Reactions of carbonylmetallate anions with 1-haloalkynes

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The main regularities of the reactions of 1-haloalkynes RC≡CX with carbonylmetallate anions $[(\eta^5\text{-}C_5R'_5)(CO)_3M]^-$ (R′ = H (**1**—**3**), M = Cr (**1**), M = Mo (**2**), or M = W (**3**); R′ = Me (**4**—**6**), M = Cr (**4**), M = Mo (**5**), or M = W (**6**)) were revealed. It was established that the first stage of the reactions of anions **1**—**6** with bromo- or iodoalkynes RC≡CX (X=Br or I) involved the transfer of the halogen atom from the sp-hybridized carbon atom to the transition metal atom to form carbonyl halides $(\eta^5\text{-}C_5R'_5)(CO)_3MX$. To the contrary, the reactions of anions **1**—**6** with chloroalkynes RC≡CCl proceeded selectively as a nucleophilic substitution at the unsaturated carbon atom, the reaction rate being governed by the nucleophilicity of the carbonylmetallate anions and the electron-withdrawing ability of the R group. These reaction paths are consistent with the structures of the lowest unoccupied molecular orbitals (LUMO) in the PhC≡CX molecules (X = Cl, Br, or I) calculated by the MNDO/PM3 method. In the case of the reactions of 1-chloroheptyne-1 $ClC{\equiv}CC_5H_{11}{}^n$, anions **1**—**3** appeared to be insufficiently nucleophilic, but these reactions can be performed as cross-coupling of the carbonylmetallate anions with chloroalkynes catalyzed by palladium complexes.

Key words: σ-ethynyl complexes of chromium, molybdenum, and tungsten, 1-haloalkynes, carbonylmetallate anions of chromium, molybdenum, and tungsten.

Bifunctional 1-haloalkynes RC≡CX can react with transition-metal complexes either at the carbon—halogen or at the triple carbon—carbon bond. Examples of formation of η^2-haloalkyne, halovinylidene, σ-1-alkynyl, and tetrahalometallacyclopentadiene complexes of transition metals in reactions of haloalkynes with various organometallic substrates were reported in the literature.[1]

Although haloalkynes are promising ligands, their coordination chemistry remains poorly studied. The reactions of nucleophilic substitution of the halogen atom in 1-haloalkynes are often used to form carbon—heteroatom (oxygen, sulfur, nitrogen, phosphorus, *etc.*) bonds.[2] However, these reactions have virtually not been used to form transition metal—carbon σ-bonds. The available examples of these processes concern the reactions of carbonylmetallate anions $[(\eta^5\text{-}C_5H_5)M(CO)_3]^-$ (M = Cr, Mo, or W) with PhC≡CBr[3], and XC≡CX (X = Cl, Br, or I),[4] the reactions of $(CO)_5M^-$ (M = Mn or Re) with IC≡CI,[5] and the reactions of anionic phthalocyanine rhodium complexes with RC≡CBr (R = Ph or Pr^n).[6]

Results and Discussion

With the aim of revealing the regularities and synthetic possibilities of the reactions of carbonylmetallate anions with 1-haloalkynes-1, in this work we studied the reactions of anions **1**—**6** with RC≡CX (R = Ph and X = Cl, Br, or I; R = $C_5H_{11}{}^n$ and X = Cl or Br; or R = COOMe and X = Cl):

$$[(\eta^5\text{-}C_5R'_5)(CO)_3M]^- + RC{\equiv}CX \longrightarrow (\eta^5\text{-}C_5R'_5)(CO)_3MC{\equiv}CR + X^- \qquad (1)$$

R′ = H; M = Cr (**1**), Mo (**2**), W (**3**)
R′ = Me; M = Cr (**4**), Mo (**5**), W (**6**)

The reactions of anions **1**—**3** with phenylethynyl halides PhC≡CX (X = Cl, Br, or I) were studied in close detail. The course of the reaction and the composition of the reaction products are governed by the nature of M, X, and R, the nature of halogen X being of prime importance. Thus, the regularities of the reactions of anions **1**—**6** with 1-chloro-2-phenylacetylene differ sharply from those of the reactions of the same carbonylmetallate anions with 1-bromo- and 1-iodo-substituted analogs.

Reactions with 1-bromo- and 1-iodoalkynes-1

The reactions with 1-bromo-2-phenyl- and 1-iodo-2-phenylacetylenes proceeded readily even at subzero temperature. The first stage formally involved the trans-

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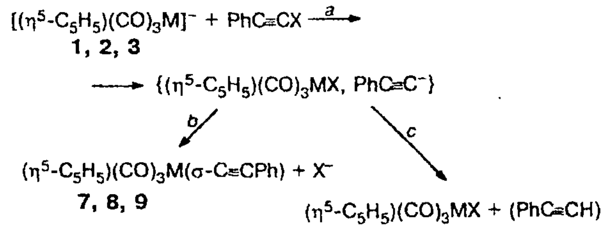
fer of the positively charged halogen atom from the sp-hybridized carbon atom to the transition metal atom (Scheme 1).

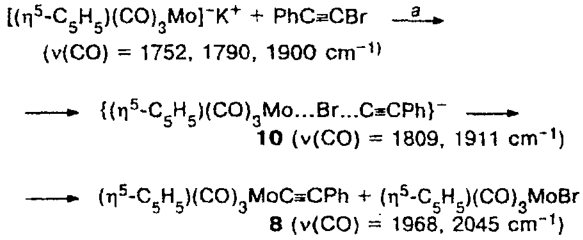
Scheme 1



M = Cr (**1**,**7**), Mo (**2**, **8**), W (**3**, **9**)

If the reactions were terminated by adding water at the early stages (M = W, X = Br, from −110 °C to −60 °C; M = W, X = I, −110 °C; or M = Mo, X = I, −110 °C), carbonyl halides of molybdenum and tungsten were obtained as the only metal-containing products (Table 1). When the reaction temperature was even slightly higher than the above-mentioned temperature range, the σ-phenylethynyl compounds $(\eta^5\text{-}C_5H_5)(CO)_3M(\sigma\text{-}C{\equiv}CPh)$ (M = Mo (**8**) or M = W (**9**)) were detected in the reaction mixture, *i.e.*, the transfer of the halogen atom from the sp-hybridized carbon atom to the metal atom (see Scheme 1, path *a*) was followed by the replacement of the halogen atom by the phenylethynyl group (path *b*). As a result, a mixture of the σ-phenylethynyl compounds $(\eta^5\text{-}C_5H_5)(CO)_3M(\sigma\text{-}C{\equiv}CPh)$ and carbonyl halides $(\eta^5\text{-}C_5H_5)(CO)_3MX$ was formed. Apparently, residual amounts of halides were present because the phenylethynyl anions were partially removed from the reaction zone as a result of side processes (see Scheme 1, path *c*), which were not studied in detail. The presence of phenylacetylene in the reaction mixture was determined by GLC. The yield of σ-ethynyl complex **7** in the reactions of chromium anion **1** was as high as 50—60%, while we failed to accurately determine the content of halides $(\eta^5\text{-}C_5H_5)(CO)_3CrX$ because of their instability.

