The pK_{R^+} values for coordinated propargyl cations $[Cp_2M_2(CO)_4(\mu-\eta^2,\eta^3-HC{\equiv}CCR^1R^2)]^+$ (M = Mo, W)

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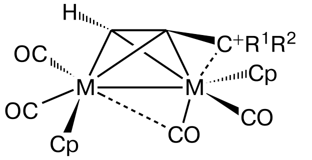
The pK_{R^+} values for metal-stabilized carbocations $[Cp_2M_2(CO)_4(\mu-\eta^2,\eta^3-HC{\equiv}CCR^1R^2)]^+$ (M = Mo, W) containing primary ($R^1 = R^2 = H$), secondary ($R^1 = H$, $R^2 = Me$), or tertiary ($R^1 = R^2 = Me$) coordinated propargyl cations were measured in 50% aqueous acetonitrile. Their stability increases from the tertiary to primary cation, and the stability of the tungsten-containing cations is higher than that of the corresponding molybdenum analogs.

Key words: pK_{R^+}, stability, metal-stabilized carbocations, molybdenum, tungsten, coordinated propargyl cations.

The pK_{R^+} value is a measure of thermodynamic stability of metal-stabilized carbocations relatively to the corresponding carbinols. These values have been measured for the series of such carbocations, in particular, ferrocenyl,[1] alkynyldicobalthexacarbonyl,[2] cyclobutadieneirontricarbonyl,[3] cymanthrenyl[4,5] and their phosphine analogs,[6] benchrothrenyl,[7] and cynichronidyl.[8] In the most part of presented systems, the C_α carbocationic center (formally, the C atom on which a positive charge is generated) is bound to both the organometallic radical and one or two alkyl or aryl radicals, which can compete with the organometallic radical in the carbocationic center stabilization. In the series of alkyl and aryl substituents, the alkyl groups exhibit the minimal competition, and among the latter (taking into account possible steric effects), the Me group competes minimally.

The pK_{R^+} values have been measured only for two series of metal-stabilized carbocations in which the C_α atom is bound to the H atom or Me radical only. The first series is a sequence of ferrocenylmethyl cations. In this series, the substitution of H by Me enhances pK_{R^+} and, hence, stability.[9,10] In the second series including alkynyldicobalthexacarbonyl cations, the substitution of H by Me exerts almost no effect on the stability.[2] In this work, we report the third possible method used to influence of the alkyl substitution on the stability of metal-stabilized carbocations, namely, a decrease in the stability of the latter in the substitution of H by Me at the carbocationic center of the binuclear carbocationic molybdenum and tungsten complexes.



1a—c, 2a—c

1, 2: $R^1 = R^2 = H$ (**a**); $R^1 = H$, $R^2 = Me$ (**b**); $R^1 = R^2 = Me$ (**c**)
M = Mo (**1a—c**), W (**2a—c**)

These compounds contain the tetrahedral M_2C_2 framework. Preliminary results of pK_{R^+} determination have been published elsewhere.[11]

Results and Discussion

Crystalline tetrafluroborates of cations **1a—c** are rather stable toward hydrolysis. Their syntheses do not require anhydrous reagents (for example, HBF_4 etherate), and application of aqueous HBF_4 is quite admissible. Our preliminary experiments showed that cations **1a,b** and **2a,b** are stable for some time in aqueous solutions, and their hydrolysis occurs rather slowly and to a rather low extent. The pK_{R^+} values were estimated as close to 4.8 and 3.7, respectively, from the data on hydrolysis of cations **1a,b** in an aqueous solution. Thus, the rough estimate of the stability of cations **1a,b** revealed their closeness to cyclopropenyl cations, which are referred to the most stable carbenium ions.[12] Since the pK_{R^+} values of the cyclopropenyl cations were measured in 50% aqueous MeCN, pK_{R^+} of cations **1a—c** and **2a—c** were determined in the same medium for comparison. We convinced that these cations are stable in this solvent for the time sufficient for equilibration. The ^1H NMR spectra of cations **1a,b** (concentration ~0.18 mol L^{-1}) for >24 h exhibit no foreign signals with a noticeable intensity, so that even significant times of equilibration have no effect on correctness of pK_{R^+} determination for these cations.

