Reduction of Metal-Stabilized α-CF_3-Carbenium Ion Complexes under Mild Conditions: Synthesis, Structures, and Reactivity

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Complexed α-CF_3 propargyl alcohols of the general formula $[(M_2L_6)\{\mu\text{-}\eta^2,\eta^2\text{-RC}\equiv\text{CCH(CF}_3\text{)(OH)}\}]$ were prepared with M_2L_6 = $Co_2(CO)_6$, R = $CH_3(CH_2)_4$– (**1**), R = C_6H_5– (**2**); M_2L_6 = $Co_2(CO)_5P(C_6H_5)_3$, R = $CH_3(CH_2)_4$– (**3a**,**b**), R = C_6H_5– (**4a**,**b**); M_2L_6 = $Co_2(CO)_4$dppm, R = C_6H_5– (**5**); M_2L_6 = $Co(CO)_3MoCp(CO)_2$, R = $CH_3(CH_2)_4$– (**6a**,**b**), R = C_6H_5– (**7a**,**b**). An X-ray molecular structure of the propargyl-alcohol complex $[\{Co_2(CO)_4\text{dppm}\}\{\mu\text{-}\eta^2,\eta^2\text{-}C_6H_5C\equiv CCH(CF_3)(OH)\}]$ (**5**) was also determined. The related carbenium ions $[(M_2L_6)\{\mu\text{-}\eta^2,\eta^3\text{-RC}\equiv\text{CCH(CF}_3)\}][BF_4]$ (**8–12**) were obtained from the parent propargyl alcohol complexes by direct protonation with $HBF_4 \cdot Et_2O$ in diethyl ether. These carbenium ions were reduced further by Zn in CH_2Cl_2 to give the alkyne adducts $[(M_2L_6)\{\mu\text{-}\eta^2,\eta^2\text{-RC}\equiv\text{CCH}_2(\text{CF}_3)\}]$ (**13–17**), as confirmed by the X-ray molecular structure of $[(Co_2(CO)_4\text{dppm})\{\mu\text{-}\eta^2,\eta^2\text{-}C_6H_5\text{-}C\equiv CCH_2(CF_3)\}]$ (**17**). Treatment of the carbenium ion complex $[\{Co(CO)_3MoCp(CO)_2\}\{\mu\text{-}\eta^2,\eta^3\text{-}CH_3(CH_2)_4C\equiv CCH(CF_3)\}][BF_4]$ (**8**) with NaSMe unexpectedly afforded the reduced alkyne adduct $[\{Co(CO)_3MoCp(CO)_2\}\{\mu\text{-}\eta^2,\eta^2\text{-}CH_3(CH_2)_4C\equiv CCH_2\text{-}(CF_3)\}]$ (**13**), along with the alkyne-thioether diastereomers $\{Co(CO)_3MoCp(CO)_2\}\{\mu\text{-}\eta^2,\eta^2\text{-}CH_3(CH_2)_4C\equiv CCH(CF_3)(SMe)\}]$ (**18a**,**b**). Presumably, all the reduction reactions proceed primarily by the formation of the transient radical species, which are subsequently transformed into the reduced alkyne complexes by hydrogen abstraction from the solvent medium. Interestingly, in the case of the complexed alcohols $[\{Co_2(CO)_5P(C_6H_5)_3\}\{\mu\text{-}\eta^2,\eta^2\text{-RC}\equiv\text{CCH(CF}_3\text{)(OH)}\}]$ (**3a**,**b**) and (**4a**,**b**), the reduction process occurs in acidic medium in THF/CH_2Cl_2. An extensive study of the electronic and steric factors that influence the stability and reactivity of the carbenium ions were performed, which allowed us to explain the behavior of the related radical species in solution during the reduction process.

Introduction

Trifluoromethyl propargyl alcohols are easily available,[1] however their synthetic interest is still limited, due to the difficulty of preparing the related α-CF_3 carbenium ions prior to nucleophilic addition. Functionalization of the carbenium ion in the α-position relative to the CF_3 group is therefore a hard task.[2] Furthermore, the CF_3 function is a strong electron-withdrawing group and thus strengthens the C−O bond, which prevents the formation of a carbenium center (CF_3−C^+). In addition, the steric effects and electronic repulsion of the incoming nucleophiles with fluorine atoms of the α-CF_3 group decrease the reaction rate, and harsh conditions are often required.[3][4] To overcome such difficulties it is vital to stabilize the carbenium center (CF_3−C^+). This can be achieved by introducing a dinuclear cluster such as M_2L_6 = [$-Co_2(CO)_6$]; = [$-Cp_2Mo_2(CO)_4$] or a mixed dinuclear complex = [$-Co(CO)_3MoCp(CO)_2$] to the acetylenic unit of the trifluoromethyl propargyl alcohols. A direct metal···C^+ interaction with carbenium center therefore occurs, which stabilizes the whole complex and allows further functionalization to proceed under mild conditions.

Metal-stabilized carbon electron deficient systems of the type $[(M_2L_6)(\mu\text{-}\eta^2,\eta^3\text{-RC}\equiv\text{CCR}_2)]^+$ have been the focus of several reviews.[5] The analogous carbon-radical complexes were also reported.[6] In the latter, coupling reactions were observed.[7] A synthetic application of this chemistry is the preparation of cyclic diacetylenic compounds promoted by recombination of $[Co_2(CO)_6]_2$ diacetylenic di-radicals.[8]

Pursuing our research investigations in this field we prepared a new class of α-CF_3-propargyl alcohol complexes, in which a dinuclear cluster of the type [$Co_2(CO)_6$], [$Co_2(CO)_5P(C_6H_5)_3$], [$Co_2(CO)_4\{P(C_6H_5)_2\}_2CH_2$], or heterobimetallic [$Co(CO)_3MoCp(CO)_2$] is coordinated to the acetylenic unit (−C≡C−) (Figure 1).

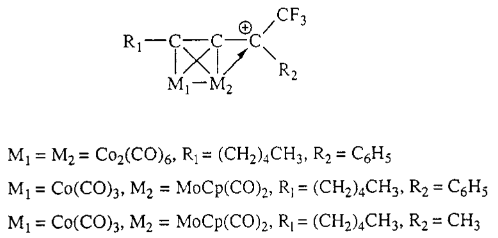

Figure 1. General formula of metal-stabilized carbenium ion

In a preliminary communication,[9] we have shown that it is possible to obtain and isolate α-CF_3 methyl- or phenyl-substituted propargylium ions, when they are stabilized by

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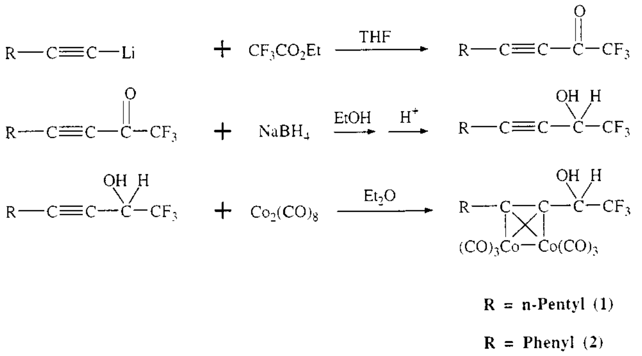
an adjacent bimetallic $[Co_2(CO)_6]$- or $[Co(CO)_3MoCp(CO)_2]$-acetylenic cluster. Through out the paper we will use the abbreviations $[Co_2]$ for $[Co_2(CO)_6]$, and [Co,Mo] for $[Co(CO)_3MoCp(CO)_2]$.

In this paper we describe the synthesis of bimetallic $[Co_2]$ and [Co,Mo] complexed acetylenic α-CF_3 alcohols and describe their ability to give carbenium ions in acidic medium. The capacity of these ions to be reduced, either directly from the complexed propargyl alcohols or starting from the related metal-stabilized carbenium ions, has also been investigated.

Results and Discussion

Synthesis, Structure, and Characterization of α-CF_3-Propargyl Alcohol Complexes $[(M_2L_6)\{\mu\text{-}\eta^2,\eta^2\text{-}RC{\equiv}CCH(CF_3)(OH)\}]$

The α-CF_3 propargyl alcohols were synthesized by treatment of the ethyltrifluoroacetate with the appropriate lithiated acetylenic compound: RC≡CLi [R = $CH_3(CH_2)_4$–; C_6H_5–]. The obtained ketones were then reduced by $NaBH_4$ in alcoholic medium, and the resulting alcohols are subsequently complexed by $Co_2(CO)_8$ leading to the alkyne complexes $[\{Co_2(CO)_6\}\{\mu\text{-}\eta^2,\eta^2\text{-}RC{\equiv}CC(OH)(CF_3)H\}]$ {R = $CH_3(CH_2)_4$-(**1**); R = C_6H_5-(**2**)} according to Scheme 1.



