η^3-Propargyl complexes of molybdenum, tungsten, and rhenium

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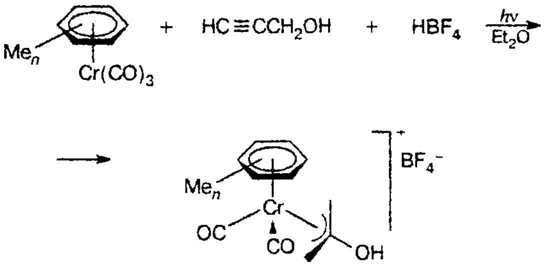
The reactions of the $Me_nC_6H_{6-n}M(CO)_3$ (M = Cr, Mo, W; n = 3, 5, 6) and $C_5R_5M(CO)_3$ (M = Mn, Re; R = H, Me) complexes with propargyl alcohol in acidic media under UV irradiation were studied. Novel $Me_nC_6H_{6-n}M(CO)_2(\eta^3\text{-}C_3H_3)BF_4$ (M = Mo, W; n = 3, 5, 6) and $C_5R_5Re(CO)_2(\eta^3\text{-}C_3H_3)CF_3SO_3$ complexes with the $3\bar{e}$-propargyl ligand were synthesized, and their properties compared with those of similar η^3-allyl derivatives. The structure and dynamic properties of the compounds obtained are discussed.

Key words: 2-hydroxyallyl complexes, η^3-propargyl complexes, synthesis, temperature dependence, IR spectra, ^{1}H and ^{13}C NMR spectra.

Generation of the carbenium center at the α-position to the double bond coordinated with the transition metal atom results in the formation of stable cationic complexes with the η^3-allyl ligand. These transformations have previously been studied[1,2] in detail for complexes of Group VI—VIII metals with olefinic ligands based on allyl alcohol or conjugated dienes in acidic media. The works on studying stabilization of carbenium ions at the α-position to the coordinated triple bond resulted in synthesis of sufficiently stable cationic complexes of Mo,[3,4] W,[3] Re,[5—7] Zr,[8] Pd,[9,10] and Pt [9,11—14] with the three-electron η^3-propargyl ligand. This work is devoted to studying the regularities of formation of mononuclear cationic complexes of Group VI and VII metals with the $3\bar{e}$-η^3-propargyl ligand and their structure.

We have previously found[1] that UV irradiation of arenechromiumtricarbonyl derivatives in the presence of propargyl alcohol and aqueous tetrafluoroboric acid or its etherate (Scheme 1) results in the formation of cationic complexes with the 2-hydroxyallyl ligand (**1a—c**).

Scheme 1

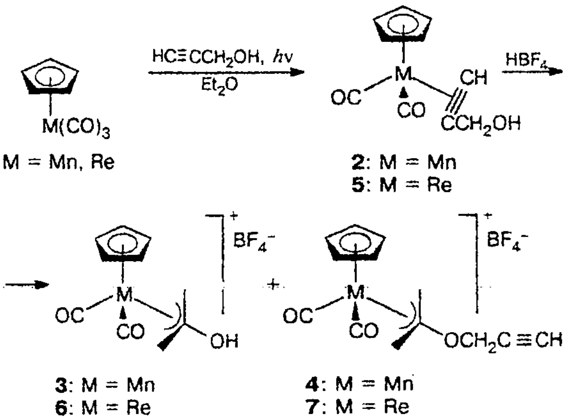


1a—c

n = 0 (**a**), 3 (1,3,5-Me$_3$) (**b**), 6 (**c**)

Unlike arenechromiumtricarbonyls, a similar one-stage reaction of $CpM(CO)_3$ (M = Mn, Re) resulted in the formation of cationic complexes in low yields and was accompanied by a considerable decomposition of the reagents. For example, according to the data of ^{1}H NMR spectroscopy, UV irradiation of an ethereal solution of $CpMn(CO)_3$ and propargyl alcohol followed by treatment of the π-complex with propargyl alcohol (**2**) formed *in situ* with 48% aqueous HBF_4 (Scheme 2) affords a mixture of two π-allyl complexes **3** and **4** approximately in a ratio of 2.5 : 1.0, which, however, does not necessarily reflect the initial ratio of reaction products, because their multiple precipitation with ether from nitromethane was required to obtained a satisfactory ^{1}H NMR spectrum.