Scheme 2



The reaction of anion **2** with PhC≡CBr was studied by low-temperature IR spectroscopy. Solutions of the reagents in THF were mixed at −90 °C and placed in a CaF_2 cell, which was cooled to the same temperature and enclosed in a cryostat. The IR spectra in the CO stretching regions (ν(CO)) were recorded with a gradual increase in the temperature from −90 °C to 23 °C. Under these conditions, the intensities of the ν(CO) bands of the initial anion **2** (1752, 1790, and 1900 cm^{-1}) were decreased, which was accompanied by the appearance of absorption bands (1968 and 2045 cm^{-1}) of the product (a mixture of σ-phenylethynyl compound **8** and carbonyl halide $(\eta^5\text{-}C_5H_5)(CO)_3MoBr$; their frequencies coincide) followed by an increase in their intensities. In addition to the above-mentioned bands, the IR spectra had two new medium-intensity bands at 1809 and 1911 cm^{-1}, which were absent in the spectra of the initial compounds and reaction products and which, in our opinion, belong to an intermediate adduct (**10**) of the

Table 1. Results of the reactions of $(\eta^5\text{-}C_5H_5)(CO)_3M^-$ (M = Mo or W) with PhC≡CX (X = I or Br)

$[CpM(CO)_3]^-$	PhC≡CX	T_{form} /°C	Time of storage/min at T_{form}	Products (%)		
				$CpM(CO)_3C{\equiv}CPh$	$CpM(CO)_3X$	$[CpM(CO)_3]_2$
W	X = I	−110	5	—	54.4	—
		−90	25	59.0	23.7	—
		−75	5	57.4	24.7	—
		−30	15	68.7	15.0	—
		0	15	66.0	16.0	—
		25	15	66.4	17.0	—
	X = Br	−110	10	—	79.0	—
		−60	30	—	98.0	—
		0	30	46.6	41.5	—
		25	30	69.5	20.5	—
Mo	X = I	−110	20	—	94.0	—
		25	60	45.0	16.7	24.5
	X = Br	−75	30	—	54.3	—
		25	35	7.4	70.8	9.0

Note: Cp = $[\eta^5\text{-}C_5H_5]$; T_{form} — Temperature of termination of the reaction with water.

carbonylmetallate anion with haloalkyne (Fig. 1, Scheme 2). In this adduct, the halogen atom is located between the carbon and metal atoms. The fact that the low-frequency band (*E*) is not split in the IR spectrum (compound **10**) indicates that the halogen atom is coordinated to the metal atom because coordination of the bromine atom to one of the carbonyl groups would lead to splitting of the *E*-type band at 1809 cm^{-1}.

The reactions of pentamethylcyclopentadienyl anions **4—6** with $PhC{\equiv}CBr$ (Eq. (2)) proceeded in the same temperature range as in the case of the reactions of **1—3**, to give products of ethynylation in approximately identical yields.

$$\begin{array}{l} \underset{\mathbf{4,\ 5,\ 6}}{[C_5Me_5(CO)_3M]^-K^+} + PhC{\equiv}CBr \longrightarrow \\ \longrightarrow C_5Me_5(CO)_3MC{\equiv}CPh + C_5Me_5(CO)_3MBr \qquad (2) \\ \quad \mathbf{11}\ (30\%) \qquad\qquad\qquad — \\ \quad \mathbf{12}\ (59\%) \qquad\qquad\quad (24\%) \\ \quad \mathbf{13}\ (52\%) \qquad\qquad\quad (25\%) \\ M = Cr\ (\mathbf{4,\ 11}),\ Mo\ (\mathbf{5,\ 12}),\ W\ (\mathbf{6,\ 13}) \end{array}$$

Apparently, reaction (2) also proceeded according to Scheme 1. The reactions of the indenyltungsten anion $(\eta^5\text{-}C_9H_7)(CO)_3W^-$ (**14**) with $PhC{\equiv}CBr$ afforded products of its ethynylation, *viz.*, $(\eta^5\text{-}C_9H_7)(CO)_3WC{\equiv}CPh$ (**15**) and carbonyl bromide $(\eta^5\text{-}C_9H_7)(CO)_3WBr$, in low yields (3 and 15%, respectively). The reasons for this fact remain unclear.

The reactions of anions **2** and **3** with 1-bromoheptyne-1 also proceeded as the transfer of the halogen atom to the transition metal atom. When the reagents were mixed in THF at −100 °C and the reaction mixture was gradually warmed to room temperature, bromides $(\eta^5\text{-}C_5H_5)(CO)_3MBr$ were obtained as the only metal-containing reaction products.

$$\begin{array}{l} \underset{\mathbf{2,\ 3}}{[(\eta^5\text{-}C_5H_5)(CO)_3M]^-} + C_5H_{11}{}^nC{\equiv}CBr \longrightarrow \\ \quad \longrightarrow (\eta^5\text{-}C_5H_5)(CO)_3MBr + \{C_5H_{11}{}^nC{\equiv}CH\} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (3) \\ \quad \not\longrightarrow (\eta^5\text{-}C_5H_5)(CO)_3MC{\equiv}CC_5H_{11}{}^n + Br^- \end{array}$$

According to the data of IR spectroscopy, reaction (3) proceeded at a noticeable rate at a temperature higher than −10 °C. In the case of reaction (3), secondary processes, which removed $C_5H_{11}{}^nC{\equiv}C^-$ from the reaction zone, were, apparently, more pronounced than in the case of $PhC{\equiv}C^-$ (see Scheme 1), due to which the σ-1-heptynyl complexes were absent from the reaction products.

Therefore, the reactions of carbonylmetallate anions **1—3** with bromo- and iodoacetylenes $RC{\equiv}CX$ proceeded as the transfer of the halogen atom regardless of the nature of the R substituent.

The formation of metal carbonyl halides has been observed previously in the reactions of anions **1—3** with dibromo- and diiodoacetylenes[4] as well as in the reaction of $(CO)_5Re^-$ with diiodoacetylene.[5] In the reaction of $(CO)_5Mn^-$ with diiodoacetylene, two competitive processes occurred, *viz.*, the elimination of iodine to form $Mn_2I_2(CO)_8$ and the nucleophilic replacement of the iodide anion to form $(CO)_5MnC{\equiv}CMn(CO)_5$.[5] The different results of the reactions of $(CO)_5Mn^-$ and $(CO)_5Re^-$ with diiodoacetylene were interpreted on the assumption that the reactions were orbital-controlled.[5] The elimination of the halogen atom observed in the reactions of 1-haloalkynes-1 with organic nucleophiles is commonly attributed to charge control over the reaction because the halogen atom acquires a positive charge (the value of which is determined by the nature of the halogen atom; I > Br >> Cl) due to interactions between the lone electron pairs of the halogen atoms and the π- and π*-orbitals of the triple carbon—carbon bond.[2] With the aim of revealing the factors that control the course of the above-considered reactions, we calculated the $PhC{\equiv}CX$ molecules (X = Cl, Br, or I) by the MNDO/PM3 method. According to the results of calculations, the structure of LUMO changes substantially on going from X = Cl to X = Br or I. In the case of bromo- and iodoalkynes, LUMO are σ-orbitals. The p_x-orbitals of the bromine and iodine atoms are involved in these MOs with the largest coefficients (0.74 and 0.77, respectively; the *x* axis is directed along the X—C bond), the phenyl ring being located in the *xy* plane. The contributions of the s- and p_x-orbitals of the carbon atoms bound to the halogen atoms are also rather high: 0.5 (s) and 0.35 (p_x) for X = Br and 0.47 (s) and 0.36 (p_x) for X = I. The coefficients of AOs of other atoms are substantially smaller and they may be ignored. Therefore, the nucleophilic attack on the halogen atom in $PhC{\equiv}CX$ (X = Br or I) can be predicted based on the structure of LUMO. In the case of $PhC{\equiv}CCl$, LUMO is the π-orbital in which the p_z-orbital of the carbon atom of the C—Cl bond is involved with the largest coefficient (−0.37), while the contribution of the p_z-orbital of the chlorine atom is substantially smaller (0.11). Hence, the nucleophilic attack on the carbon atom of the C—Cl bond in $PhC{\equiv}CCl$ can be predicted based on the results of calculations.