Scheme 1. Preparation of complexed $[Co_2(CO)_6]$propargyl alcohols

Substitution of a carbonyl ligand of complexes **1**–**2** by either a monophosphane $[P(C_6H_5)_3]$ or a chelating phosphane such as dppm = $[\{P(C_6H_5)_2\}_2CH_2]$ using standard methods[10] leads to the phosphane–$[Co_2]$-complexed alcohols **3a**, **3b**, **4a**, **4b**, and **5**. All compounds were completely characterized further, and the X-ray molecular structure of $[\{Co_2(CO)_4dppm\}\{\mu\text{-}\eta^2,\eta^2\text{-}C_6H_5C{\equiv}CCH(CF_3)(OH)\}]$ (**5**) was determined. This compound crystallizes in the monoclinic unit cell, space group *P*21/n. The bonding and molecular geometry of **5** are shown in a CAMERON[24] diagram in Figure 2. Crystallographic data and parameters for **5** are given in Table 4, selected bond lengths and angles are listed in Table 1. Complex **5** consists of a tetrahedral Co_2C_2 core with –C≡C– bond of the acetylene unit in a perpendicular orientation at a almost 90° angle relative to Co–Co bond. The metal-metal bond length of 2.473 Å conforms with previous literature values for a single Co–Co bond.[11] The coordination geometry of each Co center is a distorted octahedron occupied by the acetylene carbons, two carbonly ligands and a coordinated phosphane ligand of the bridged dppm unit.

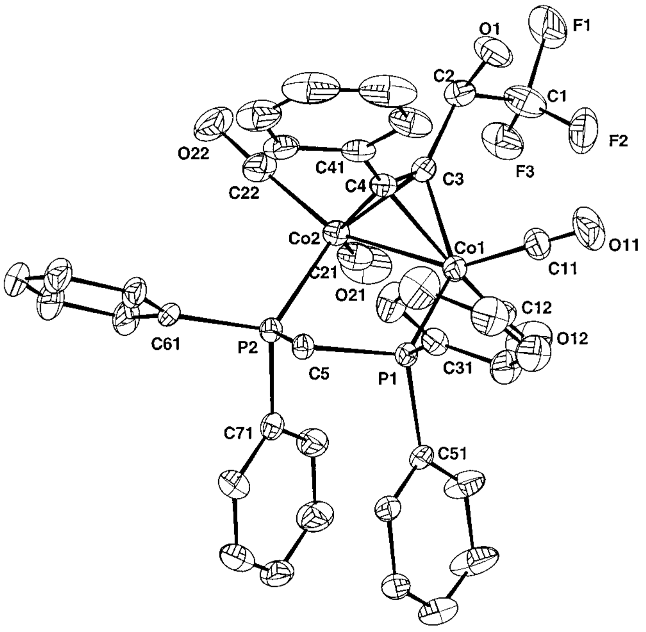


Figure 2. X-ray molecular structure of $[\{Co_2(CO)_4dppm\}\{\mu\text{-}\eta^2,\eta^2\text{-}C_6H_5C{\equiv}CCH(CF_3)(OH)\}]$ (**5**) with atom numbering system

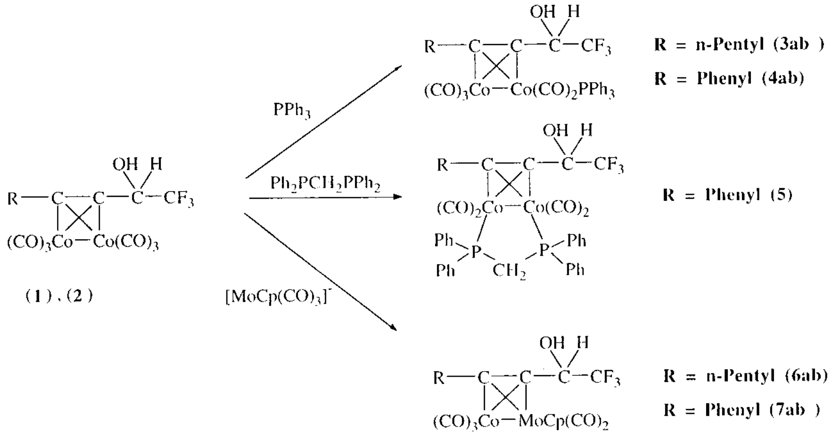
Table 1. Selected bond lengths [Å] and angles [°] for complex **5**

Co(1)–Co(2)	2.473(1)	Co(1)–P(1)	2.227(2)
Co(1)–C(3)	1.942(6)	Co(2)–P(2)	2.222(2)
Co(1)–C(4)	1.974(7)	Co(2)–C(3)	1.947(6)
Co(2)–C(4)	1.970(6)	C(3)–C(4)	1.357(9)
Co(1)–C(4)–Co(2)	77.7(2)	Co(1)–C(3)–Co(2)	79.0(2)
C(3)–C(4)–C(41)	141.5(6)	C(2)–C(3)–C(4)	126.6(7)

Furthermore, the α-CF_3-alcohol complexes **3a**, **b** and **4a**, **b** exist as a pair of diastereomers (Scheme 2). Starting from the $[Co_2]$-complexed alcohols **1**–**2**, the substitution of the metallic vertex $[Co(CO)_3]$ by the isolobal $[MoCp(CO)_2]$ leads to the hetero-bimetallic [Co,Mo]-complexed alcohols[12] obtained also as two diastereomers **6a**, **b** and **7a**, **b**, respectively. The complexed alcohols **1**–**7** thus obtained have the α-CF_3 substituent on the carbon atom bearing the hydroxyl function, while the C-4 acetylenic carbon is either substituted by an alkyl or an aryl substituent.

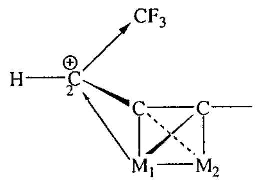
Mayr et al.[13] recently reported that alkyl or aryl substituents at C-4 do not affect the electronic density of the cluster unit, and consequently do not affect the electrophilicity of the corresponding $[Co_2]$–carbenium ions. The major differences among these complexed propargyl alcohols (**1**–**7**) therefore reside in the electronic nature of the bimetallic moieties coordinated to the acetylenic function.

It is well established that a cluster unit, or its electron donating ability, alleviates the positive charge of the adjacent α-carbenium center. It was previously shown by pK_R^+ measurements that the $[MoCp(CO)_2]$ vertex is much more



Scheme 2. Preparation of heterobimetallic [Co−Mo]- and [Co_2]-phosphane propargyl aclohols

efficient as an electron donating group than the [$Co_2(CO)_6$] unit[14][15] Consequently, the [Mo_2] or [Co,Mo] are much more stable and less reactive than the [Co_2]-complexed carbenium ions. Due to their low reactivity several X-ray structures of [Mo_2]- or [Co,Mo]-stabilized carbenium ions were reported in the literature.[1][5] However, very recently an X-ray structure of a [Co_2]−carbenium ion complex has been described. In this particular example, the carbenium center is flanked by two [Co_2] cluster units.[16] Spectroscopic results based on ^1H- and ^{13}C-NMR analysis and MO calculations on these metal-stabilized carbenium ions have shown that the electronic transfer occurs from the ligand to the carbon-deficient electronic center through the metal atom.[17] For instance, substituting a carbonyl ligand by a monophosphane or a diphosphane ligand has the dramatic effect of increasing the electronic density of the cluster core. This electronic density change is reflected on the ν_{CO} absorptions, which shift to low frequency.[18] Such behavior is illustrated by complex [$\{Co_2(CO)_6\}\{\mu$-η^2,η^2-$CH_3(CH_2)_4$-$C{\equiv}CCH(CF_3)(OH)\}$] (**1**), which shows three ν_{CO} bands at 2097, 2057, and 2029 cm^{-1}. The related monophosphane complex [$\{Co_2(CO)_5P(C_6H_5)_3\}\{\mu$-$\eta^2,\eta^2$-$CH_3(CH_2)_2$-$C{\equiv}CCH(CF_3)(OH)\}$] (**3**) exhibits ν_{CO} absorptions at 2063, 2015, 2005, 1987, and 1962 cm^{-1} (see Table 4). These results are in accord with those reported by Mayr et al,[13] which show that the carbenium ion complex [$\{Co_2(CO)_5P(C_6H_5)_3\}\{\mu$-$\eta^2,\eta^3$-$HC{\equiv}CCH(C_6H_5)\}$]$^+$ is less electrophilic than the parent carbenium ion [$Co_2(CO)_6\{\mu$-η^2,η^3-$HC{\equiv}CCH(C_6H_5)\}$]$^+$. In summary, based on the literature data and our own experiments, we have classified the electron density on the cluster moieties of these α-CF_3-propargyl alcohols, in decreasing order as follows: [Co,Mo] > [Co_2P_2] > [Co_2P] > [Co_2]. As for carbenium ion complexes, it is noteworthy to remark that the carbenium center C-2 will be stabilized by the cluster unit, but to a different extent depending on the scale shown above. This should also overcome the withdrawing effect exerted by the α-CF_3 group. These two opposing effects (Figure 3) were examined by monitoring the reactivity of these carbenium ions in solution towards reduction. The results are presented in the next section.