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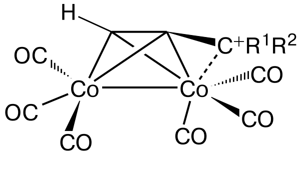
Table 1. The pK_{R^+} values for the metal-stabilized carbocations $[(\mu\text{-}\eta^2,\eta^3\text{-}R^1C{\equiv}CCR^2R^3)Cp_2M_2(CO)_4]^+$ (M = Mo, W) and some other cations

Cation	pK_{R^+}	Solvent	Refs.
	M = Mo		
1a ($R^1 = R^2 = R^3 = H$)	4.82±0.04 [a]	50% aqueous MeCN	— [b]
1b ($R^1 = R^2 = H$, $R^3 = Me$)	3.81±0.04 [a]	The same	— [b]
1b	3.79±0.02 [c]	»	— [b]
1c ($R^1 = H$, $R^2 = R^3 = Me$)	3.12±0.06 [a]	»	— [b]
1d ($R^1 = CH_2OH$, $R^2 = R^3 = H$)	5.13±0.04 [a]	»	— [b]
1d	5.35±0.04 [a]	40% aqueous MeCN	— [b]
1a	3.5	— [d]	13
	M = W		
2a ($R^1 = R^2 = R^3 = H$)	5.53±0.05 [a]	50% aqueous MeCN	— [b]
2b ($R^1 = R^2 = H$, $R^3 = Me$)	4.97±0.05 [a]	The same	— [b]
2c ($R^1 = H$, $R^2 = R^3 = Me$)	4.25±0.04 [a]	»	— [b]
	Ferrocenylmethyl cations		
$FcCH_2^+$ (**3a**)	−1.28	50% aqueous MeCN	9, 10
$FcCHMe^+$ (**3b**)	−0.66	То же	9, 10
$FcCMe_2^+$ (**3c**)	−0.01	»	9, 10
	Cyclopropenyl cations		
Di-*n*-propylcyclopropenylium (**4a**)	2.7	50% aqueous MeCN	12
Bis(*p*-anisyl)phenylcyclopropenylium (**4b**)	5.2	The same	12
	Other cations		
$[Co_2(CO)_6(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCH_2)]^+$ (**5a**)	−6.8±0.02	— [d]	2
$[Co_2(CO)_6(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCMe_2)]^+$ (**5b**)	−7.2±0.02	— [d]	2
$[Mo_2Cp_2(CO_4)(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CC_{19}H_{25}O)]^+$ (**6**)	2.7	— [d]	13
$[Mo_2Cp_2CO_4(\mu\text{-}\eta^2,\eta^3\text{-}n\text{-}C_5H_{11}{\equiv}CCHC_{10}H_9Fe)]^+$ (**7**)	−1.0	— [d]	13

[a] The concentration is ~0.002 mol L^{-1}.
[b] The data of this work.
[c] The concentration is ~0.004 mol L^{-1}.
[d] The exact composition of the solvent is not known.

It follows from Table 1 that cations **1a—c** are indeed the most stable metal-stabilized carbocations, exceeding much, in this respect, ferrocenylmethyl cations **3a—c**. Cations **1a—d** are comparable in stability with cyclopropenyl cations **4a,b**. Their stability monotonically increases from the tertiary (**1c**) to primary cation (**1a**) in the series of dimolybdenum compounds, which is opposite to the usually observed order in changing the stability of metal-stabilized carbocations (primary < secondary < tertiary). Thus, this is the first example for a decrease in stability when the H atom is substituted by the Me group at the carbocationic center. The series of alkynyldicobalthexacarbonyl cations (see Table 1, cations **5a,b**) to the recent time has been the only series that was not characterized by an increase in stability in the order primary < secondary < tertiary. The structures of cations **5a,b** are presented by analogy to those of the dimolybdenum cations (X-ray diffraction data for cations **5a,b** are unknown to date).



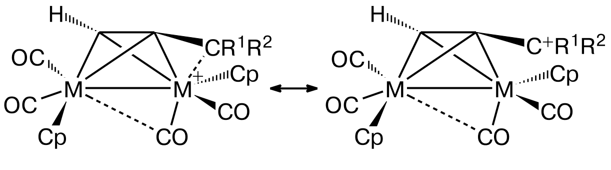
5a,b

5: $R^1 = R^2 = H$ (**a**); $R^1 = R^2 = Me$ (**b**)

The repeated determination of pK_{R^+} for cation **5a** gave a much higher value of –5.5.[13] It is impossible to compare stabilities of cations **1a—c** and their non-coordinated analogs **8a—c** because none of them exist in condensed media. The relative stability of the latter can be estimated only in the gas phase. It follows from measurements of heterolytic dissociation ($D_{R^+—H^-}$) that $D_{R^+—H^-}$ is a linear function of the logarithm of the number of C atoms in the carbenium ion. In other words, the stability of these cations enhances in the usual order characteristic of the classical carbenium ions, *viz.*, primary < secondary < tertiary.[14]

$HC{\equiv}C{-}CH_2^+$ **8a** $HC{\equiv}C{-}CHMe^+$ **8b** $HC{\equiv}C{-}CMe_2^+$ **8c**

It has long ago been assumed[15] that the stability of metal-stabilized carbocations is mainly caused by the interaction of a metal with the carbocationic center. The metal—C_α distance can serve as a measure for this interaction. Cations **1a—c** represent the first series of metal-stabilized carbocations (with different types of the carbocationic center, *viz.*, primary, secondary, and tertiary) with the known molecular structures.[16,17] The Mo—C_α distance increases monotonically (0.2439 (**1a**), 0.2613 (**1b**), and 0.2747 nm (**1c**)), which indicates weakening of the Mo—C_α interaction in this series. The elongation of the Mo—C_α distance on going from cation **1a** to cation **1c** can be explained by strengthening of steric hindrances for the Mo—C_α interaction from the Me groups. It is most likely that for cation **1a** the contribution from structure **A** is somewhat greater and that from structure **B** is somewhat less; the situation is opposite for cation **1c**. Thus, the structure of cation **1a** is closer to the four-coordinate carbonium ion, and that of cation **1c** is closer to the three-coordinate carbenium ion.