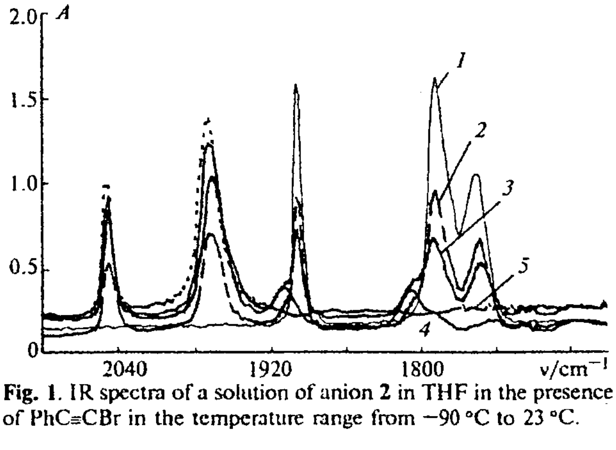


Fig. 1. IR spectra of a solution of anion **2** in THF in the presence of $PhC{\equiv}CBr$ in the temperature range from −90 °C to 23 °C.

Note that the structure of LUMO in PhC≡CX is in qualitative agreement with the results of theoretical studies of the reactions of RC≡CX with the SH^- anion performed by the extended Hückel method.[7]

Reactions of carbonylmetallate anions with phenylethynyl chloride

The reactions of tungstate and molybdate anions **3** and **2** with PhC≡CCl in THF proceeded only upon heating above 50 °C to form the corresponding σ-phenylethynyl compounds **8** (in 72% yield) and **9** (78%) as virtually the only reaction products (reaction (4)). In the case of the molybdate anion, an insignificant amount of the $[(\eta^5\text{-}C_5H_5)(CO)_3Mo]_2$ dimer was also detected.

$$\underset{\mathbf{2,\,3}}{[(\eta^5\text{-}C_5H_5)(CO)_3M]K} + C_6H_5C{\equiv}CCl \longrightarrow$$

$$\longrightarrow \underset{\mathbf{8,\,9}}{(\eta^5\text{-}C_5H_5)(CO)_3MC{\equiv}CPh} + KCl \qquad (4)$$

M = Mo (**2**, **8**), W (**3**, **9**)

Figure 2 shows changes in the concentrations of the σ-phenylethynyl complexes with time. As can be seen from this figure, reaction (4) proceeded without an induction period.

We performed a preliminary study of the kinetics of reaction (4) of tungstanate anion **3** in THF at 65 °C by IR spectroscopy. It was established that the reaction had an overall second order and a first order with respect to the carbonylmetallate anion and haloacetylene. The rate constant was (0.12±0.02) L $(\text{mol min})^{-1}$. (The results of kinetic studies of reaction (4) will be published elsewhere.) Apparently, this reaction, like other processes of nucleophilic substitution at an unsaturated carbon atom, proceeded according to an addition—elimination scheme (Scheme 3).

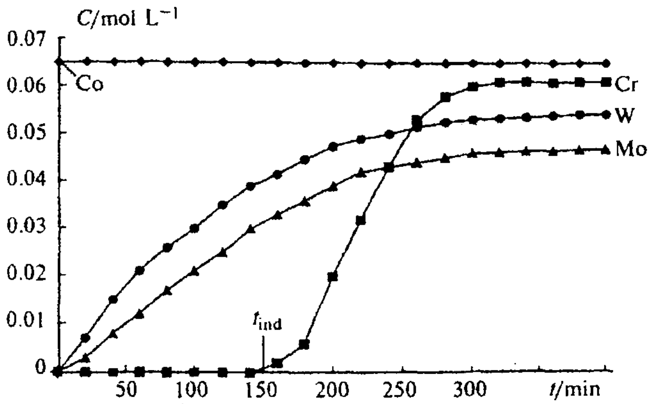
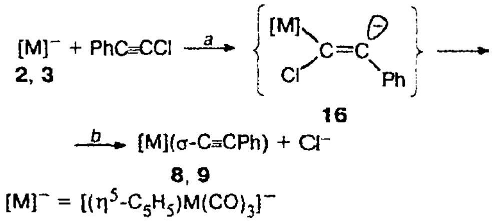


Fig. 2. Changes in the concentrations of the σ-phenylethynyl complexes $(\eta^5\text{-}C_5R'_5)(CO)_3MC{\equiv}CPh$ in the course of the reactions of anions **1**—**3** with PhC≡CCl.

Scheme 3



The yield of the σ-phenylethynyl derivative remained virtually unchanged upon addition of alcohol (20 vol.%) to THF. This indicates that the rate of elimination of the chloride anion (see Scheme 3, path *b*) is substantially higher that the rate of protonation of adduct **16**.

The reactions of $(\eta^5\text{-}C_5Me_5)(CO)_3Mo^-$ (**5**) and $(\eta^5\text{-}C_5Me_5)(CO)_3W^-$ (**6**) with PhC≡CCl in THF proceeded analogously to reaction (4) of cyclopentadienyl analogs, to give the corresponding σ-phenylethynyl compounds **12** and **13** in 53 and 48% yields, respectively. The reaction of indenyltungstanate anion **14** with PhC≡CCl was accompanied by noticeable decomposition, and the yield of σ-derivative **15** was 10%.

Unlike reactions (4) of anions **2** and **3**, analogous processes with carbonylchromate anions **1** and **4** (Eq. (5)) were characterized by pronounced induction periods. For the reaction of anion **1** in THF at 65 °C, the induction period was 2.5 h (Fig. 2).

$$\underset{\mathbf{1,\,4}}{(\eta^5\text{-}C_5R'_5)(CO)_3Cr^-} + PhC{\equiv}CCl \longrightarrow$$

$$\longrightarrow \underset{\mathbf{7,\,11}}{(\eta^5\text{-}C_5R'_5)(CO)_3CrC{\equiv}CPh} + Cl^- \qquad (5)$$

R′ = H (**1**, **7**), Me (**4**, **11**)

After completion of the induction period, the reaction was accelerated and completed in a time shorter than that observed in the reactions of the molybdate and tungstanate anions. This course of the reaction corresponds to the formation of catalytically active species in the first stage. We have demonstrated that the addition of the reaction product (σ-ethynyl complex **7**) to the reaction mixture did not accelerate reaction (5). We believe that the reaction proceeded according to Scheme 4:

Scheme 4

$$(\eta^5\text{-}C_5H_5)(CO)_3Cr^-K^+ + 3\,THF \rightleftharpoons$$

$$\rightleftharpoons \underset{\mathbf{17}}{(THF)_3Cr(CO)_3} + (\eta^5\text{-}C_5H_5)K \qquad (a)$$

$$\mathbf{17} + PhC{\equiv}CCl \rightleftharpoons \underset{\mathbf{18}}{(CO)_3Cr(\eta^6\text{-}PhC{\equiv}CCl)} + 3\,THF \qquad (b)$$

$$\mathbf{18} + (\eta^5\text{-}C_5H_5)Cr(CO)_3{}^- \rightleftharpoons$$

$$\rightleftharpoons \underset{\mathbf{19}}{(CO)_3Cr[\eta^6\text{-}PhC{\equiv}CCr(CO)_3(\eta^5\text{-}C_5H_5)]} + Cl^- \qquad (c)$$

$$\mathbf{19} + THF \rightleftharpoons \mathbf{17} + (\eta^5\text{-}C_5H_5)(CO)_3CrC{\equiv}CPh \qquad (d)$$

The catalytically active species (**17**) was formed as a result of replacement of the cyclopentadienyl ring in the initial carbonylmetallate anion by the THF molecule (see Scheme 4, stage *a*). The reaction of **17** with PhC≡CCl afforded compound **18**, in which the chromium atom is coordinated by the six-membered ring. In the case of compound **18**, the nucleophilic substitution of the chlorine atom proceeded more readily compared to PhC≡CCl due to coordination to the acceptor tricarbonylchromium group. The final replacement of $(\eta^5\text{-}C_5H_5)(CO)_3CrC{\equiv}CPh$ in (**19**) under the action of THF regenerated catalytically active species **17** and allowed the process to persist. Apparently, the rate determining step of the reaction involved the replacement of the π-ligand (see Scheme 4, stage *a*). Consequently, the possibility of generation of the $L_3Cr(CO)_3$ molecule, which can produce $(\eta^6\text{-}PhC{\equiv}CCl)Cr(CO)_3$ by replacing readily leaving ligands L, under mild conditions is of paramount importance for accelerating this reaction (see Scheme 4, stage *b*). The validity of this suggestion was confirmed by the fact that reaction (5) was accelerated upon addition of catalytic amounts of (η^6-naphthalene)tricarbonylchromium (**20**) as well as by the fact that this reaction was accelerated when acetonitrile was used as the solvent instead of THF.