[M_1-M_2] = [Co-Mo] = [$Co(CO)_3$-$MoCp(CO)_2$]
[Co_2] = [$Co_2(CO)_6$]
[Co_2P] = [$Co_2(CO)_5\ P(Ph)_3$]
[Co_2P_2] = [$Co_2(CO)_4(P(Ph_2)_2CH_2$]

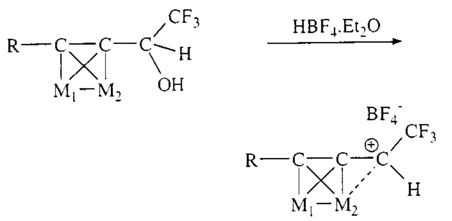
Figure 3. Schematic drawing showing two opposite interactions at the cabenium center: (a) metal-stabilized effect; (b) CF_3-distabilization attactive effect

Synthesis and Reduction of the Metal-Stabilized α-CF_3-Propargyl Carbenium Ion Complexes [(M_2L_6)-$\{\mu$-η^2,η^3-$RC{\equiv}CCH(CF_3)\}$][BF_4]

Treatment of the propargyl alcohol complexes [$\{Co_2(CO)_6\}\{\mu$-η^2,η^2-$RC{\equiv}CC(OH)(CF_3)H\}$] (**1−2**) by $HBF_4 \cdot Et_2O$ in ether did not afford any precipitate, as expected for the formation of the related carbenium ion salts. In contrast, the complexed alcohols **3−7** gave, under the same experimental conditions, the corresponding carbenium ions **8**, **9**, **10**, **11**, and **12**, respectively (Scheme 3). These results demonstrate that the electron donating effect of the [Co_2] cluster in Complexes (**1−2**) is not sufficient to overcome the α-CF_3 withdrawing effect. The ν_{CO} frequencies in the starting alcohols and their corresponding carbenium ions are listed in Table 3.

Furthermore, we noticed that protonation of the [Co_2P] complexed alcohols **3a**, **b** and **4a**, **b** by $HBF_4 \cdot Et_2O$ in a CH_2Cl_2/THF readily afforded the reduced complexes **15** and **16**, but not the related carbenium ion complexes

(Scheme 4). In the previous reaction the THF plays the role of the reducing agent, by acting as a mono-electron donor, as was previously reported.[19] Surprisingly, complexes **1−2**, were not reduced using CH_2Cl_2/THF as a solvent.



$M_1 = Co(CO)_3$, $M_2 = MoCp(CO)_2$
$R = (CH_2)_4CH_3$ (**8**)
$R = C_6H_5$ (**9**)
$M_1 = Co(CO)_3$, $M_2 = Co(CO)_2P(Ph)_3$
$R = (CH_2)_4CH_3$ (**10**)
$R = C_6H_5$ (**11**)
M_1, $M_2 = Co_2(CO)_4CH_2(P(Ph)_3)_2$
$R = C_6H_5$ (**12**)

Scheme 3. Synthesis of the metal-stabilized carbenium ions (**8−12**).

It is also interesting to note that under the same experimental conditions the propargyl alcohols **5−7** afforded the carbenium ions **8−9** and **12**, therefore these compounds are very stable and cannot be reduced by the CH_2Cl_2/THF system. Carbenium ions **8−9** and **12** can readily be reduced, however, by using Zn/CH_2Cl_2 as reducing agent leading to compounds **13−14** and **17** (Scheme 5). The structures of these compounds were all identified by spectroscopic methods and elemental analysis (see Experimental Section), furthermore, the X-ray molecular structure of compound **17** was determined. The compound crystallizes with one molecule of acetone in the triclinic unit cell, space group *P*1. The bonding and molecular geometry of **17** are shown in a CAMERON[24] diagram in Figure 4. Crystallographic data and parameters for **17** are given in Table 4, selected bond lengths and angles are listed in Table 2. Complex **17** displays a tetrahedral Co_2C_2 core with -C≡C- bond of the acetylene unit in a perpendicular orientation at a almost 90° angle relative to Co−Co bond. The metal-metal bond length is 2.4876 Å, slightly longer than that of complex **5**.

The coordination geometry of each Co center is a distorted octahedron, occupied by the acetylene carbons, two carbonly ligands, and a coordinated phosphane ligand of the bridged dppm unit. Overall, the structure of **17** looks very similar to that of the parent molecule, **5**, and confirms its reduction since the hydroxyl group is now substituted by a hydrogen atom.

At this stage a few brief comments are required, since, according to our results, formation of a Co-complexed propargyl radical is only possible providing its related carbenium ion can be formed. This explains why the alcohol complexes **1−2** cannot be reduced by the THF/CH_2Cl_2 system. On the other hand, if the carbenium ion complex is strongly

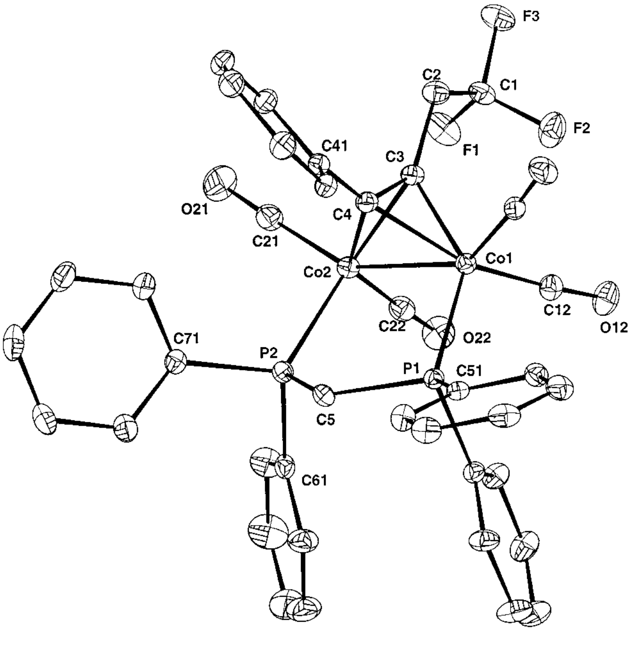


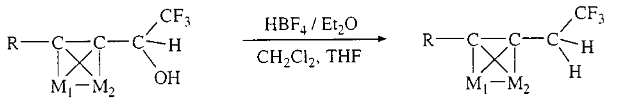
Figure 4. X-ray molecular structure of $[\{Co_2(CO)_4dppm\}\{\mu\text{-}\eta^2,\eta^2\text{-}C_6H_5C{\equiv}CCH_2(CF_3)\}]$ (**17**) with atom numbering system

Table 2. Selected bond lengths [Å] and angles [°] for complex **17**

Co(1)−Co(2)	2.4876(7)	Co(1)−P(1)	2.227(1)
Co(1)−C(3)	1.950(4)	Co(2)−P(2)	2.225(2)
Co(1)−C(4)	1.939(4)	Co(2)−C(3)	1.934(4)
Co(2)−C(4)	1.967(4)	C(3)−C(4)	1.341(6)
Co(1)−C(4)−Co(2)	79.1(2)	Co(1)−C(3)−Co(2)	79.6(2)
C(3)−C(4)−C(41)	135.5(4)	C(2)−C(3)−C(4)	135.1(4)

Table 3. Comparison of ν(CO) (cm^{-1}) frequencies between the complexed alcohols and their corresponding carbenium ions

Alcohol	ν(CO) [cm^{-1}]	Cations	ν(CO) [cm^{-1}]
[Co_2]-(**1**)	2097, 2057, 2029		unstable, not isolated
[Co_2]-(**2**)	2048, 2050, 2020		unstable, not isolated
[Co_2P]-(**3**)	2063, 2015, 2005, 1987, 1967	**8**	2104, 2065, 2055, 2006, 1989
[Co_2P]-(**4**)	2068, 2018	**9**	2108, 2072, 2005
[Co_2P_2]-(**5**)	2066, 2029, 2001, 1974	**10**	2138, 2063, 2005
[Co,Mo]-(**6**)	2051, 2001, 1984, 1942	**11**	2123, 2071, 2022, 1973
[Co,Mo]-(**7**)	2057, 2002, 1949	**12**	2090, 2065, 2004, 1978

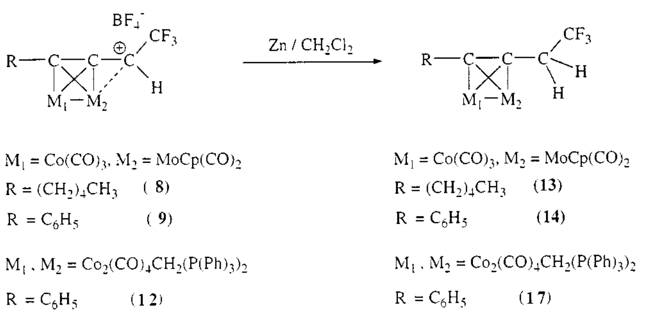


3ab, 4ab

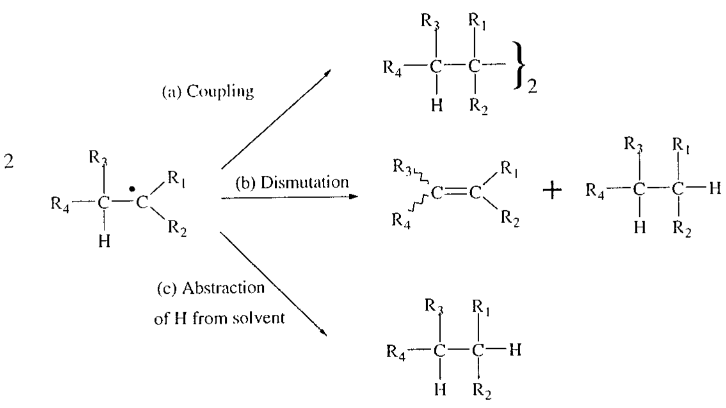
$M_1 = Co(CO)_3$, $M_2 = Co(CO)_2P(Ph)_3$