A **B**

The pK_{R^+} value and the Mo—C_α distance are related by a linear function (Fig. 1), which is the first experimentally observed example for an increase in the stability of metal-stabilized carbocations with a decrease in the metal—C_α distance.

A substituent in the propargyl ligand that is remote from the C_α atom, such as the CH_2OH group in cation **1d**, has almost no effect on the stability, and the pK_{R^+} value of cation **1d** in 50% aqueous MeCN is by 0.32 higher than that for cation **1a**. In the absence of a polar or any other effect, the increase in pK_{R^+} should be 0.3 because the probability of proton addition to μ-η^2,η^2-($HOCH_2C{\equiv}CCH_2OH$)$Cp_2Mo_2(CO)_4$ (**9**), which is the precursor of cation **1d**, increases twofold compared to that for μ-η^2,η^2-($HC{\equiv}CCH_2OH$)$Cp_2Mo_2(CO)_4$ (**10a**), which is the precursor of cation **1a**. A good agreement between these values is observed within the experimental error.

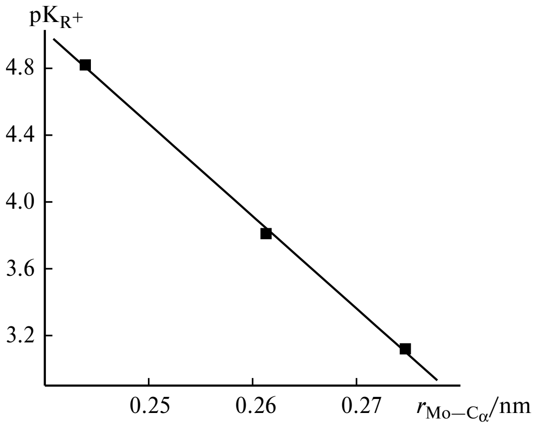
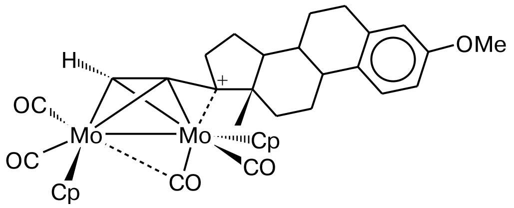


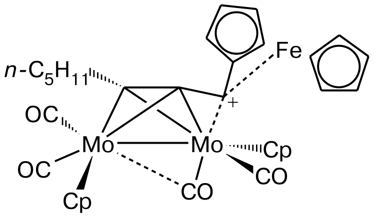
Fig. 1. Plot of pK_{R^+} *vs.* Mo—C_α distance ($r_{Mo—C_\alpha}$) in cations **1a—c** (pK_{R^+} = 18.3 – 55.33$r_{Mo—C_\alpha}$).

The Mo—C_α distances in cations **1c** and **6** are almost the same and amount to 0.275 and 0.274 nm,[13] while the pK_{R^+} values are 3.12 and 2.7, respectively (see Table 1). This difference can be a consequence of considerable steric hindrances for solvation of the carbocationic center. They are created by the bulky propargyl ligand in cation **6**. Exact composition of the solution, in which pK_{R^+} of the latter was determined, is unknown.[13] Therefore, the observed scatter in the pK_{R^+} values of these cations can depend, to a greater extent, on the solvent composition (content of the organic component) rather than on differences in solvation.



6

A peculiarity of cation **7** is related to the unexpectedly low pK_{R^+} value,[13] which is by ~5 units lower than that for cation **1b** and by 0.34 units lower than that for cation **3b**. It was assumed[13] that the ferrocenyl and alkyl ligands with the long chain exert a greater effect on the C_α atom in cation **7** than in the C_2Mo_2 cluster. Above we have already presented arguments against the significant influence of the alkyl radical when the latter is not bound to the carbocationic center. Structural data for cation **7** are unknown. For analog of **7** containing the *n*-C_3H_7 group instead of the n-C_5H_{11} substituent, the Mo—C$_\alpha$ interaction (r_{Mo-C_α} = 0.263 nm) is almost the same as that in cation **1b**, while the Fe—C$_\alpha$ interaction (r_{Fe-C_α} = 0.303 nm) is much less[18] than that in the known ferrocenyl cations.[19,20] It is reasonable to assume that these interactions are the same in cation **7**. The difference in the pK_{R^+} values for cations **1b** and **7** is too high to be explained by a change in the solvent composition (see below the discussion about the plot of pK_{R^+} *vs.* solvent), and a reason for such a high difference remains unclear.