Catalysis of reaction (5) by $(\eta^6\text{-}C_{10}H_8)Cr(CO)_3$

It is known that compound **20** dissociates to a significant degree in THF at room temperature[8] (reaction (6)), this dissociation being the basis of the preparative procedure for the synthesis of arenetricarbonylchromium complexes through naphthalene—arene exchange in complex **20** in diethyl ether with an addition of THF.

$$\underset{\mathbf{20}}{Cr(CO)_3(\eta^6\text{-}C_{10}H_8)} + 3\ THF \rightleftharpoons \underset{\mathbf{17}}{Cr(CO)_3(THF)_3} + C_{10}H_8 \quad (6)$$

We found that the addition of catalytic amounts of compound **20** resulted in acceleration of reaction (5) of $(\eta^5\text{-}C_5H_5)(CO)_3Cr^-$ to an extent that it proceeded even at room temperature (the reaction time was less than 20 h and the yield of complex **7** was 33%). This reaction in THF at 65 °C was completed in 3 h to form compound **7** in approximately the same yield. In the presence of **20**, the reactions of the anions $(\eta^5\text{-}C_5H_5)(CO)_3Mo^-$ (**2**) and $(\eta^5\text{-}C_5H_5)(CO)_3W^-$ (**3**) were also accelerated and proceeded with a rate approximately identical to that observed in the reaction of chromate anion **1**. We believe that under these conditions anions **2** and **3** reacted with PhC≡CCl according to Scheme 4 with the participation of anions **2** and **3** at stage (*b*) accompanied by elimination of σ-phenylethynyl complexes **7** and **8** at stage (*d*) rather than according to Scheme 3 ("addition—elimination"). Apparently, a comparatively low yield of the target σ-phenylethynyl complexes and the necessity of using rather large amounts of catalysts (no less than 10%) for the purpose of providing reproducibility are associated with the fact that (as we have demonstrated in the control experiments) (η^6-naphthalene)tricarbonylchromium **20** underwent decomposition under the action of anions **1**—**3**. Because of this, a portion of the catalyst and the initial anionic complex were removed from the reaction zone.

Reactions of anions 1—3 with PhC≡CCl in acetonitrile

Carbonylchromate anion **1** reacted with PhC≡CCl in acetonitrile more rapidly than in THF. Reaction (5) proceeded without an induction period even at 35 °C. This is attributable to the fact that the stage of replacement of the cyclopentadienyl ligand in MeCN (reaction (7)) is less endothermic than the same stage in THF (see Scheme 4, stage *a*).*

To the contrary, the reaction of tungsten anion **3** with PhC≡CCl in MeCN proceeded approximately 1.5 times more slowly than that in THF. We believe that reaction (4) in both solvents proceeded according to the "addition—elimination" scheme and the difference in the rate is due to the difference in the cation—anion interaction in the salt and in **3** (anion **3** exists as a solvent-separated ion pair and a contact ion pair in MeCN and THF, respectively). In the reactions of carbonylmetallate anions with perfluoroaryl and perfluorovinyl halides, which are phenomenologically similar to reaction (4), contact ion pairs react faster than solvent-separated ion pairs.[11,12] If these regularities are also true for reaction (4), a change from THF to MeCN should cause a decrease in its rate.

Reactions of carbonylmetallate anions 1—3 with 1-chloro-2-methoxycarbonylacetylene and perfluoro-tert-butylacetylene

The electron-deficient haloalkynes ClC≡CCOOMe and $FC{\equiv}CC(CF_3)_3$ readily reacted with carbonylmetallate anions **1**—**3** even under mild conditions. In the reactions with 1-chloro-2-methoxycarbonylacetylene in THF, the complete conversion of the initial carbonylmetallate anions was observed even at −80 °C.

$$\underset{\mathbf{1,\ 2,\ 3}}{(\eta^5\text{-}C_5H_5)(CO)_3M^-} + ClC{\equiv}C{-}COOMe \longrightarrow$$

$$\longrightarrow \underset{\mathbf{21}\ (65\%),\ \mathbf{22}\ (64\%),\ \mathbf{23}\ (44\%)}{(\eta^5\text{-}C_5H_5)(CO)_3MC{\equiv}C{-}COOMe} \quad (7)$$

M = Cr (**1**, **21**), Mo (**2**, **22**), W (**3**, **23**)

The reactions with perfluoro-*tert*-butylacetylene also proceeded very readily (reaction (12)). However, these reactions, unlike those described above, were reversible.

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*This fact can be rather rigorously demonstrated for the molybdenum complexes based on the values of the enthalpies of the replacement of the arene ligand in (η^6-toluene)tricarbonylmolybdenum under the action of C_5H_5Na, THF, or MeCN.[10] The same regularities may also be true for the chromium complexes and, consequently, reaction (5) should proceed more rapidly in acetonitrile than in THF.

According to the data of IR spectroscopy, the equilibrium was shifted to the initial compounds in the case of the chromate anion and to the reaction products in the case of the molybdenum and tungsten anions.

$$\underset{\mathbf{1,\ 2,\ 3}}{(\eta^5\text{-}C_5H_5)(CO)_3M^-} + FC{\equiv}C{-}C(CF_3)_3 \rightleftharpoons$$

$$\rightleftharpoons \underset{\mathbf{24}\ (10\%),\ \mathbf{25}\ (38\%),\ \mathbf{26}\ (30\%)}{(\eta^5\text{-}C_5H_5)(CO)_3MC{\equiv}C{-}C(CF_3)_3} \qquad (8)$$

M = Cr (**1**, **24**), Mo (**2**, **25**), W (**3**, **26**)

In reactions (11) and (12), the reactivities of anions **1**—**3** were reduced to a minimum. Apparently, these reactions with all the above-mentioned anions proceeded according to Scheme 3.