$R = (CH_2)_4CH_3$ (**15**) ; $R = C_6H_5$ (**16**)

Scheme 4. Reduction of α-CF_3-propargyl alcohol complexes (**3−4**) using THF/CH_2Cl_2 in acidic medium



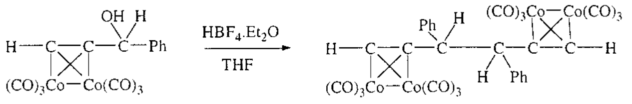
Scheme 5. Reduction of the metal-stabilized carbenium ions (**8**, **9**, and **12**) by Zn in CH_2Cl_2



Scheme 7. Possible reactions of carbon-centered radicals

stabilized by the bimetallic cluster, then the mono-electronic transfer from THF to the deficient electronic center is not possible, as shown by the alcohol complexes **5−7**, and the reaction stops at the carbenium ion stage. This hypothesis is also confirmed by the fact that the complex $[\{Mo_2Cp_2(CO)_4\}\{\mu\text{-}\eta^2,\eta^2\text{-}HC{\equiv}CCH(C_6H_5)(OH)\}]$, which is isolobal to the compound $[\{Co_2(CO)_6\}\{\mu\text{-}\eta^2,\eta^2\text{-}HC{\equiv}CCH(C_6H_5)(OH)\}]$, does not lead to coupling products. Finally, Co-stabilized carbenium ion exhibiting a stability between the two previous examples can be reduced by mono-electron transfer from THF to give the reduced compounds.

We would also like to outline that by either using the THF/CH_2Cl_2 system or by the action of Zn/CH_2Cl_2, our α-CF_3-propargyl alcohol complexes $[\{Co_2(CO)_4L_2\}\{\mu\text{-}\eta^2,\eta^2\text{-}RC{\equiv}CC(OH)(CF_3)H\}]$ (**3−7**) gave exclusively the reduction products, and never the coupling reaction products, which is the major product observed with $[\{Co_2(CO)_6\}\{HC{\equiv}CCH(C_6H_5)(OH)\}]$ (Scheme 6).[19]



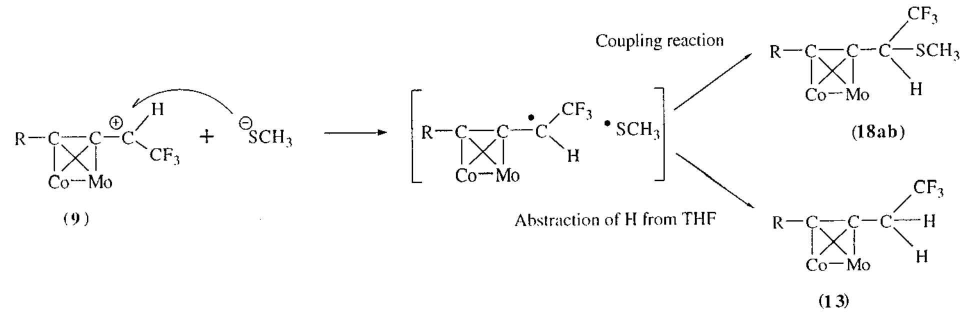
Scheme 6. Coupling reaction observed for a $[CO_2]$-complexed acetylenic alcohol in acidic medium

Generally, in carbon-centered radical reactions, the competition between coupling reactions, dismutation and abstraction of a hydrogen from the solvent, is a well documented area.[20](Scheme 7). For instance, primary carbon centered radical next to a hydrogen atom in the β position favors the dismutation reaction over the other reactions. Increasing the size of the substituents at the radical center favors the abstraction of a hydrogen from the solvent relative to recombination and dismutation. In our propargyl alcohol compounds, the presence of a CF_3 group in the alpha position to the carbon centered radical would impede the coupling reaction, due to electron repulsion, and hence abstraction of a proton from the solvent becomes the major reaction.

Another important feature of this chemistry was demonstrated when the carbenium ion complex $[\{Co(CO)_3MoCp(CO)_2\}\{\mu\text{-}\eta^2,\eta^3\text{-}CH_3(CH_2)_4C{\equiv}CCH(CF_3)\}][BF_4]$ (**8**) was treated by NaSMe to give two compounds in 1:1 ratio. These compounds were identified, respectively, as the reduced compound $[\{Co(CO)_3MoCp(CO)_2\}\{\mu\text{-}\eta^2,\eta^2\text{-}CH_3(CH_2)_4C{\equiv}CCH(CF_3)H\}]$ (**13**) and the substituted thio-ether complexes $[\{Co(CO)_3MoCp(CO)_2\}\{\mu\text{-}\eta^2,\eta^2\text{-}CH_3(CH_2)_4C{\equiv}CCH(CF_3)(SMe)\}]$ (**18a** and **b**) obtained as a pair of diastereomers. These results illustrate that the reaction between the isolated [Co,Mo] stabilized carbenium ion **9** and the methyl thiolato anion proceed through a radical pathway, whereby the transient radical pair species can either recombine in the solvent cage to give coupling reaction[21] as illustrated by formation of **18a**, **b** or, after diffusion from the solvent cage, would abstract a hydrogen atom from the solvent to afford the reduced alkyne adduct **13** (Scheme 8).

Conclusion

Co-complexed propargyl radicals may be formed during the reduction of α-CF_3 complexed acetylenic alcohols in acidic medium providing that their related carbenium ions are formed and are slightly stabilized. The stability of these carbenium ions depends on the electron donor ability of the bimetallic cluster. Our α-CF_3-complexed carbenium ions system seems to offer a new insight into, and the comprehension of the factors that allow certain cobalt-stabilized carbenium ions to undergo one electron reduction process rather than a substitution reaction. The present study shows that three classes of propargyl alcohol complexes can be distinguished. These classes could be defined as follows: class (a) − the parent alcohol complexes $[\{Co_2(CO)_6\}\{\mu\text{-}\eta^2,\eta^2\text{-}RC{\equiv}CCH(CF_3)(OH)\}]$ (**1−2**) cannot be reduced by THF/CH_2Cl_2 in acidic medium because the related $[Co_2]$-carbenium ions cannot be formed, class (b) − weakly stabilized carbenium ions such as $[Co_2P]$ complexes **10** and **11** are easily reduced in acidic medium by THF/CH_2Cl_2, and class (c) − stable carbenium ions such as complexes **8**, **9**, and **12** can only be reduced when a strong reducing agent is used.

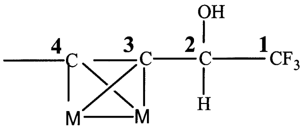


Scheme 8. Abstraction and coupling reactions occurring from a radical pair process

Experimental Section

General Methods: All reactions were carried out under an atmosphere of dry argon. Solvents were dried and distilled using standard techniques. Diethyl ether and THF were distilled from sodium benzophenone ketyl, dichloromethane and acetonitrile from sodium hydride, pentane was treated by sulfuric acid and distilled on sodium. Ethylrifluoroacetate, heptyne triphenylphosphane, Bis(diphenylphosphanyl)methane, $Mo_2Cp_2(CO)_6$, $Co_2(CO)_8$, HBF_4/Et_2O, aqueous 40% HBF_4, CD_2Cl_2, CD_3Cl, [D$_6$]acetone were used as purchased. − IR spectra were recorded on a Bio-rad FTS 165 spectrometer from KBr disks. All absorptions are expressed in wave numbers (cm^{-1}). − ^{1}H-, ^{13}C-, ^{19}F and ^{31}P-NMR spectra were recorded on a Bruker AM instrument, using standard programs for proton (299.MHz), carbon (75 MHz), fluoride (282 MHz) and phosphorus (124 MHz) spectra. NMR chemical shifts are reported in δ (ppm) relative to TMS (^{1}H, ^{13}C), $CFCl_3$ (^{19}F) or 85% H_3PO_4 (^{31}P); Data (^{13}C, ^{31}P) are proton decoupled. − Elemental analyses were performed by: "Centre régional de microanalyse-Université Pierre et Marie Curie".

Throughout the experimental section the carbon numbering system for the α-CF_3-propargyl alcohol complexes is shown on this diagram.