7

The study of substituted propargyl cations includes the determination of pK_{R^+} for cations, some of which contain hydrocarbon radicals in position 3. It can be assumed that for similar compounds the solubility of the initial carbinols, which can generate the corresponding cations, is lower than the solubility of the carbinols, which are precursors of cations **1a—c**. For comparison, we determined pK_{R^+} for cation **1a** in aqueous solutions with different concentrations of MeCN (Table 2). In addition, we estimated to estimate pK_{R^+} for cation **1a** in neat water. Cation **1a** was chosen because it is the first member of the series. In addition, it has the highest stability and solubility in water compared to other cations of this series. Its pK_{R^+} values were determined in aqueous MeCN with a variable content of the latter (0.19—0.76 molar fractions of MeCN) at 20 °C. Reproducible results were not always obtained for solutions with a molar fraction of MeCN (x_2) of 0.19 because of precipitation of the initial carbinol during measurements. The pK_{R^+} values for cation **1a** in a solution with a lower x_2 cannot be determined because of restricted solubility of the initial carbinol.

It is seen from the data in Table 2 that in the studied interval of concentrations the pK_{R^+} value of cation **1a** decreases with an increase in x_2. The plot of pK_{R^+} *vs.* x_2 (Fig. 2) is close to linear and is described by the equation pK_{R^+} = 5.13(0.02) – 1.19(0.04)x_2 (root-mean-square deviations are presented in parenthesis; r^2 = 0.996 for six points). The pK_{R^+} value in water equal to 5.13 was found by the linear extrapolation. The square approximation (pK_{R^+} = 5.16 – 1.37x_2 + 0.19x_2^2, r^2 = 0.997) gives a very close value. Its difference from the value obtained by linear extrapolation is insignificant. The curve, whose shape resembles a hockey stick,[21] is observed when the third power polynomial pK_{R^+} = 5.37 – 3.07x_2 + 4.16x_2^2 – 2.79x_2^3 is used for the approximation of experimental data. Since data on the dependence of pK_{R^+} of the metal-stabilized carbocations on the molar fraction of the organic solvent are lacking, the pK_{R^+} value obtained by linear extrapolation seems more reliable. Another possible approach to estimation of pK_{R^+} for cation **1a** in water could be based on such its modification due to which the solubility of the corresponding precursor would strongly be enhanced. This modification is usually associated with the introduction of the hydrophilic group into the molecule. For this purpose we determined pK_{R^+} for cation **1d** in aqueous MeCN with a variable content of the latter. In this case, in spite of two OH groups in compound **9**, which is the precursor of cation **1d**, measurements in a solution with $x_2 \leq 0.19$ also failed. The pK_{R^+} value in this solvent is 5.35 and, as for cation **1a**, pK_{R^+} increases with a decrease in the content of MeCN in the mixed solvent.

Table 2. The pK_{R^+} values for cation **1a** in aqueous MeCN

Content MeCN (vol/vol)	Molar fraction MeCN	pK_{R^+}
40	0.19	4.92±0.06
50	0.26	4.81±0.06
60	0.34	4.70±0.04
70	0.45	4.58±0.06
80	0.58	4.45±0.06
90	0.76	4.22±0.05

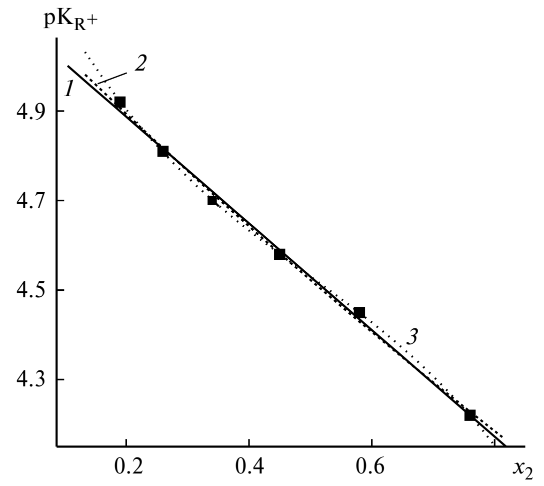
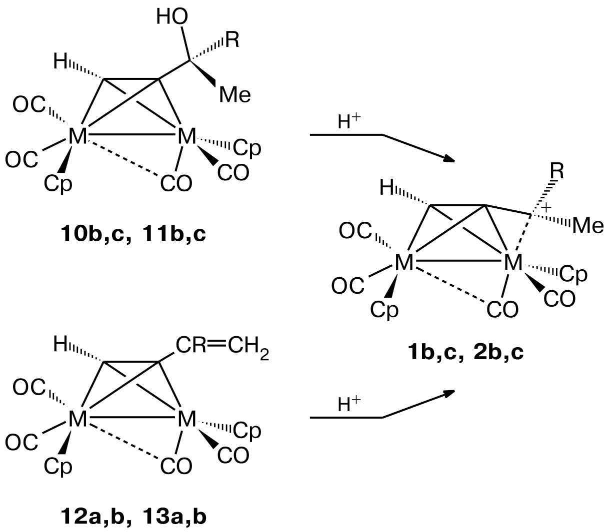