Reactions of carbonylmetallate anions 1—3 with 1-chloroheptyne-1. Catalytic cross-coupling under the action of palladium complexes

Anions **1**—**3** did not react with $C_5H_{11}{}^nC{\equiv}CCl$ upon prolonged boiling in THF. Thus, boiling of carbonyltungstanate anion **3** with $C_5H_{11}{}^nC{\equiv}CCl$ in THF for 24 h afforded insignificant amounts of the dimer $[(\eta^5\text{-}C_5H_5)(CO)_3W]_2$ (3%) and the σ-1-heptynyl complex $(\eta^5\text{-}C_5H_5)(CO)_3WC{\equiv}CC_5H_{11}{}^n$ (**27**) (4%), while even trace amounts of analogous complexes were not detected in the case of carbonylchromate anion **1** under these conditions. Apparently, the low electrophilicity of chloroalkyne retards the replacement according to the "addition—elimination" scheme (see Scheme 3). Unlike the above-considered reactions of anions **1**—**3** with 1-chloro-2-phenylacetylene, the addition of **20** did not accelerate the reaction of the above-mentioned anions with 1-chloroheptyne-1 according to Scheme 4. This is because of the fact that 1-chloroheptyne-1 does not contain a six-membered ring capable of being coordinated to the tricarbonylchromium group. We found that the addition of catalytic amounts of palladium complexes to a mixture of 1-chloroheptyne with carbonylmetallate anions **1**—**3** sharply accelerated the reaction. The process went to completion even at room temperature. The yields of complex **27**, $(\eta^5\text{-}C_5H_5)(CO)_3CrC{\equiv}CC_5H_{11}{}^n$ (**28**), and $(\eta^5\text{-}C_5H_5)(CO)_3MoC{\equiv}CC_5H_{11}{}^n$ (**29**) were as high as 20—46%.

$$(\eta^5\text{-}C_5H_5)(CO)_3M^- + ClC{\equiv}CC_5H_{11}{}^n \xrightarrow{[Pd]}$$

$$\longrightarrow (\eta^5\text{-}C_5H_5)(CO)_3MC{\equiv}CC_5H_{11}{}^n \qquad (9)$$

M = W (**27**), Cr (**28**), Mo (**29**)

Apparently, reaction (9) proceeded according to the scheme of the typical cross-coupling, which involves oxidative addition of chloroalkyne to the Pd^0 complex to form the chloroethynyl intermediate $Pd(\sigma\text{-}C{\equiv}CC_5H_{11}{}^n)Cl$, nucleophilic substitution of the carbonylmetal group for the chlorine atom to form $(\eta^5\text{-}C_5H_5)(CO)_3M{-}Pd(\sigma\text{-}C{\equiv}CC_5H_{11}{}^n)$, followed by reductive elimination of σ-heptynyl complexes **27**—**29**. The reactions of Pd-catalyzed cross-coupling of 1-chloroalkynes-1 will be published elsewhere.

To summarize, the results of our investigations allow us to state the following regularities of the reactions of carbonylmetallate anions **1**—**6** with 1-haloalkynes:

— the reactions with bromo- and iodoalkynes proceed as a halogen atom transfer from haloalkyne to the metal atom;

— the reactions of carbonylmetallate anions of molybdenum and tungsten **2**, **3**, **5**, and **6** with chloroalkynes $RC{\equiv}CCl$ (R = Ph or COOMe) proceed as a nucleophilic substitution at the sp-hybridized carbon atom;

— the reactions of carbonylmetallate anions **1** and **4** with $Ph{\equiv}CCl$ proceed according to a complex scheme involving the replacement of the cyclopentadienyl ligand in the carbonylchromate anions at the first stage and the formation of $(THF)_3Cr(CO)_3$ as a catalyst;

— the reactions of carbonylmetallate anions with nonactivated chloroalkyne $C_5H_{11}{}^nC{\equiv}CCl$ can be performed as cross-coupling catalyzed by Pd^0 complexes.

Experimental

All operations associated with the preparation of the solvents, synthesis of the initial organometallic compounds, isolation of the reaction products, and their purification, except for thin-layer chromatography, were performed under an atmosphere of dry purified argon. Silica gel (Aldrich, 70—230 mesh, 60 Å) and aluminum oxide (Brockmann II) were used for chromatography.

The IR spectra were measured on UR-20 and Specord M-82 spectrophotometers. The degree of conversion of the metal carbonyl complexes in the reactions was determined from the change in the carbonyl regions (ν(CO) = 1700—2100 cm^{-1}) of the IR spectra. The ^1H and ^{13}C NMR spectra were recorded on Varian VXR-400, Bruker WP-200 SY, and Bruker AMX-400 instruments. Samples were prepared with the use of standard deuterated solvents under argon. The chemical shifts are given in the δ scale. The mass spectra were measured on a Kratos MS-890 instrument (the energy of ionizing electrons was 70 eV, the current of emission was 100 μA, the temperature of the ionization chamber was 150—250 °C.)

The initial compounds $[(\eta^5\text{-}C_5H_5)(CO)_3Cr]_2Hg$[13] (**30**), $[(\eta^5\text{-}C_5H_5)(CO)_3Mo]_2$[14] (**31**), $[(\eta^5\text{-}C_5H_5)(CO)_3W]_2$[14] (**32**), $[(\eta^5\text{-}C_5Me_5)(CO)_3Cr]_2Hg$[13,15] (**33**), $[(\eta^5\text{-}C_5Me_5)(CO)_3Mo]_2$[14,15] (**34**), $[(\eta^5\text{-}C_5Me_5)(CO)_3W]_2Hg$[13,15] (**35**), $[(\eta^5\text{-}C_9H_7)(CO)_3W]_2Hg$[16] (**36**), $PhC{\equiv}CI$,[17] $PhC{\equiv}CBr$,[18] $PhC{\equiv}CCl$,[20] $MeOOCC{\equiv}CCl$,[20] $C_5H_{11}{}^nC{\equiv}CCl$,[21] and $C_5H_{11}{}^nC{\equiv}CBr$[21] were prepared according to known procedures.

The anions were prepared by reducing the corresponding dimers with a Na/K alloy in THF (10 mL per 0.3 mmol of the carbonylmetal substrate) and with Na amalgam in acetonitrile.

Calculations of the $PhC{\equiv}CX$ molecules (X = Cl, Br, or I) were carried out by the semiempirical quantum-chemical MNDO/PM3 method[22] (in the valence approximation) using the GAMESS program package[23] on a Workstation DEC 3000 AXP-400X.

Reactions of carbonylmetallate anions 2 and 3 with $PhC\equiv CBr$ and $PhC\equiv CI$. Anions 2 and 3 were prepared in THF from compounds **31** (0.147 g, 0.3 mmol) and **32** (0.2 g, 0.3 mmol), respectively. A solution of $PhC\equiv CI$ (0.137 g, 0.6 mmol) or $PhC\equiv CBr$ (0.11 g, 0.6 mmol) in THF (3 mL) was added with stirring to solutions of the anions in THF, which were preliminarily filtered and cooled to −110 °C. The temperature of the reaction mixture was gradually increased and aliquot samples (2 mL of the reaction mixture) were drawn at different temperatures. Water (2—3 drops) was added to the aliquot samples to terminate the reaction. The solvent was removed from all aliquot samples *in vacuo* and the residues were transferred to a column with Al_2O_3 (0.5×2 cm) and washed with petroleum ether. Red-orange bands were eluted with benzene. These bands contained a mixture of σ-ethynyl complexes with carbonyl halides, whose ratio was determined by ^1H NMR spectroscopy. Organic admixtures, which were washed off with petroleum ether on a column, were studied by GLC. $PhC\equiv CH$ was detected in all samples. The yield of the latter depends on the temperature of termination of the reaction. When the reactions of anions **2** and **3** were terminated at −110 °C, $PhC\equiv CH$ was obtained in 100% yield (see Table 1).

IR spectral studies of the reaction of anion 2 with $PhC\equiv CBr$. Low-temperature IR studies were performed in the temperature range from −90 to 23 °C on a Specord M-82 spectrophotometer equipped with a cryostat (Carl Zeiss). Anion **2** was prepared from **31** (0.367 g, 0.75 mmol) in THF, filtered off, and cooled to −100 °C. Then $PhC\equiv CBr$ (0.271 g, 0.15 mmol) was added with stirring. The mixture of the reagents at −90 °C was placed in a CaF_2 cell cooled to the same temperature. The IR spectra were recorded, the mixture being gradually warmed to room temperature.