Synthesis of [{$Co_2(CO)_6$}-μ,η^2,η^2-(1,1,1-trifluoronon-3-yne-2-ol)] (1): To 1-heptyne (2.9 g, 3·10^{-2} mol) in THF (40 mL) was added dropwise at 0°C, butyllithium (11.5 mL of a 2.5 M solution). After stirring 0.5 h, the mixture was cooled to −50°C and 2.48 g of ethyltrifluoroacetate (2·10^{-2} mol) were added dropwise. The mixture was stirred for 1 h and after attaining room temperature, 50 mL of NH_4Cl saturated aqueous solution were added. The organic phase was extracted by 3 × 25 mL of diethyl ether. The extracts were dried with $MgSO_4$ and the solvent removed under vacuum; The colorless oil was dissolved in 30 mL of ethanol and $NaBH_4$ (1.2 g) was added, progressively. The reaction was monitored by TLC on silica gel (eluent pentane/ether 5:1). The reaction was complete in one hour. After addition of water (50 mL) the organic phase was extracted by 3 × 25 mL of diethyl ether, dried ($MgSO_4$), and the solvent removed under vacuum to give a colorless oil (4.73 g). To the obtained oil in 50 mL of diethyl ether was added, at room temperature under argon, dicobalt octacarbonyl (1.2 g, 2.5 .10^{-2} mol). The reaction was monitored by TLC on silica gel (eluent pentane/ether, 6:1). The reaction was complete in one hour. After adsorption of the crude product on silica gel, flash chromatography (pentane then pentane/ether, 10:1) leads to a dark red oil in 50% yield (5.1 g). − ^{1}H NMR ($CDCl_3$): δ = 5.12 (dq, *J* = 14.0 Hz, *J* = 7.2 Hz, 1 H, 2-H), 5.81 (t, *J* = 8.2 Hz, 2 H, 5-H), 2.53 (d, *J* = 7.2 Hz, 1 H, OH), 1.62 (m, 2 H, 6-H), 1.43 (m, 4 H, 7,8-H), 0.93 (t, *J* = 7.2 Hz, 3 H, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 198.6 (CO), 123.2 (q, *J* = 282.0 Hz, C-1), 100.1 (C-3), 86.1 (C-4), 70.9 (q, *J* = 33.0 Hz, C-2), 32.9 (C-5), 31.3 (C-6), 31.0 (C-7), 22.0 (C-8), 13.5 (C-9). − ^{19}F NMR ($CDCl_3$): δ = −75.9 (d, *J* = 6.1 Hz). − IR ν(CO): ṽ = 2095, 2057, 2029 cm^{-1}. − $C_{15}H_{13}Co_2F_3O_7$ calcd. C 37.52, H 2.73; found C 37.70, H 2.81.

[{$Co_2(CO)_6$}-{μ-η^2,η^2-(1,1,1-trifluoro-4-phenylbut-3-yne-2-ol)] (2): The same synthetic procedure was used for the preparation of compound (**2**) as was used for (**1**). − ^{1}H NMR ($CDCl_3$): δ = 7.36 (m, 3 H, C_6H_5), 5.57 (m, 2 H, C_6H_5), 5.37 (dq, *J* = 13.5 Hz, *J* = 6.1 Hz, 1 H, 2-H), 2.86 (d, *J* = 6.1 Hz, 1 H, OH). − ^{13}C NMR ($CDCl_3$): δ = 198.3 (CO), 137.2, 129.5, 128.9, and 128.2 (C_6H_5), 124.1 (q, *J* = 283.0 Hz, C-1), 92.8 (C-3), 85.6 (C-4), 71.3 (q, *J* = 31.9 Hz). − ^{19}F NMR ($CDCl_3$): δ = −76.58 (d, *J* = 6.1 Hz). − IR ν(CO): ṽ = 2089, 2050, 2020 cm^{-1}. − $C_{16}H_7Co_2F_3O_7$ calcd: C 39.54,H 1.45; found C 40.41, H 1.65.

[{$Co_2(CO)_5P(C_6H_5)_3$}-μ-η^2,η^2-(1,1,1-trifluoronon-3-yne-2-ol)] (3a, 3b): To 0.58 g of (**1**) (1.21 mmol) in THF (15 mL) was added $P(C_6H_5)_3$ (0.40 g, 1.52 mmol) in THF (35 mL) and 2.3 mL of a 1 M solution of sodium/benzophenone in THF. The reaction was monitored by TLC (silica gel, eluent pentane/ether 4:1). The reaction was left for one hour at room temperature, then the mixture was purified by flash chromatography, giving the two diastereomers, which were separated in the order of increasing polarity (**3a**) then (**3b**), as red oils, 0.35 g and 0.06 g (40% and 7% yield, respectively).

Compound 3a: ^{1}H NMR ($CDCl_3$): δ = 7.56−7.31 (m, 15 H, C_6H_5), 3.96 (dq, *J* = 14 Hz, *J* = 8.0 Hz, 1 H, 2-H), 2.22 (m, 1 H, 5-H), 1.99 (d, *J* = 8.0 Hz, 1 H, OH), 1.72 (m, 1 H, 5-H), 1.51 (m, 2 H, 6-H), 1.25 (m, 4 H, 7,8-H), 0.89 (t, *J* = 7.1 Hz, 3 H, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 206.2, 204.8, and 200.9 (CO), 134.3 (d, *J* = 53.4 Hz, C$_{ipso,}$ C_6H_5), 133.0 (d, *J* = 10.1 Hz, C$_{ortho,}$ C_6H_5), 130.8 (C$_{para,}$ C_6H_5), 129.0 (d, *J* = 9.5 Hz, C$_{meta,}$ C_6H_5), 123.0 (q, *J* = 283.5 Hz, C-1), 96.1 (C-3), 92.7 (C-4), 68.9 (q, *J* = 32.5 Hz, C-2), 31.7, 31.5, and 31.2 (C-5-6-7), 22.7 (C-8), 14.2 (C-9). − ^{19}F NMR ($CDCl_3$): δ = −76.5 (d, *J* = 6.1 Hz, CF_3). − ^{31}P NMR ($CDCl_3$): δ = 52.9 (broad). − IR ν(CO): ṽ = 2063, 2015, 2005, 1987, and 1962 cm^{-1}.

Compound 3b: ^{1}H NMR ($CDCl_3$): δ = 7.62−7.55 (m, 15 H, C_6H_5), 4.13 (dq, *J* = 14 Hz, *J* = 7.8 Hz, 1 H, 2-H), 2.36 (m, 1 H, 5-H), 2.04 (m, 1 H, 5-H), 1.86 (d, *J* = 7.8 Hz, 1 H, OH), 1.51 (m, 2 H, 6-H), 1.29 (m, 4 H, 7,8-H), 0.90 (t, *J* = 7.1 Hz, 3 H, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 206.1−201.1 (CO), 134.6 (d, *J* = 39.6 Hz,C$_{ipso}$), 133.0 (d, *J* = 10.4 Hz,C$_{ortho}$), 130.7 (C$_{para}$), 128.9 (d,

J = 8.4 Hz,C_{meta}), 123.5 (q, J = 234.7 Hz, C-1), 98.8 (C-3), 79.9 (C-4), 71.5 (q, J = 32.0 Hz, C-2), 32.7, 31.9, and 22.7 (C-6-7-8), 14.1 (C-9). − ^{19}F NMR ($CDCl_3$): δ = −76.7.(d, J = 6.1 Hz, CF_3). − ^{31}P NMR ($CDCl_3$): δ = 51.3.(broad). − IR ν(CO): $\tilde{\nu}$ = 2062, 2015, 1998, 1963 cm^{-1}. − $C_{32}H_{28}Co_2F_3O_6P$ calcd: C 53.81, H 3.94; found C 55.65, H 4.14.

[{Co_2(CO)5P(C_6H_5)$_3$}-µ-$η^2$,$η^2$-(1,1,1-trifluoro-4-phenylbut-3-yne-2-ol)] (4a,4b): Compounds (**4a**) and (**4b**) were prepared in the same way described for **3a** and **3b**, and were isolated in 35% and 25% yield, respectively.

Compound 4a: ^{1}H NMR ($CDCl_3$): δ = 7.41−7.19 (m, 20 H, C_6H_5), 3.97 (qui, J = 14.0 Hz, J = 7.8 Hz 1 H, 2-H), 2.03 (d, J = 7.8 Hz, 1 H, OH). − ^{13}C NMR ($CDCl_3$): δ = 200.5 (CO), 138.8 ($C_{ipso,}$ C_6H_5), 133.9 (d, J = 40.3 Hz, $C_{ipso,}$ PC_6H_5), 133.2 (d, J = 11.6 Hz, $C_{ortho,}$ PC_6H_5), 130.7 ($C_{meta,}$ PC_6H_5), 130.4 (C_6H_5), 128.8 (C_6H_5), 128.7 (d, J = 9.7 Hz, $C_{meta,}$ C_6H_5), 128.2 (C_6H_5), 124.0 (q, J = 284.0 Hz, C-1), 85.7 (C-3), 82.4 (C-4), 70.0 (q, J = 31.8 Hz, C-2). − ^{19}F NMR ($CDCl_3$): δ = −75.77(d, J = 6.0 Hz, CF_3). − ^{31}P NMR ($CDCl_3$): δ = 48.27(broad). − IR ν(CO): $\tilde{\nu}$ = 2068, 2018 cm^{-1}.