Fig. 2. Plot of pK_{R^+} for cation **1a** *vs.* molar fraction of acetonitrile (x_2): pK_{R^+} = 5.13 – 1.19x_2 (*1*), pK_{R^+} = 5.16 – 1.37x_2 + 0.19x_2^2 (*2*), and pK_{R^+} = 5.37 – 3.07x_2 + 4.16x_2^2 – 2.79x_2^3 (*3*).

The published results[13] on determination of pK_{R^+} for cation **1a** differ strongly from those found by us (see Table 1) and need some clarification. The potentiometric method was used in this work, whereas the authors[13] used the spectrophotometric method. Concordant results were obtained by different methods for cations **1c** and **6** (see Table 1) containing the coordinated tertiary propargyl ligand. The experimental description[13] for determination of pK_{R^+} shows that increasing amounts of aqueous H_2SO_4 were added to a solution of the initial carbinol in an organic solvent (usually acetone or MeCN) in such a way that the fraction of the organic solvent in the final solution ranged from 10 to 50%. However, the composition of a solution with pK_{R^+} equal to 3.5 is unknown. It is important to know the solvent composition because the pK_{R^+} value, as indicated above, depends on the content of organic solvent. If the authors[13] determined pK_{R^+} in 10% aqueous MeCN, then the change in pK_{R^+} (ΔpK_{R^+}) on going from 10% to 50% aqueous MeCN should be 1.31. The data in Table 2 show that for a greater concentration interval (40—90%) $\Delta pK_{R^+} = 0.7$, and since on going from 40% to 50% aqueous MeCN $\Delta pK_{R^+} = 0.11$, then for a much smaller concentration interval (10—40%) ΔpK_{R^+} should be 1.2. When pK_{R^+} for cation **1a** was determined at a concentration of the organic solvent much higher than 10%, ΔpK_{R^+} became the realistic. It is assumed in the above analysis that on going from 10 to 50% MeCN the pK_{R^+} value for cation **1a** can increase, which contradicts the dependence of pK_{R^+} on the composition of the solution found in this work.

Cations **2a—c** are tungsten analogs of cations **1a—c** and represent the second series of metal-stabilized carbocations in which the stability increases from the tertiary to primary cation (see Table 1). Among them, only cation **2c** has a known molecular structure. The W—C_α distance in this cation is 0.2837 nm,[22] which is almost the same as the value for the corresponding dimolybdenum cation (0.275±0.01 nm). The closeness of the covalent radii of molybdenum and tungsten[23] allows one to expect the metal—C_α interaction in these compounds to be approximately the same. In fact, the stability of the tungsten-containing cations is also higher than that of the corresponding analogs. The difference in the pK_{R^+} values for cations **1c** and **2c** ($\Delta pK_{R^+} = 1.13$) is approximately the same as that for cations **1b** and **2b** ($\Delta pK_{R^+} = 1.17$) and decreases in the case of cations **1a** and **2a** ($\Delta pK_{R^+} = 0.72$).

Scheme 1

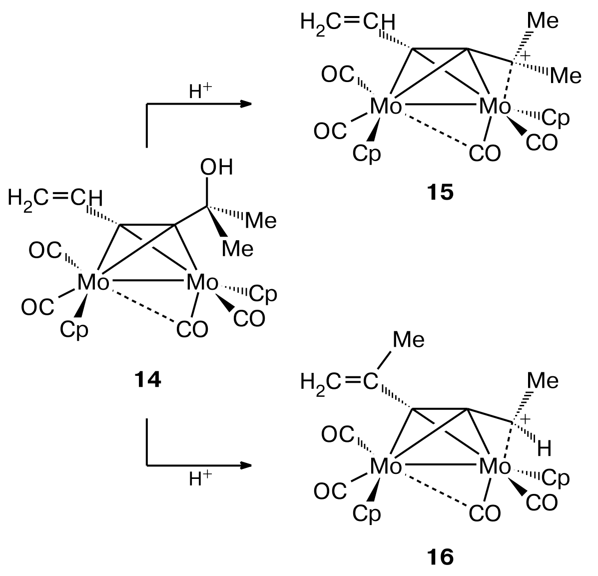


1, 2, 10, 11: R = H (**b**), Me (**c**)
12, 13: R = H (**a**), Me (**b**)
1, 10, 12: M = Mo; **2, 11, 13:** M = W

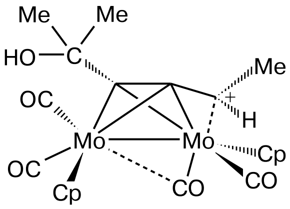
Cations **1b,c** and **2b,c** can be synthesized from different precursors, *viz.*, alcohols or alkenes[24] (Scheme 1).