Reactions of carbonylmetallate anions 4—6 with $PhC\equiv CBr$. A solution of phenylethynyl bromide (0.24 g, 1.34 mmol; 0.29 g, 1.58 mmol; and 0.21 g, 1.2 mmol in the cases of anions **4**, **5**, and **6**, respectively) in THF (3 mL) was added with stirring at −110 °C to anions **4—6**, which were prepared from solutions of compounds **33**, **34**, and **35** (0.5 g, 0.67 mmol; 0.5 g, 0.79 mmol; and 0.6 g, 0.6 mmol, respectively) in THF and filtered. The course of the reaction was monitored by IR spectroscopy. At −70 °C (within 15 min after the addition of $PhC\equiv CBr$) in the case of anion **5** and at −110 °C (within 10 min after the addition of $PhC\equiv CBr$) in the cases of anions **4** and **6**, bands of the initial anions disappeared. Then the reaction mixture was gradually warmed to room temperature during 45 min. The solvent was removed *in vacuo*. The residue was separated on a column with SiO_2 (2.5×12 cm). The yellow band containing the σ-ethynyl complex and the orange band containing carbonyl bromide were successively eluted with a 3 : 1 benzene—hexane mixture. The resulting complexes were additionally purified by reprecipitation with hexane from benzene.

The reaction with anion **4** afforded the **$(\eta^5$-$C_5Me_5)(CO)_3CrC\equiv CPh)$** complex (**11**) in a yield of 0.15 g (30%). IR (hexane), ν/cm^{-1}: 2030, 1969, 1949 (CO); 2109 ($C\equiv C$). ^1H NMR (C_6D_6), δ: 1.49 (s, C_5Me_5). MS, *m/z*: 372 $[M]^+$, 316 $[M - 2CO]^+$, 288 $[M - 3CO]^+$. Found (%): C, 67.76; H, 5.71; Cr, 13.97. For $C_{21}H_{20}O_3Cr$, calculated (%): C, 67.48; H, 5.41; Cr, 13.93.

The reaction with anion **5** gave complex **12** and $(\eta^5$-$C_5Me_5)(CO)_3MoBr$ in yields of 0.39 g (59%) and 0.15 g (24%), respectively. **$(\eta^5$-$C_5Me_5)(CO)_3MoC\equiv CPh$ (12).** IR (THF), ν/cm^{-1}: 2053, 1979 (CO); 2110 ($C\equiv C$). ^1H NMR (C_6D_6), δ: 1.59 (s, C_5Me_5). MS, *m/z*: 416 $[M]^+$, 388 $[M - CO]^+$, 360 $[M - 2CO]^+$, 332 $[M - 3CO]^+$, 231 $[C_5Me_5Mo]^+$. Found (%): C, 60.65; H, 4.88; Mo, 23.12. For $C_{21}H_{20}O_3Mo$, calculated (%): C, 60.58; H, 4.84; Mo, 23.05. **$(\eta^5$-$C_5Me_5)(CO)_3MoBr$.** IR (THF), ν/cm^{-1}: 2053, 1979 (CO); 2110 ($C\equiv C$). ^1H NMR (C_6D_6), δ: 1.45 (s, C_5Me_5). MS, *m/z*: 395 $[M]^+$, 339 $[M - 2CO]^+$, 311 $[M - 3CO]^+$, 231 $[C_5Me_5Mo]^+$. Found (%): C, 39.55; H, 4.15; Br, 20.18; Mo, 23.68. For $C_{13}H_{15}O_3BrMo$, calculated (%): C, 39.52; H, 3.83; Br, 20.22; Mo, 24.28.

The reaction with anion **6** gave complex **13** and $(\eta^5$-$C_5Me_5)(CO)_3WBr$ in yields of 0.31 g (52%) and 0.14 g (25%), respectively. **$(\eta^5$-$C_5Me_5)(CO)_3WC\equiv CPh$ (13).** IR (CH_2Cl_2), ν/cm^{-1}: 2031, 1945 (CO); 2108 ($C\equiv C$). ^1H NMR (C_6D_6), δ: 1.72 (s, C_5Me_5). Found (%): C, 50.18; H, 3.99; W, 36.28. For $C_{21}H_{20}O_3W$, calculated (%): C, 50.03; H, 3.96; W, 36.47.

Reaction of anion 14 with $PhC\equiv CBr$. A solution of phenylethynyl bromide (0.142 g, 0.78 mmol) in THF (3 mL) was added with stirring at −70 °C to anion **14**, which was prepared from a solution of **36** (0.38 g, 0.39 mmol) in THF and filtered. The reaction mixture was warmed to room temperature during 1 h. At room temperature, bands of the initial anion **14** were absent in the IR spectra. The solvent was removed *in vacuo* and the residue was separated on plates with SiO_2 in a 2 : 1 benzene—hexane system. Two bands were collected: the yellow band corresponded to complex **15** and the orange band corresponded to the $(\eta^5$-$C_9H_7)(CO)_3WBr$ complex. The resulting compounds were additionally purified by reprecipitation from a benzene/hexane mixture. $(\eta^5$-$C_9H_7)(CO)_3WBr$ and **15** were obtained in yields of 0.055 g (15%) and 0.011 g (3%), respectively.

Reactions of anions 2 and 3 with $C_5H_{11}{}^nC\equiv CBr$. $C_5H_{11}{}^nC\equiv CBr$ (0.1 g, 0.6 mmol) was added with stirring at −100 °C to anions **2** and **3**, which were prepared from solutions of **31** (0.15 g, 0.3 mmol) and **32** (0.2 g, 0.3 mmol), respectively, in THF and filtered. The reaction mixture was gradually warmed to room temperature, the course of the reaction being monitored by IR spectroscopy. The mixture was stirred at room temperature for 20 min and the solvent was removed *in vacuo*. The residue was separated on a column with SiO_2 in a 2 : 1 benzene—hexane mixture. Orange bands were isolated and characterized as $(\eta^5$-$C_5H_5)(CO)_3MoBr$ and $(\eta^5$-$C_5H_5)(CO)_3WBr$ by comparing with known samples. The compounds $(\eta^5$-$C_5H_5)(CO)_3MoBr$ and $(\eta^5$-$C_5H_5)(CO)_3WBr$ were obtained in yields of 0.13 g (65%) and 0.17 g (68%), respectively.

Reactions of anions 2, 3, 5, 6, and 14 with $PhC\equiv CCl$. A solution of phenylethynyl chloride in THF (3 mL) was added at room temperature to the anions, which were preliminarily filtered. The reaction mixture was gradually warmed to 65 °C and refluxed, the course of the reaction being monitored by IR spectroscopy. After bands of the initial anion disappeared in the IR spectrum, the solvent was removed *in vacuo*, the residue was transferred to a column with SiO_2, and the major yellow band of the σ-ethynyl complex was eluted with benzene. The complexes eluted from the column were additionally purified by reprecipitation with hexane from benzene.

Anion **2** was prepared from **31** (0.147 g, 0.3 mmol) and then phenylethynyl chloride (0.09 g, 0.6 mmol) was added. Complex **8** was obtained in a yield of 0.15 g (72%).

Anion **3** was prepared from **32** (0.5 g, 0.75 mmol) and then phenylethynyl chloride (0.2 g, 1.5 mmol) was added. Complex **9** was obtained in a yield of 0.5 g (78%).

Anion **5** was obtained from **34** (1.5 g, 2.38 mmol) and then phenylethynyl chloride (0.64 g, 4.7 mmol) was added. Complex **12** was obtained in a yield of 1 g (53%).

Anion **6** was obtained from **35** (0.81 g, 0.8 mmol) and then phenylethynyl chloride (0.218 g, 1.6 mmol) was added. Complex **13** was obtained in a yield of 0.38 g (48%).

