]^+$ with BF_4^- as a counteranion. The Ortep view of the cation with the labeling scheme is shown in Figure 1; selected intramolecular bond lengths and angles are presented in the supplementary material. Complex **2b′** contains a normal Mo–Mo single bond of 3.018 Å bridged by the C20–C21 acetylene moiety and a

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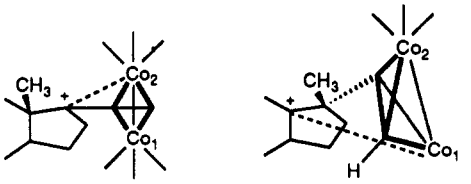
(19) Some spectra were also recorded at 25 °C on a Bruker AM 500 spectrometer for the compounds **4a**. Proton spectra were acquired at 500.135 MHz with use of a 5-mm dual-frequency $^1H/^{13}C$ probe.

Chart I



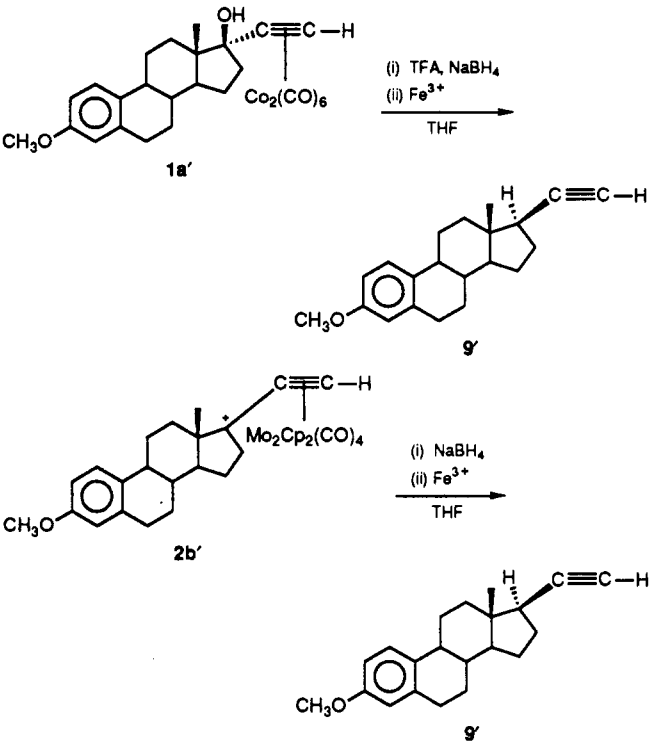
2a′ **2a″**

semibridging carbonyl group. The IR spectrum of compound **2b′** recorded in CH_2Cl_2 solution shows a carbonyl band at 1861 cm^{-1}, which is consistent with the presence of a semibridging carbonyl group.

The coordination around the molybdenum can be described as a distorted octahedron. A π-bonded cyclopentadienyl group, a terminal carbonyl group, and a semibridging group attached to Mo2, the C20–C21 bridging acetylene group, and a weak interaction between Mo2 and C17 complete the coordination sphere of Mo2. A similar environment is observed for Mo1, but with two terminal carbonyl ligands and a π-cyclopentadienyl group. Further, a weak interaction between the semibridging carbonyl group and Mo1 (d(Mo1–C) = 2.76 (2) Å) is observed, indicating that Mo1 is an electron-deficient center. This correlates with electron-counting arguments whereby a formal dative bond from Mo2 to Mo1 is proposed in order to achieve an 18-electron count for each metal. A similar formulation was suggested by Curtis[3] for the complex $[Mo_2Cp'_2(CO)_4(C_3H_3)]^+BF_4^-$. Finally the angle about the central carbon C17–C20–C21 in **2b′** is 144.0 (10)°, similar to that in μ-alkyne adducts.[3] Structural data also indicate that the organometallic moiety plays a role in stabilizing the carbenium ion. The interaction between C17 and Mo2 (d(Mo2–C17) = 2.74 Å) is weaker than that reported for the compound $[Mo_2Cp'_2(CO)_4(C_3H_3)]^+BF_4^-$ (d(C–Mo) = 2.47 Å),[3] and this difference may be attributable to the conformational constraints imposed by the bioligand. The C17–C20 bond is below the plane of the D ring at an angle of 40°, indicating that the organometallic moiety is shifted below the D ring, resulting in a weak Mo–C_α interaction. In the case of the analogous dicobalt compound **2a′**, this kind of interaction is expected to be even weaker (since this situation is a general trend in cobalt carbenium ions with respect to the molybdenum series), allowing the formation of both carbenium ions **2a′** and **2a″**, where **2a″** results from the migration of the methyl group in **2a′**. In addition, stabilization of a carbenium ion at C13 may be achieved by Co1–C13 interaction in this conformation of the organometallic entity (see Chart I).

In order to obtain some stereochemical information on the behavior of **2b′**, we have investigated the reactivity of this complex with $NaBH_4$. Treatment of **2b′** with $NaBH_4$ followed by oxidation with Fe^{3+} afforded the major product **9′**, where the hydrogen is situated below the D ring. This result is not without precedent; Nicholas has reported that the reduction of the dicobalt analogue **2a′** with $NaBH_4$ leads to the same product **9′**[18] and has shown that hydrogen attack occurs at the α-face (see Scheme III). The stereochemistry of this product supports the premise that the orientation of the organometallic moiety is similar for both the dicobalt and the dimolybdenum derivatives **2a′** and **2b′**.

Scheme III



Conclusion

We have shown the important role of organometallic moieties of the type M_2L_6 (M_2L_6 = $Co_2(CO)_6$, $Mo_2Cp_2(CO)_4$) in stabilizing the propargylic carbenium ion derivatives of steroids. In addition, the complexity of the ligand appears to impose constraints that consequently modify the stability and reactivity of such complexes with respect to those of basic model molecules. Isomerization reactions such as those observed with the dicobalt estradiol derivative **2a′** provide examples of this situation.

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Registry No. **1a**, 93122-00-0; **1a′**, 56544-38-8; **1b**, 129620-67-3; **1b′**, 129620-68-4; **2a**, 129620-70-8; **2a′**, 129620-74-2; **2b**, 129620-72-0; **2b′**, 129620-76-4; **3a′**, 129620-78-6; **3b′**, 129620-77-5; **4a′**, 129620-79-7; **9′**, 21321-94-8; **11a**, 123503-24-2; **11b**, 123503-26-4; $Co_2(CO)_8$, 10210-68-1; $Mo_2Cp_2(CO)_4$, 56200-27-2; $Co_2(CO)_6(\mu$-$CH{\equiv}CCH_2)^+$, 62866-99-3; $Mo_2(CO)_4Cp_2(\mu$-$CH{\equiv}CCH_2)^+$, 84079-80-1; $FeCHCH_3^+$, 12129-73-6.

Supplementary Material Available: Details of the spectroscopic data collection, tables of crystallographic data, bond distances, angles, and anisotropic thermal parameters for **2b′**, and NMR spectra (13 pages); a listing of observed and calculated structure factors for **2b′** (11 pages). Ordering information is given on any current masthead page.