Carbinols **10b,c** transform into cations **1b,c** upon potentiometric titration, while alkenes **12a,b** are not protonated under these conditions. The titration curves for compounds **12a,b**, are in fact the dilution curves, indicating a much higher basicity of the precursor alcohols compared to that of precursor alkenes. The great difference in basicity of the precursors allowed a less stable cation (with a considerable predomination) of two possible cations to be obtained by the variation of their structure. For example, compound **14** transforms into cation **15** containing almost no admixture of cation **16** (Scheme 2).

Scheme 2



Cation **16** forms instead of assumed cation **17** due to the dehydration of alkene **14** during synthesis of this cation.*



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* Detailed data on the synthesis of cations **15** and **16** from different precursors and their rearrangements will be presented elsewhere.

Experimental

Initial compounds for measurements of pK_{R^+} were synthesized by cross-addition of $Cp_2M_2(CO)_4$ (M = Mo, W) to the corresponding alkynes.[25] All reactions of substituted alkynes with $Cp_2M_2(CO)_4$ were carried out under nitrogen or argon. Distilled solvents and alumina for chromatography, hereafter Al_2O_3 (activity between III and IV), were used for chromatography. ^{1}H NMR spectra were recorded on a Bruker WP-80 spectrometer in acetone-d_6 dried above molecular sieves 4 A.

(μ-η^2,η^2-Propynol)bis(η^5-cyclopentadienyl)tetracarbonyldimolybdenum (10a). In degassed CH_2Cl_2 (25 mL) $Cp_2Mo_2(CO)_4$ (1.74 g, 4 mmol) was dissolved, propynol (0.5 mL, 8.66 mmol) was added to the solution, and the mixture was stirred for 50 min at ~20 °C. The solution changed its color from brown to cherry-red. An equal volume of benzene was added to the reaction mixture, and CH_2Cl_2 was removed (if possible, completely) *in vacuo* at ~20 °C. The remaining benzene solution was chromatographed on Al_2O_3. The pink band was eluted with benzene, and this eluate containing insignificant amounts $Cp_2Mo_2(CO)_6$ was given up. Then the red band was eluted with CH_2Cl_2. After the solvent was removed *in vacuo*, dark red crystals of compound **10a** were obtained from the red eluate in 95% yield (1.61 g). Found (%): C, 41.61; H, 2.99; Mo, 38.82. $C_{17}H_{14}Mo_2O_5$. Calculated (%): C, 41.66; H, 2.88; Mo, 39.15. ^{1}H NMR, δ: 3.48 (t, 1 H, OH, ^3J = 6.1 Hz); 4.59 (dd, 2 H, CH_2, ^3J = 6.1 Hz, ^4J = 0.7 Hz); 5.40 (s, 10 H, Cp); 6.03 (t, 1 H, CH, ^4J = 0.7 Hz).

(μ-η^2,η^2-3-Butyn-2-ol)bis(η^5-cyclopentadienyl)tetracarbonyldimolybdenum (10b). In degassed CH_2Cl_2 (30 mL) $Cp_2Mo_2(CO)_4$ (1.74 g, 4 mmol) was dissolved, a ~53% aqueous solution of 3-butyn-1-ol (1.2 mL) in acetone (3 mL) was added to the solution, and the mixture was stirred for 1 h at ~20 °C. The brown color of the solution turned to be cherry-red. An equal volume of benzene was added to the reaction mixture, and CH_2Cl_2 was removed *in vacuo* at ~20 °C. The remaining benzene solution was chromatographed on Al_2O_3. The pink band was eluted with benzene, and this eluate containing insignificant amounts of $Cp_2Mo_2(CO)_6$ was given up. Then the red band was eluted with CH_2Cl_2. After the solvent was removed *in vacuo*, dark red crystals of **10b** were obtained from the red eluate in 83% yield (1.68 g). Found (%): C, 42.74; H, 3.09. $C_{18}H_{16}Mo_2O_5$. Calculated (%): C, 42.88; H, 3.20. ^{1}H NMR, δ: 1.25 (d, 3 H, Me, ^3J = 6.3 Hz); 3.10 (d, 1 H, OH, ^3J = 5.4 Hz); 4.62 (m, 1 H, $C\underline{H}(OH)Me$); 5.40, 5.43 (both s, 5 H each, Cp); 6.22 (d, 1 H, CH, ^4J = 0.7 Hz).