Anion **14** was obtained from **36** (1.26 g, 1.3 mmol) and then phenylethynyl chloride (0.356 g, 2.6 mmol) was added. Complex **15** was obtained in a yield of 0.13 g (10%).

Reaction of tungstanate anion 3 with $PhC\equiv CCl$ in the presence of MeOH. Anion **3** was prepared from compound **32** (0.2 g, 0.3 mmol) in THF. Anhydrous MeOH (3 mL, 20% with respect to the volume of the solution) was added to a solution of the anion at room temperature and then a solution of $PhC\equiv CCl$ (0.09 g, 0.6 mmol) in THF (3 mL) was added with stirring. The reaction mixture was refluxed for 10 h. After bands of the initial anion disappeared in the IR spectra, the mixture was treated as described above. $CpW(CO)_3C\equiv CPh$ was obtained in a yield of 0.19 g (73%) and traces of $[CpW(CO)_3]_2$ were detected.

Reactions of chromate anions 1 and 4 with $PhC\equiv CCl$. A solution of phenylethynyl chloride (0.082 g, 0.6 mmol) in THF (3 mL) was added with stirring at room temperature to solutions of anions **1** and **4**, which were prepared from solutions of **30** (0.18 g, 0.3 mmol) and **33** (0.22 g, 0.3 mmol), respectively, in THF and filtered. The reaction mixture was gradually warmed to 65 °C and refluxed for 6.5 h. The IR spectra were recorded every 20 min. After bands of the initial anions disappeared in the IR spectra, the solvent was removed *in vacuo*, the residues were applied to a column with SiO_2, and the yellow bands of compounds **7** and **11** were eluted with a 1 : 1 benzene—hexane mixture. Complexes **7** and **11** were obtained in yields of 0.13 g (70%) and 0.15 g (67%), respectively.

Reactions of anions 1 and 3 with $PhC\equiv CCl$ in the presence of $(\eta^6\text{-}C_{10}H_8)Cr(CO)_3$ (20). *A.* $PhC\equiv CCl$ (0.082 g, 0.6 mmol) and complex **20** (10%, 0.016 g, 0.06 mmol) were added with stirring at room temperature to a solution of anion **1**, which was prepared from **30** (0.18 g, 0.3 mmol) in THF and filtered. The reaction was performed at room temperature during 24 h. The course of the reaction was monitored by IR spectroscopy. After bands of the initial anion disappeared in the IR spectra, the solvent was removed *in vacuo* and the resulting complex **7** was purified on a column with SiO_2 (benzene as the eluent). Compound **7** was obtained in a yield of 0.06 g (33%).

B. Compound **20** (5%, 0.0079 g, 0.03 mmol) was added with stirring at room temperature to anion **1**, which was prepared as described above and filtered. After 0.5 h, $PhC\equiv CCl$ (0.082 g, 0.6 mmol) was added to this solution. The flask with the reaction mixture was placed in a bath warmed to 65 °C and the mixture was refluxed for 3 h until bands of the initial anion disappeared in the IR spectrum. The resulting complex **7** was purified on a column with SiO_2 (benzene as the eluent). Compound **7** was obtained in a yield of 0.05 g (28%).

C. Complex **20** (10%, 0.016 g, 0.6 mmol, in THF (5 mL)) and $PhC\equiv CCl$ (0.082 g, 0.6 mmol) were added at room temperature to a solution of anion **3** in THF, which was prepared from **32** (0.2 g, 0.3 mmol) and filtered. The reaction mixture was stirred for 22 h at room temperature until bands of the initial anion disappeared in the IR spectra. The resulting complex **9** was purified from decomposition products on plates with SiO_2 (a 2 : 1 benzene—hexane mixture as the eluent). Compound **9** was obtained in a yield of 0.04 g (15%).

Reactions of anions 1 and 3 with $PhC\equiv CCl$ in acetonitrile. Anions **1** and **3** were prepared from solutions of **30** (0.18 g, 0.3 mmol) and **32** (0.2 g, 0.3 mmol), respectively, in MeCN. $PhC\equiv CCl$ (0.082 g, 0.6 mmol) was added with stirring at room temperature to the filtered anions and the reaction mixture was gradually warmed to 65 °C. The course of the reaction was monitored by IR spectroscopy. In the case of chromate anion **1**, absorption bands of the product appeared in the IR spectra even at 35 °C. The reaction was completed in 1.5 h. In the case of tungstate anion **3**, the reaction mixture was refluxed for 10 h until the reaction was completed. The solvent was removed *in vacuo* and the residue was applied to a column with SiO_2 and eluted with benzene. The resulting σ-complexes were additionally purified by reprecipitation with hexane from benzene. Complexes **7** and **9** was isolated in yields of 0.06 g (33%) and 0.096 g (37%), respectively.

Reactions of anions 1—3 with $ClC\equiv CCOOMe$. Anions **1—3** were prepared from solutions of **30** (0.36 g, 0.6 mmol), **31** (0.29 g, 0.6 mmol), and **32** (0.2 g, 0.3 mmol), respectively, in THF. Equimolar amounts of $ClC\equiv CCOOMe$ were added with stirring to the anions (0.071 g, 0.6 mmol to anion **1** and 0.14 g, 1.2 mmol to anions **2** and **3**), which were preliminarily filtered and cooled to −110 °C. At −80 °C, bands of the initial anion disappeared in the IR spectra. The reaction mixture was gradually warmed to room temperature and the solvent was removed *in vacuo*. The residues were applied to a column with SiO_2 and the σ-methoxycarbonylethynyl complexes were eluted with benzene. The compounds eluted from the column were recrystallized from a benzene—hexane mixture. Complexes **21**, **22**, and **23** were obtained in yields of 0.22 g (65%), 0.26 g (64%), and 0.11 g (44%), respectively.

$(\eta^5\text{-}C_5H_5)(CO)_3CrC\equiv CCOOMe$ (21). IR (CH_2Cl_2), ν/cm^{-1}: 2112 ($C\equiv C$); 2050, 1987 (CO); 1700 (>C=O). ^{1}H NMR (C_6D_6), δ: 4.03 (s, C_5H_5); 3.39 (s, COOMe). ^{13}C NMR (C_6D_6), δ: 52.04 (—COO*Me*); 90.46 (*C*$_5$H$_5$); 110.56, 119.08 (C(α), C(β)); 152.96 (—*C*OOMe); 233.1, 244.51 (*C*O). Found (%): C, 50.75; H, 3.1; Cr, 18.32. For $C_{12}H_8CrO_5$, calculated (%): C, 50.72; H, 2.84; Cr, 18.3.

$(\eta^5\text{-}C_5H_5)(CO)_3MoC\equiv CCOOMe$ (22). IR (THF), ν/cm^{-1}: 2120 ($C\equiv C$); 2055, 1982 (CO); 1708 (>C=O). ^{1}H NMR (C_6D_6), δ: 4.47 (s, C_5H_5); 3.38 (s, COOMe). ^{13}C NMR (C_6D_6), δ: 51.3 (−COO*Me*); 92.86 (*C*$_5$H$_5$); 101.45, 122.15 (C(α), C(β)); 153.11 (−*C*OOMe); 223.07, 237.18 (*C*O). Found (%): C, 44.3; H, 2.49; Mo, 29.19. For $C_{12}H_8MoO_5$, calculated (%): C, 43.92; H, 2.45; Mo, 29.24.