Compound 4b: ^{1}H NMR ($CDCl_3$): δ = 7.41−7.18 (m, 20 H, C_6H_5), 3.97 (dq, J = 14.0 Hz, J = 7.8 Hz, 1 H, 2-H), 1.88 (d, J = 7.8 Hz, 1 H, OH). − ^{13}C NMR ($CDCl_3$): δ = 205.9−203.9−200.5 (CO), 139.5 ($C_{ipso,}$ C_6H_5), 133.8 (d, J = 41.1 Hz, $C_{ipso,}$ PC_6H_5), 133.3 (C_6H_5), 133.2 (d, J = 10.7 Hz, $C_{ortho,}$ PC_6H_5), 130.6 (C_6H_5), 130.5 (d, J = 10.4 Hz, $C_{meta,}$ PC_6H_5), 128.8 (C_6H_5), 128.7 (d, J = 8.2 Hz, $C_{para,}$ PC_6H_5), 128.2 (C_6H_5), 124.6 (q, J = 283 Hz, C-1), 88.1 (C-3), 79.6 (C-4), 70.3 (q, J = 30.5 Hz, C-2). − ^{19}F NMR ($CDCl_3$): δ = −76.34 (broad). − ^{31}P NMR ($CDCl_3$): δ = 48.29 (broad). − IR ν(CO): $\tilde{\nu}$ = 2068, 2018 cm^{-1}. − $C_{33}H_{22}Co_2F_3O_6P$ calcd: C 55.02, H 3.08; found C 56.22, H 3.06.

[{$Co_2(CO)_4$dppm}-µ-$η^2$,$η^2$-(1,1,1-trifluoro-4-phenylbut-3-yne-2-ol)] (5): To a solution of **2** (0.5 g, 1.27 mmol) in 50 mL of hexane was added dppm (0.5 g, 1.30 mmol). After 0.5 h of reflux, the reaction was completed. The mixture was purified by flash chromatography on silica gel, using pentane as eluent then using pentane/ether (1:4). Complex **5** was obtained in 58% yield (0.66 g). − ^{1}H NMR ($CDCl_3$): δ = 7.25−6.91 (m, 25 H, C_6H_5), 5.20 (dq, J = 14.0 Hz, J = 7.5 Hz, 1 H, 2-H), 3.22 (m, 2 H, PCH_2P), 2.34 (d, J = 7.5 Hz, 1 H, OH). − ^{13}C NMR ($CDCl_3$): δ = 205.8, 202.4, and 202.0 (CO), 141.7 ($C_{ipso,}$ C_6H_5), 130.7, 128.8, and 126.4 ($C_{o,m,p}$, C_6H_5), 138.1, 134.1, 132.8, 130.2, 129.7, and 128.3 (m, PC_6H_5), 124.6 (q, J = 281.4 Hz, C-1), 93.9 (C-4), 91.7 (C-3), 72.4 (q, J = 31.6 Hz, C-2), 34.4 (t,.J = 21.7 Hz, PCH_2P). − ^{19}F NMR ($CDCl_3$): δ = −76.7 (d, J = 6.0 Hz, CF_3). − ^{31}P NMR ($CDCl_3$): δ = 37.7 (broad). − IR ν(CO): $\tilde{\nu}$ = 2066, 2029, 2001, 1974 cm^{-1}. − $C_{39}H_{29}F_3O_5P_2Co_2$ calcd: C 57.51, H 3.59; found C 54.37, H 3.54.

[{$Co(CO)_3MoCp(CO)_2$}-µ-$η^2$,$η^2$-(1,1,1-trifluoronon-3-yne-2-ol)] (6a, 6b): To 0.15 g (0.3 mmol) of **1** in 15 mL THF was added a solution of $NaMoCp(CO)_2$ in 15 mL THF, prepared from 0.15 g (0.3 mmol) of $Mo_2Cp_2(CO)_6$ and 0.014 g (0.6 mmol) of Na/1.4 g Hg [for the detailed preparation of $NaMoCp(CO)_3$ see reference[12]]. This mixture was stirred for 7 h at room temperature and monitored by TLC-silica gel using pentane/ether (2:1) as eluent. After chromatography on silica gel, two products were recovered, **2a** and **2b**, in the order of increasing polarity. Complexes **2a** and **2b** were obtained in 58.8% (0.10 g) and 35.3% (0.06 g) yield, respectively.

Compound 6a: ^{1}H NMR ($CDCl_3$): δ = 5.47 (s, 5 H, Cp), 5.07 (dq, J = 13 Hz, J = 5.8 Hz, 1 H, 2-H), 2.91 (t, J = 8.0 Hz, 2 H, 5-H), 2;39 (d, J = 5.8 Hz, OH), 1.75 (m, 1 H, 6-H), 1.60 (m, 1 H, 6-H), 1.40 (m, 4 H, 7,8-H), 0.92 (t, J = 6.8 Hz, 3 H, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 203.0 (CO), 123.5 (q, J = 276.0 Hz, C-1), 105.2 (C-3), 90.3 (Cp), 79.8 (C-4), 73.4 (q, J = 32.0 Hz, C-2), 34.9 (C-5), 31.8 (C-6), 30.9 (C-7), 22.2 (C-8), 13.7 (C-9). − ^{19}F NMR ($CDCl_3$): δ = −75.9 (d, J = 6.1 Hz). − IR ν(CO): $\tilde{\nu}$ = 2051, 2001, 1984, 1942 cm^{-1}. − $C_{19}H_{18}CoF_3MoO_6$ calcd: C 41.17, H 3.27; found C 42.99, H 3.12.

Compound 6b: ^{1}H NMR ($CDCl_3$): δ = 5.42 (s, 5 H, Cp), 4.94 (dq, J = 13.0 Hz, J = 7.4 Hz, 1 H, 2-H), 2.96 (m, 2 H, 5-H), 2;19 (d, J = 7.4 Hz, 1 H, OH), 1.63 (m, 2 H, 6-H), 1.40 (m, 4 H, 7,8-H), 0.91 (t, J = 6.8 Hz, 3 H, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 202.9 (CO), 124.0 (q, J = 281.0 Hz, C-1), 104.1 (C-3), 90.4 (Cp), 78.6 (C-4), 73.5 (q, J = 31.0 Hz, C-2), 35.1 (C-5), 31.9 (C-6), 30.9 (C-7), 22.2 (C-8), 13.8 (C-9). − ^{19}F NMR ($CDCl_3$): δ = −75.15(d, J = 6.5 Hz). − IR ν(CO): $\tilde{\nu}$ = 2052, 2003, 1987, and 1940 cm^{-1}. − $C_{19}H_{18}CoF_3MoO_6$ calcd: C 41.17, H 3.27; found C 43.11, H 3.16.

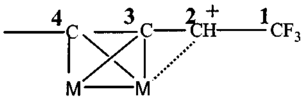
[{$Co(CO)_3MoCp(CO)_2$}-µ-$η^2$,$η^2$-(1,1,1-trifluoro-4-phenylbut-3-yne-2-ol)] (7a, 7b): A slightly modified procedure was used relative to that of (**6a**, and **6b**). A THF solution of **2** was heated under reflux for two hours with $NaMoCp(CO)_3$. The diastereomers **7a** and **7b** were separated by flash chromatography in the order of increasing polarity, and were obtained in 35% and 53% yield respectively (0.2 g) and (0.3 g).

Compound 7a: ^{1}H NMR ($CDCl_3$): δ = 7.43−7.33 (m, 5 H, C_6H_5), 5.46 (s, 5 H, Cp), 5.28 (dq, J = 13.0 Hz, J = 5.7 Hz, 1 H, 2-H), 2.27 (d, J = 5.7 Hz, 1 H, OH). − ^{13}C NMR ($CDCl_3$): δ = 225.6 (CO), 222.3 (CO), 202.7−202.3 (CO), 140.4 (C_{ipso}), 129.3 (C_{meta}), 128;6 (C_{ortho}), 127.6 (C_{para}), 124.7 (q, J = 282.2 Hz,C-1), 98.2 (C-3), 90.4 (Cp), 88.4 (C-4), 73.4 (q, J = 30.7 Hz, C-2). − ^{19}F NMR ($CDCl_3$): δ = −75.87 (d, J = 5.7 Hz). − IR ν(CO): $\tilde{\nu}$ = 2057, 2002, 1949 cm^{-1}.

Compound 7b: ^{1}H NMR ($CDCl_3$): δ = 7.43−7.32 (m, 5 H, C_6H_5), 5.46 (s, 5 H, Cp), 5.16 (dq, J = 13.0 Hz, J = 5.7 Hz, 1 H, 2-H), 2.34 (d, J = 5.7 Hz, 1 H, OH). − ^{13}C NMR ($CDCl_3$): δ = 225.4 (CO), 222.8 (CO), 203.0−201.8 (CO), 140.1 (C_{ipso}), 129.8 (C_{meta}), 128.5 (C_{ortho}), 127.9 (C_{para}), 124.9 (q, J = 283.0 Hz, C-1), 104.9 (C-3), 98.8 (C-4), 90.9 (Cp), 73.2 (q, J = 30.3 Hz, C-2). − ^{19}F NMR ($CDCl_3$): δ = −75.89 (d, J = 6.4 Hz). − IR ν(CO): $\tilde{\nu}$ = 2058, 1994, 1948 cm^{-1}. − $C_{20}H_{12}CoF_3MoO_6$ calcd: C 42.88, H 2.16; found C 43.90, H 2.54.