Scheme 2



In the case of $CpRe(CO)_3$, this reaction in ether is impeded by the formation of a sufficiently stable

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dicarbonyl complex with ether (with the characteristic bands in the IR spectrum: νCO(Et$_2$O) 1846, 1917 cm^{-1}), which is present in a considerable excess as compared to the corresponding complex 5 with propargyl alcohol (with the characteristic bands in the IR spectrum: νCO(C$_6$H$_6$) 1880, 1944 cm^{-1}). Therefore, benzene was used as a solvent instead of ether, which afforded a mixture of cationic complexes **6** and **7** with a ratio of 1 : 1, according to the data of ^{1}H NMR spectroscopy.

Complexes **3** and **4** are sand-colored solid substances, and complexes **6** and **7** are light-sandy solids, sufficiently stable in air and soluble only in polar solvents.

The IR spectra of compounds **3**, **4**, **6**, and **7** exhibit two absorption bands in the region of 2000—2050 cm^{-1}. In the ^{1}H NMR spectra of complexes **3** and **4**, the signals of protons of the 2-hydroxyallyl ligand are close to those observed for compound **1**. A noticeable value of the geminal spin-spin coupling constant ($J_{H_{syn}-H_{anti}}$ = 3—4 Hz) is the characteristic feature of complexes **6** and **7**, which was also observed for rhenium allyl complexes with the unsubstituted allyl ligand.[2]

The picture observed in the ^{1}H NMR spectra of complexes **4** and **7** is close, as a whole, to that in the spectra of compounds **3** and **6**, except for the signals characteristic of the noncoordinated propargyl fragment.

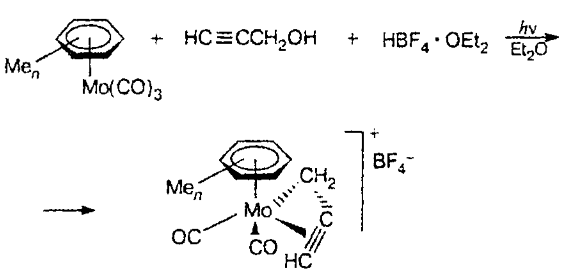
The formation of a mixture of products **3**, **4** and **6**, **7** can be explained by the competitive addition of water or propargyl alcohol to an intermediate reactive species, which was not detected by IR spectra. This is confirmed when the reaction is performed in two stages: with the formation of sufficiently stable complex **2** followed by its protonation, which afford complex **3** as a single product.

It is most likely, in all cases, that π-complexes with propargyl alcohol are formed at the first stage after elimination of the CO ligand under UV irradiation (which is confirmed by the IR spectra in the carbonyl stretching region), and in the case of CpMn(CO)$_3$, this complex was isolated and characterized.[15] At the next stage, this complex is protonated at the oxygen atom of the OH group followed by dehydration and formation of a propargyl complex, the attack of which by water or alcohol should result in products of the type of **1**, **3**, **6** or **4**, **7**, respectively.

In the examples considered, we failed to detect intermediate cationic species, in particular, the coordinated propargyl cation, because of their high reactivity. Therefore, we attempted to increase their stability, using similar derivatives of heavier metals from the same subgroup and ligands with stronger donating properties. Molybdenum and tungsten arenemetaltricarbonyl complexes were chosen as starting compounds, because it could be expected that stabilization of cationic species on the atoms of these metals is higher than on the chromium atom.