$(\eta^5\text{-}C_5H_5)(CO)_3WC\equiv CCOOMe$ (23). IR (CH_2Cl_2), ν/cm^{-1}: 2120 ($C\equiv C$); 2051, 1971 (CO); 1710 (>C=O). ^{1}H NMR (C_6D_6), δ: 4.42 (s, C_5H_5); 3.38 (s, COOMe). ^{13}C NMR (C_6D_6), δ: 51.36 (—COO*Me*); 91.35 (*C*$_5$H$_5$); 86.15, 122.56 (C(α), C(β)); 153.25 (—*C*OOMe); 212.0, 227.19 (*C*O). Found (%): C, 35.62; H, 2.1; W, 43.51. For $C_{12}H_8WO_5$, calculated (%): C, 34.64; H, 1.94; W, 44.19.

Reactions of anions 1—3 with $FC\equiv CC(CF_3)_3$. *A. Reaction of anion 1.* A solution of $FC\equiv CC(CF_3)_3$ (0.21 g, 0.8 mmol) in THF (3 mL) was added with stirring to anion **1**, which was prepared from **30** (0.24 g, 0.4 mmol) in THF, filtered, and cooled to −90 °C. The reaction mixture was warmed to room temperature and stirred for 6 days. The solvent was removed *in vacuo*. The residue was extracted with anhydrous hexane and the extract was filtered under an argon atmosphere. The mixture was concentrated to one-half of the initial volume and the product was precipitated at −10 °C. The yellow σ-complex $(\eta^5\text{-}C_5H_5)(CO)_3CrC\equiv CC(CF_3)_3$ (**24**) was obtained in a yield of 0.035 g (10%). IR (hexane), ν/cm^{-1}: 2141 ($C\equiv C$); 2058, 1999, 1982 (CO). ^{1}H NMR (C_6D_6), δ: 3.92 (s, C_5H_5). ^{19}F NMR (C_6D_6), δ: 8.99 (s, *t*-C_4F_9). MS, *m/z*: 444 $[M]^+$, 416 $[M - CO]^+$, 388 $[M - 2CO]^+$, 360 $[M - 3CO]^+$.

B. Reactions of anions 2 and 3. Anions **2** and **3** were prepared from solutions of **31** (0.19 g, 0.4 mmol) and **32** (0.27 g, 0.4 mmol), respectively, in THF. A solution of $FC\equiv CC(CF_3)_3$ (0.21 g, 0.8 mmol) in THF (3 mL) was added with stirring to the anions, which were preliminarily filtered and cooled to −90 °C. The reaction mixture was warmed to room temperature during 1 h. The ratio of the intensities of the bands of the carbonylmetallate anions and σ-ethynyl complexes was no longer changed when the mixture was warmed to room temperature. The solvent was removed *in vacuo*, the products were extracted with hexane, and the extract was filtered off, concentrated in vacuo, and cooled to −10 °C until yellow crystals precipitated. Yellow σ-ethynyl complexes **25** and **26** were obtained in yields of 0.15 g (38%) and 0.14 g (30%), respectively.

$(\eta^5\text{-}C_5H_5)(CO)_3MoC\equiv CC(CF_3)_3$ (25). IR, ν/cm^{-1}: in hexane, 2128 ($C\equiv C$); 2079, 1994, 1982 (CO); in CH_2Cl_2, 2140 ($C\equiv C$); 2061, 1985 (CO). M.p. = 110—112 °C (with decomp.). ^{1}H NMR (C_6D_6), δ: 4.28 (s, C_5H_5). ^{19}F NMR (C_6D_6), δ: 8.94 (s, *t*-C_4F_9). ^{13}C NMR (C_6D_6), δ: 37.5 (*C*—CF_3); 92.5 (C_5H_5); 101.57 (C(α)); 106.14 (C(β)); 123.01 (CF_3); 222.5, 237.3 (*C*O). MS, *m/z*: 490 $[M]^+$, 462 $[M - CO]^+$, 406 $[M]^+$, 387 $[M - 3CO - F]^+$, 330 $[M - 3CO - 3F]^+$. Found (%): C, 34.77; H, 1.01; F, 35.04; Mo, 19.63. For $C_{14}H_5F_9O_3Mo$, calculated (%): C, 34.46; H, 1.02; F, 35.04; Mo, 19.67.

$(\eta^5\text{-}C_5H_5)(CO)_3WC\equiv CC(CF_3)_3$ (26). IR, ν/cm^{-1}: in hexane, 2135 ($C\equiv C$); 2060, 1981, 1970 (CO); in CH_2Cl_2, 2130 ($C\equiv C$); 2055, 1970 (CO). M.p. = 124—125°C (with decomp.). ^{1}H NMR (C_6D_6), δ: 4.25 (s, C_5H_5). ^{19}F NMR (C_6D_6), δ: 8.97 (s, *t*-C_4F_9). ^{13}C NMR (C_6D_6), δ: 86.18 (*C*—CF_3); 91.48 (C_5H_5); 107.0 (C(α)); 120.85 (C(β)); 123.72 (CF_3); 212.24, 227.51 (*C*O). MS, *m/z*: 576 $[M]^+$, 548 $[M - CO]^+$, 492 $[M - 3CO]^+$. Found (%): C, 30.13; H, 1.17; F, 29.66; W, 31.61. For $C_{14}H_5F_9O_3W$, calculated (%): C, 29.2; H, 0.87; F, 29.69; W, 31.92.

Reactions of anions 1 and 3 with $C_5H_{11}{}^nC\equiv CCl$. $C_5H_{11}{}^nC\equiv CCl$ (0.078 g, 0.6 mmol) was added with stirring at room temperature to anions **1** and **3**, which were prepared from solutions of **30** (0.18 g, 0.3 mmol) and **33** (0.2 g, 0.3 mmol), respectively, in THF and filtered. The reaction mixtures were refluxed with stirring for 18 and 24 h, respectively. The solvent was removed *in vacuo*. The residues were separated on plates with SiO_2 in a 2 : 1 benzene—hexane mixture. In the case of anion **1**, only decomposition products were detected. In the case of anion **3**, two complexes were isolated, namely, dimer **32** (0.012 g, 3%) and σ-complex **27** (0.01 g, 4%).

$(\eta^5\text{-}C_5H_5)(CO)_3WC\equiv CC_5H_{11}{}^n$ (27). IR (THF), ν/cm^{-1}: 2130 ($C\equiv C$); 2040, 1956 (CO). ^{1}H NMR (C_6D_6), δ: 0.8—0.95 (t, Me); 1.22—1.32, 1.4—1.5, 1.52—1.65 (m, 3 CH_2); 2.5—2.6 (m, CH_2); 4.62 (s, C_5H_5). ^{13}C NMR (C_6D_6), δ: 14.31 (CH_3); 22.68, 22.95, 30.5, 31.51 (CH_2); 53.82 (C(α)); 91.24 (C_5H_5); 129.6 (C(β)); 212.95, 231.95 (*C*O). MS, *m/z*: 428 $[M]^+$, 400 $[M - CO]^+$, 372 $[M - 2\,CO]^+$, 344 $[M - 3\,CO]^+$, 329 $[M - 3\,CO - Me]^+$, 316 $[M - 3\,CO - Et]^+$.

Reaction of tungstate anion 3 with $C_5H_{11}{}^nC\equiv CCl$ in the presence of $PdCl_2(PPh_3)_2$. A solution of anion **3** in THF (10 mL) was prepared from **32** (0.22 g, 0.62 mmol). $C_5H_{11}{}^nC\equiv CCl$ (0.078 g, 0.62 mmol) and $PdCl_2(PPh_3)_2$ (5%, 0.022 g, 0.031 mmol) were added with stirring at room temperature. The reaction mixture was stirred for 40 min until bands of the initial anion disappeared in the IR spectra. The solvent was removed *in vacuo* and the residue was applied to plates with SiO_2 and eluted with a 1 : 1 benzene—hexane mixture. Dimer **32** and complex **27** were obtained in yields of 0.04 g (10%) and 0.12 g (46%), respectively.

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