[{$Co(CO)_3MoCp(CO)_2$}-µ-$η^2$,$η^3$-(1,1,1-trifluoronon-3-yn-2-onium)] Tetrafluoroborate (8): To a solution of a mixture of (**6a**) and (**6b**) (0.277 g, 0.5 mmol) in 5 mL of ether was added HBF_4/Et_2O (0.25 mL). The red solution turns dark with the formation of an insoluble oil. The reaction was left for 1 h at room temperature, then the supernatant was removed and the oily material washed five times with diethyl-ether and finally dried under vacuum for several hours.

The carbon numbering system for the α-CF_3-carbenium complexes is illustrated by the following diagram:



^{1}H NMR (CD_2Cl_2): δ = 5.99 (s, 5 H, C_p), 5.94 (q, J = 7.2 Hz, 1 H, 2-H), 2.98 (m, 2 H, 5-H), 1.73 (m, 2 H, 6-H),1.38 (m, 4 H, 7,8-H), 0.93 (t, J = 6.6 Hz, 3 H, 9-H). − ^{13}C NMR (CD_3COCD_3): δ = 215.5, 209.2, and 198.2 (CO), 123.5 (q, J = 275.9 Hz, C-1), 107.3−84.7 (C-3,4), 94.0 (q, J = 36.9 Hz, C-2), 93.4 (s, Cp) (C-5), 35.7 (C-5), 32.6 (C-6), 31.4 (C-7), 22.4 (C-8), 13.9 (C-9). − ^{19}F

NMR (CD_2Cl_2): δ = −59.2 (broad). − IR ν(CO): ṽ = 2104, 2065, 2055, 2006, 1989, and 1947 cm^{-1}. − $C_{19}H_{17}BCoF_7MoO_5$ calcd: C 36.57, H 2.74; found C 34.88, H 3.00.

[{$Co(CO)_3MoCp(CO)_2$}-μ-$η^2$,$η^3$-(1,1,1-trifluoro-4-phenylbut-3-yn-2-onium)] Tetrafluoroborate (9): The same procedure was used as for compound **8**. − ^{1}H NMR (CD_2Cl_2): δ = 7.77 (m, 2 H, C_6H_5), 7.59 (m, 3 H, C_6H_5), 6.06 (q, *J* = 6.5 Hz, 1 H, C_6H_5), 7.43 (m, 2 H, C_6H_5), 7.35 (m, 3 H, C_6H_5), 6.06 (q, *J* = 6.5 Hz, 1 Hz), 6.04 (s, 5 H, Cp−Mo). − IR ν(CO): ṽ = 2108, 2072, 2005 cm^{-1}.

[{$Co_2(CO)_5P(C_6H_5)_3$}-μ-$η^2$,$η^3$-(1,1,1-trifluoronon-3-yne-2-onium)] Tetrafluoroborate (10): This compound hydrolyses rapidly in solution, therefore the ^{1}H-NMR spectrum could not be recorded, however the IR data are reminiscent of a cobalt−carbenium ion complex. − IR ν(CO): ṽ = 2138, 2063, and 2005 cm^{-1}.

[{$Co_2(CO)_5P(C_6H_5)_3$}-μ-$η^2$,$η^3$-(1,1,1-trifluoro-4-phenylbut-3-yne-2-onium)] Tetrafluoroborate (11): This compound hydrolyses rapidly in solution, therefore the ^{1}H-NMR spectrum could not be recorded. The infrared data are characteristic of a cobalt−carbenium ion complex. − IR ν(CO): ṽ = 2123, 2071, 2022 cm^{-1}.

[{$Co_2(CO)_4$dppm}-μ-$η^2$,$η^3$-(1,1,1-trifluoro-4-phenylbut-3-yne-2-onium)] Tetrafluoroborate (12): This complex hydrolyses rapidly in solution, therefore the ^{1}H-NMR spectrum could not be recorded. − IR ν(CO): ṽ = 2090, 2065, 2004, 1978 cm^{-1}. − $C_{39}H_{28}BCo_2F_7O_4P_2$ calcd: C 52.97, H 3.19; found C 52.52, H 3.85.

[{$Co(CO)_3MoCp(CO)_2$}-μ-$η^2$,$η^2$-(1,1,1-trifluoronon-3-yne)] (13): The carbenium ion complex **8** (0.11 mmol) was dissolved in CH_2Cl_2 (20 mL) and an excess of Zn powder (a small spatula portion) was added, and the reaction stirred for 20 minutes at room temperature then filtered, and the solvent removed under vacuum. The residue was purified by chromatography on silica gel using an Et_2O/pentane (10:90) mixture. Complex **13** was isolated as red-orange oily material in 85% yield (65 mg). − ^{1}H NMR ($CDCl_3$): δ = 5.37 (s, 5 H, C_p), 3.48 (oct, *J* = 10.6−4.3 Hz, 2 H, 2-H), 2.88 (t, *J* = 8.6 Hz, 2 H, 5-H), 1.61 (m, 2 H, 6-H),1.40 (m, 4 H, 7,8-H), 0.92 (t, *J* = 7.2 Hz, 3 H, 9-H).

[{$Co(CO)_3MoCp(CO)_2$}-μ-$η^2$,$η^2$-(1,1,1-trifluoro-4-phenylbut-3-yne)] (14): The preparation of this complex is similar to that of compound **13**. Thus, starting with 0.11 mmol of the carbenium ion complex **9** in CH_2Cl_2, the target compound **14** was isolated as a red-orange oily material in 80% yield (48 mg). − ^{1}H NMR (CD_3COCD_3): δ = 7.01 (m, 5 H, C_6H_5), 5.10 (s, 5 H, C_p), 3.37 (q, *J* = 9.75 Hz, 2 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 233.1, 225.7, and 213.0 (CO), 141.2 ($C_{ipso,}$ C_6H_5), 128.9, 128.5, and 127.1 ($C_{o,m,p,}$ C_6H_5), 126.5 (q, *J* = 272 Hz, C-1), 91.4 (Cp), 95.5−90.8 (C-3, C-4), 39.2 (q, *J* = 29.3 Hz, C-2). − ^{19}F NMR ($CDCl_3$): δ = −64.43 (t, *J* = 9.8 Hz, CF_3). − IR ν(CO): ṽ = 2056, 2004, 1993, 1944 cm^{-1}. − Anal. for $C_{20}H_{12}CoF_3MoO_5$ calcd: C 44.14, H 2.22; found C44.26, H2.28.

[{$Co_2(CO)_5P(C_6H_5)_3$}-μ-$η^2$,$η^2$-(1,1,1-trifluoronon-3-yne)] (15): This complex was prepared by two different procedures:

Method A: This synthetic procedure is the same as the one described for complexes **13** and **14**. Complex **15** was obtained in 60% yield as red oily material (46 mg).

Method B: The alcohol starting materials **3a**, and **b** (100 mg, 0.142 mmol) were dissolved in 2 mL of CH_2Cl_2 in the presence of 31 μL of THF. The red solution was treated with $HBF_4 \cdot Et_2O$ (58 mL) at −5 °C, and the reaction was left to attain room temperature. The solvents were removed and the residue was purified by chromatography on silica gel using Et_2O/pentane (10:90) as eluent. Complex **15** was isolated in 30% yield (30 mg). − ^{1}H NMR ($CDCl_3$): δ = 7.59−7.47 (m, 15 H, C_6H_5), 2.63 (q, *J* = 10.4 Hz, 2 H, 2-H), 2.20 (m, 1 H, 5-H), 2.04 (m, 1 H, 5-H), 1.60 (m, 1 H, 6-H), 1.47 (m, 1 H, 6-H), 1.31 (m, 4 H, 7,8-H), 0.91 (t, *J* = 6.4 Hz, 3 H, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 206.4, 204.8, and 201.5 (CO), 134.6 (d, *J* = 40.2 Hz, $C_{ipso,}$ C_6H_5), 133.1 (d, *J* = 9.5 Hz, $C_{ortho,}$ C_6H_5), 130.7 (s, $C_{para,}$ C_6H_5), 128.9 (d, *J* = 7.3 Hz, $C_{meta,}$ C_6H_5), 125.9 (q,*J* = 279 Hz, C-1), 99.5−78.1 (C-3−4), 36.0 (q, *J* = 29 Hz, C-2), 32.1, 32.0, 31.4 (C-5, C-6, C-7), 22.7 (C-8), 14.2 (C-9). − ^{19}F NMR ($CDCl_3$): δ = −64.80.(t, *J* = 10.3 Hz, CF_3). − ^{31}P NMR ($CDCl_3$): δ = 52.84.(broad). − IR ν(CO): ṽ = 2059, 2010, 2005, 1997, 1987, and 1963 cm^{-1}. − $C_{32}H_{28}Co_2F_3O_5P$ calcd: C 55.02, H 4.04; found C 52.85 H 4.25.