(μ-η^2,η^2-2-Methyl-3-butyn-2-ol)bis(η^5-cyclopentadienyl)tetracarbonyldimolybdenum (10c). Cation **1c** (306 mg, 0.52 mmol) was dissolved in CH_2Cl_2 (60 mL), water (60 mL) was added to the solution, and the mixture was mechanically shaken for 45 min. The organic layer was separated, benzene (20 mL) was added, the solvent was removed *in vacuo* to a volume of ~10 mL, an equal volume of hexane was added to the residue, and the mixture was chromatographed on Al_2O_3. Two red bands were seen on the column. A substance from the first red band was eluted with benzene, and dark red crystals of **12b** were obtained in 11.5% yield (30 mg) after the solvent was removed *in vacuo*. Found (%): C, 45.38; H, 3.16. $C_{19}H_{16}Mo_2O_4$. Calculated (%): C, 45.62; H, 3.22. ^{1}H NMR, δ: 1.78 (dd, 3 H, Me); 4.77 (m, 1 H, CH_2); 4.94 (m, 1 H, CH_2); 5.39 (s, 10 H, Cp); 5.97 (s, 1 H, CH). A substance from the second red band was eluted with a benzene—CH_2Cl_2 (1 : 1) mixture. After the solvent was removed, dark red crystals of **10c** were obtained in 86.5% yield (233 mg). Found (%): C, 44.18; H, 3.41. $C_{19}H_{18}Mo_2O_5$. Calculated (%): C, 44.04; H, 3.50. ^{1}H NMR, δ: 1.22 (s, 6 H, 2 Me); 2.90 (s, 1 H, $C(O\underline{H})Me_2$); 5.47 (s, 10 H, Cp); 6.29 (s, 1 H, CH).

(μ-η^2,η^2-2-Butyne-1,4-diol)bis(η^5-cyclopentadienyl)tetracarbonyldimolybdenum (9). In degassed CH_2Cl_2 (30 mL) $Cp_2Mo_2(CO)_4$ (1.74 g, 4 mmol) was dissolved, a solution of 2-butyne-1,4-diol (0.53 g, ~6.2 mmol) in degassed acetone (10 mL) was added to the solution, and the mixture was stirred for 3 h at ~20 °C. The solution turned its color from brown to cherry-red. An equal volume of benzene was added to the reaction mixture, and CH_2Cl_2 and acetone were removed *in vacuo* at ~20 °C. The remaining benzene solution was chromatographed on Al_2O_3. The pink band was eluted with benzene, and this eluate containing insignificant amounts of $Cp_2Mo_2(CO)_6$ was given up. Then the red band was eluted with diethyl ether. After the solvent was removed *in vacuo*, dark red crystals of **9** were obtained in 83% yield (1.68 g). Found (%): C, 41.74; H, 3.09. $C_{18}H_{16}Mo_2O_6$. Calculated (%): C, 41.56; H, 3.10. ^{1}H NMR, δ: 4.30 (t, 1 H, OH, ^3J = 5.1 Hz); 4.86 (d, 2 H, CH_2, ^3J = 5.1 Hz); 5.39 (s, 5 H, Cp).

(μ-η^2,η^2-Propynol)bis(η^5-cyclopentadienyl)tetracarbonylditungsten (11a). In degassed CH_2Cl_2 (45 mL) $Cp_2W_2(CO)_4$ (2.44 g, 4 mmol) was dissolved, propynol (0.5 mL, 8.66 mmol) was added to the solution, and the mixture was stirred for 50 min at ~20 °C. The color of the solution turned from brown to cherry-red. An equal volume of benzene was added to the reaction mixture, and CH_2Cl_2 was removed *in vacuo* (if possible, completely) at ~20 °C. The remaining benzene solution was chromatographed on Al_2O_3. The pink band was eluted with benzene, and the eluate containing insignificant amounts of $Cp_2W_2(CO)_6$ was rejected. The red band was eluted with CH_2Cl_2. After the solvent was removed *in vacuo*, dark red crystals of **11a** were obtained from the red eluate in 95% yield (2.53 g). Found (%): C, 30.91; H, 2.21. $C_{17}H_{14}O_5W_2$. Calculated (%): C, 30.66; H, 2.12. ^{1}H NMR, δ: 3.26 (t, 1 H, OH, ^3J = 6.2 Hz); 4.67 (dd, 2 H, CH_2, ^3J = 6.2 Hz, ^4J = 0.7 Hz); 5.30 (m, 1 H, CH, ^4J = 0.7 Hz); 5.46 (s, 10 H, Cp, $^2J_{W,H}$ = 1.2 Hz).