[{$Co_2(CO)_5P(C_6H_5)_3$}-μ-$η^2$,$η^2$-(1,1,1-trifluoro-4-phenylbut-3-yne)] (16): This compound was also prepared by the two synthetic procedures outlined above: Method A: Complex **16** was obtained as red powder in 90% (70 mg). − Procedure B: Compound **16** was isolated in a lower yield of 27% (40 mg). − ^{1}H NMR ($CDCl_3$): δ = 7.36−7.19 (m, 20 H, C_6H_5), 2.87 (m, 1 H, 2-H), 2.28 (m, 1 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 204.0 (CO), 200.7 (CO), 140.0 ($C_{ipso,}$ C_6H_5), 133.9 (d, $C_{ipso,\ J}$ = 41.1 Hz, PC_6H_5), 133.3 (d, $C_{ortho,\ J}$ = 10.5 Hz, PC_6H_5), 130.5, 129.8, 128.7 (s, $C_{ortho,\ meta,\ para}$), 128.6 (d, *J* = 9.8 Hz, $C_{meta,}$ PC_6H_5), 127.0 (s, $C_{para,}$ PC_6H_5), 126.1 (q, *J* = 281 Hz, C-1), 86.3 (C-3), 90.8 (C-4), 35.2 (q, *J* = 29.3 Hz, C-2). − ^{19}F NMR ($CDCl_3$): δ = −64.75.(t, *J* = 9.1 Hz, CF_3). − ^{31}P NMR ($CDCl_3$): δ = 49.53 (broad). − IR ν(CO): ṽ = 2065, 2013, and 1983 cm^{-1}. −$C_{33}H_{22}Co_2F_3O_5P$ calcd: C 56.27, H 3.15; found C 56.34, H 3.21.

[{$Co_2(CO)_4$dppm}-μ-$η^2$,$η^2$-(1,1,1-trifluoro-4-phenylbut-3-yne)] (17): In a similar manner to that described for complexes **13** and **14**, the reduced compound **17** was obtained from 0.11 mmol of the carbenium ion complex **12**, as a red-orange powder in 90% yield (79 mg). − ^{1}H NMR ($CDCl_3$): δ = 7.33−6.99 (m, 25 H, C_6H_5), 3.63 (m, 2 H, PCH_2P), 3.13 (m, 2 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 205.9−202.6 (CO), 142.4 (s, $C_{ipso,}$ C_6H_5), 138.7, 134.4. and 132.8 (m, C_6H_5P), 132.7 (s, $C_{para,}$ C_6H_5), 130.7 (m, C_6H_5P), 130.4 ($C_{ortho,}$ C_6H_5), 128.6−128.2 (m, C_6H_5P), 125.9 (s, $C_{meta,}$ C_6H_5), 126.6 (q, *J* = 274.5 Hz, C-1), 93.8 (C-4), 88.9 (C-3), 39.1 (q, *J* = 28.9 Hz, C-2), 34.5 (t, *J* = 21.8 Hz, PCH_2P). − ^{19}F NMR ($CDCl_3$): δ = −64.90.(t, *J* = 10.49 Hz, CF_3). − ^{31}P NMR ($CDCl_3$): δ = 38.36 (s). − IR ν(CO): ṽ = 2027, 1999, 1969, 1959 cm^{-1}. − $C_{39}H_{29}Co_2F_3O_4P_2$ calcd: C 58.66, H 3.66; found C 56.67, H 3.70.

[{$Co(CO)_3MoCp(CO)_2$}-μ-$η^2$,$η^2$-(1,1,1-trifluoro-2-(methylthio)non-3-yne)] (18a, 18b) and [{$Mo_2Cp_2(CO)_4$}-μ-$η^2$,$η^3$-(prop-2-yn-1-onium)] Tetrafluoroborate (19): A mixture of the two alcohol diastereomers **6a**, and **b** (220 mg, 0.40 mmol) were dissolved in 10 mL of Et_2O. The red solution was protonated by 0.2 mL of $HBF_4 \cdot Et_2O$ at room temperature, affording a dark red oily precipitate. This material was isolated and washed 5 times with Et_2O. CH_2Cl_2 was then added (10 mL) and NaSMe (30 mg, 0.43 mmol.) was introduced, and the reaction was left to stir for 10 minutes. The solvent was removed and the residue was purified by chromatography on silica-gel using Et_2O/pentane 10:90 to yield inseparable mixture of the two diastereoisomer-substituted complexes **18a**, and **b** (1:1) in 35% yield (82 mg). The reduced complex **19** was obtained in 35% yield (74 mg).

Spectroscopic Data for 18a, and b: ^{1}H NMR ($CDCl_3$): δ = 5.44−5.40 (s, 5 H, C_p), 4.25 (m, 1 H, 2-H), 2.93 (m, 2 H, 5-H), 2.36−2.35 (s, 3 H, SCH_3), 1.7 (m, 2 H, 5-H), 1.65 (m, 2 H, 6-H), 1.42 (m, 4 H, 7,8-H), 0.92−0.93 (t, *J* = 6.3 Hz, 3 H, 9-H). − IR ν(CO): ṽ = 2051, 2000, 1985, 1939 cm^{-1}.

Table 4. Crystal data for compounds **5** and **17**

	Compound **5**	Compound **17**
Formula	$C_{39}H_{29}Co_2F_3O_5P_2$	$C_{39}H_{29}Co_2F_3O_4P_2 \cdot C_3H_6O$
mass	814.5	856.5
a [Å]	11.756(4)	11.099(5)
b [Å]	20.542(4)	11.712(2)
c [Å]	15.404(5)	15.575(7)
α [°]	90	87.57(3)
β [°]	96.98(3)	86.50(4)
γ [°]	90	76.26(4)
V [Å^3]	3692(2)	1962(1)
Z	4	2
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	*P*-1
Linear abs. coeff. μ [cm^{-1}]	10.4	9.8
Density ρ [g·cm^{-3}]	1.47	1.45
Diffractometer	CAD4 Enraf−Nonius	CAD4 Enraf−Nonius
Radiation	Mo-*K*α (λ = 0.71069 Å)	Mo-*K*α (λ = 0.71069 Å)
Scan type	ω /2θ	ω/2θ
Scan range [°]	0.8 + 0.345 tgθ	0.8 + 0.345 tgθ
θ Limits [°]	1−25	1−26
Temperature of measurement	295 K	223 K
Octants collected *h*; *k*; *l*	0,13; 0,24; −18,18	0,13; −14,14; −19,19
Decay%	<10	<10
No. of data collected	7041	8126
No. of unique data collect. (R_{int})	6483 (0.05)	7703 (0.03)
No. of unique data used for ref.	3057 $(Fo)^2 > 3\sigma(Fo)^2$	4787 $(Fo)^2 > 3\sigma(Fo)^2$
$R = \Sigma\|\|Fo\| - \|Fc\|\|/\Sigma\|Fo\|$	0.0506	0.0478
$Rw^* = [\Sigma w(Fo - Fc)^2/\Sigma w\, Fo^2]^{1/2}$	0.0597	0.0563
S	1.17	1.11
Extinction parameter	none	none
No. of variables	497	488
Δρmin [e·Å^{-3}]	−0.42	−0.48
Δρmax [e·Å^{-3}]	0.87	0.74

Spectroscopic Data for 19: ^1H NMR (CD_2Cl_2): δ = 7.39 (m, 5 H, C_6H_5), 7.15 (s, 1 H, 3-H), 7.00 (s, 1 H, 1-H), 5.38 (s, 5 H, Cp). − IR ν(CO): $\tilde{\nu}$ = 2052, 2006, 1993, 1907 cm^{-1}.

X-ray Structure Determination: Suitable crystals of [(Co_2(CO)$_4$dppm)(μ-η^2,η^2-RC≡CCH(CF_3)(OH)] (**5**) were obtained by slow evaporation of a saturated solution in pentane/Et_2O (1:4), while complex [{$Co_2(CO)_4$dppm}{μ-η^2,η^2-$C_6H_5C{\equiv}CCH_2(CF_3)$}] (**17**) was obtained by slow evaporation of an acetone saturated solution. The selected crystal of complex **5** or **17** was glued on the top of a glass rod. Accurate cell dimensions and orientation matrix were obtained by least-squares refinements of 25 accurately centered reflections on a Nonius CAD4 diffractometer equipped with graphite-monochromated Mo-*K*α radiation. No significant variations were observed in the intensities of two checked reflections during data collection. The ψ-scan curve of **5** or **17** was flat, hence no absorption correction was applied. Complete crystallographic data and collection parameters for **5** and **17** are listed in Table 4. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[22] Scattering factors and corrections for anomalous dispersion were taken from ref.[23] Complex **5** exhibited a disordered behavior for the CF_3−C−OH unit. A best structural resolution was achieved by considering two locations where the CF_3−C−OH fragment displayed occupation factor of (43%) and (57%). The asymmetric unit of complex **17** contains one molecule of solvated acetone, thus crystals of **17** decomposed at room temperature by loss of solvent and thus the X-ray data were recorded at low temperature. The structures of compounds **5** and **17** were refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were introduced in calculated positions in the last refinements and were allocated an overall refinable isotropic thermal parameter. Fractional parameters, anisotropic thermal parameters, and all bond lengths and angles are given in the Supporting Information for complexes **5** and **17**.

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