(μ-η^2,η^2-3-Butyn-2-ol)bis(η^5-cyclopentadienyl)tetracarbonylditungsten (11b). In degassed CH_2Cl_2 (30 mL) $Cp_2W_2(CO)_4$ (1.83 g, 3 mmol) was dissolved, a ~53% aqueous solution of 3-butyn-2-ol (1.5 mL) in acetone (3 mL) was added to the solution, and the mixture was stirred for 70 min at ~20 °C. The solution changed its color from brown to cherry-red. An equal volume of benzene was added to the reaction mixture, and CH_2Cl_2 and acetone were removed *in vacuo* at ~20 °C. The remaining benzene solution was chromatographed on Al_2O_3. The pink band was eluted with benzene, and this eluate containing insignificant amounts of $Cp_2W_2(CO)_6$ was rejected. The red band was eluted with CH_2Cl_2, and after the solvent was removed *in vacuo*, dark red crystals of **11b** were obtained from the red eluate in 78% yield (1.59 g). Found (%): C, 32.03; H, 2.26. $C_{18}H_{16}O_5W_2$. Calculated (%): C, 31.79; H, 2.37. ^{1}H NMR, δ: 1.26 (d, 3 H, Me, ^3J = 6.3 Hz); 2.90 (d, 1 H, OH, ^3J = 5.3 Hz); 4.62 (m, 1 H, $C\underline{H}(OH)Me$); 5.45, 5.50 (both s, 5 H each, Cp); ~5.48 (CH, signal is overlapped with signals from Cp protons).

(μ-η^2,η^2-2-Methyl-3-butyn-2-ol)bis(η^5-cyclopentadienyl)tetracarbonylditungsten (11c). Cation **2c** (458 mg, 0.6 mmol) was dissolved in CH_2Cl_2 (80 mL), water (80 mL) was added to the solution, and the mixture was mechanically shaken for 1 h.

The organic layer was separated, benzene (40 mL) was added, the solvent was removed *in vacuo* to a volume of ~25 mL, and the solution was chromatographed on Al_2O_3. Two red bands were observed on the column. A substance from the first red band was eluted with benzene, and after the solvent was removed *in vacuo*, dark red crystals of **13b** were obtained in 25% yield (103 mg). Found (%): C, 32.47; H, 2.10. $C_{19}H_{16}O_4W_2$. Calculated (%): C, 32.66; H, 2.13. ^1H NMR, δ: 1.77 (dd, 3 H, Me); 4.66 (m, 1 H, CH_2); 4.89 (m, 1 H, CH_2); 5.16 (t, 1 H, CH, $^2J_{W,H}$ = 1.55 Hz); 5.46 (s, 10 H, Cp). A substance from the second red band was eluted with CH_2Cl_2. After the solvent was removed, dark red crystals of **11c** were obtained in 64% yield (265 mg). Found (%): C, 33.12; H, 2.77. $C_{19}H_{18}O_5W_2$. Calculated (%): C, 32.88; H, 2.61. ^1H NMR, δ: 1.22 (s, 6 H, 2 Me); 2.80 (s, 1 H, C(O$\underline{H}$)Me_2); 5.53 (s, 10 H, Cp); 5.58 (s, 1 H, CH).

Determination of pK_{R+} values. Acetonitrile was purified using a procedure for electrochemical measurements.[26] Twice distilled water was used for preparation of solutions. The pK_{R+} values were determined by the potentiometric method. A weighted sample of carbinol was dissolved in MeCN (25 mL), water was added to bring the volume to 50 mL (concentration of carbinol ~0.002 mol L^{-1}), and the solution with a maintained constant temperature was titrated with a 0.1 *M* aqueous solution of HCl. The total volume of the added titrant was at most 1 mL, and the composition of the solution changed from 1 : 1 (vol/vol) at the beginning of titration to 1 : 1.02 at the end of titration. Thus, the determined pK_{R+} values lie in the concentration range from 50 to 49.5% MeCN in water. It follows from the data in Tables 1 and 2 that ΔpK_{R+} for cations **1a,d** in the 40—50% interval should be 0.011 and 0.022, respectively, at a change in the concentration by 1%, *i.e.*, ΔpK_{R+} is certainly lower than the error of determination of pK_{R+}. Although such data are presently absent for other cations, we cannot assume that their ΔpK_{R+} can be much higher than the values presented. During titration the color of the solution changed from cherry-red (color of a solution of the initial carbinol) at the beginning of titration to yellow-orange (**1a**, **2a**), brick-red (**1b**, **2b**), or brown-red (**1c**, **2c**) at the end of titration. The stability of pH-meter indications was monitored by the pH value of standard solutions before and after a series of measurements. The first and last results in the series were not used for calculations because the error of determination of pK_{R+} was maximal for them. Three or four series of measurements were carried out for each carbinol and each concentration of MeCN. To reduce to minimum the systematic error of determination of pK_{R+}, the initial carbinols prepared in different runs were used, and measurements were carried out using different instruments. The results presented (see Table 1) are averaged values of these three or four series of measurements. The measurements were carried out on an EV-74 universal ionometer and pH-150 and pH-340 pH-meters.

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