The use of an immersion lamp allowed these compounds to be efficiently involved in reactions of CO substitution. It has been found that UV irradiation of arenemolybdenumtricarbonyls with propargyl alcohol and tetrafluoroboric acid etherate in ether results in the formation of single products, stable cationic complexes containing no 2-hydroxyallyl ligand (Scheme 3). The compounds obtained were isolated and characterized by the data of elemental analysis and IR and ^{1}H and ^{13}C NMR spectra, and the pentamethylbenzene derivative was characterized by the XRD method.[4] Based on these data, we assigned to them the structure of complexes **8** containing the HC≡C—CH$_2$ fragment as the three-electron ligand.

Scheme 3

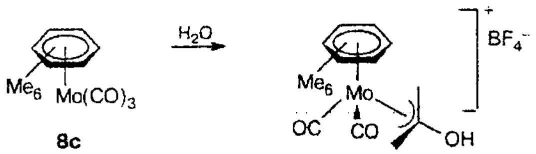


8a—c

n = 3 (1,3,5-Me$_3$) (**a**), 5 (**b**), 6 (**c**)

Complexes **8a—c** are red-brown substances soluble in polar solvents, sufficiently stable with respect to water and air oxygen. They can be stored without decomposition in a refrigerator for several months and can be precipitated from non-anhydrous solvents. At the same time, as established by ^{1}H NMR spectroscopy, in nitromethane containing 3—5% water, complex **8c** reacts with water very slowly to form 2-hydroxyallyl derivative **9** (Scheme 4). After 5 days at room temperature, signals of complex **9** with a sufficient intensity (up to 3 mol.% relative to that of **8c**) appear in the spectrum.

Scheme 4

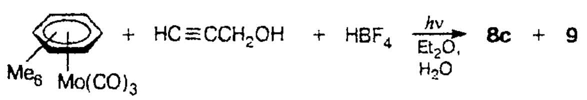


8c

9

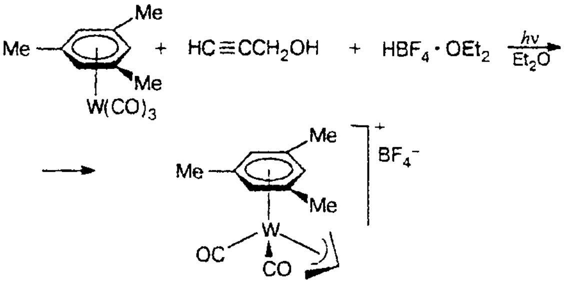
If the reaction of preparation of the propargyl complexes is carried out in the presence of 48% aqueous HBF$_4$, a mixture of two products, **8c** and **9**, is formed in a ratio of 73 : 27 (Scheme 5) (^{1}H NMR spectroscopy data). When insufficiently anhydrous ether is used, complex **9** can be formed as an admixture (to 3—4%) even in the reaction with tetrafluoroboric acid etherate.

Scheme 5



The use of mesitylenetungstentricarbonyl as the starting compound in the reaction with propargyl alcohol and tetrafluoroboric acid resulted unexpectedly in a different result. Complex **10** that formed is of allyl rather than of propargyl type (Scheme 6).

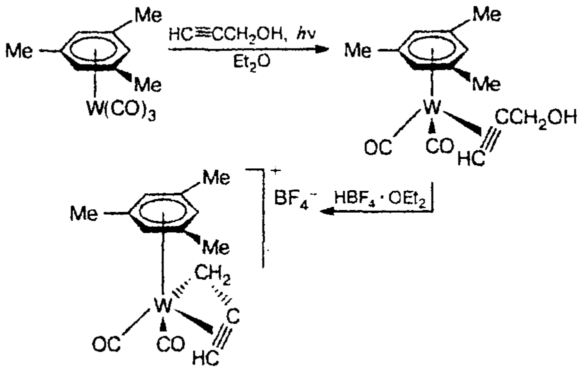
Scheme 6



10

Complex **10** is completely identical to the product obtained previously in a similar reaction[2] with allyl alcohol instead of propargyl alcohol. In this case, the tungsten propargyl complex (**11**) was not detected even as an admixture. Complex **11** was isolated in a low yield in the staged reaction (Scheme 7), and the allyl complex is not formed.

Scheme 7



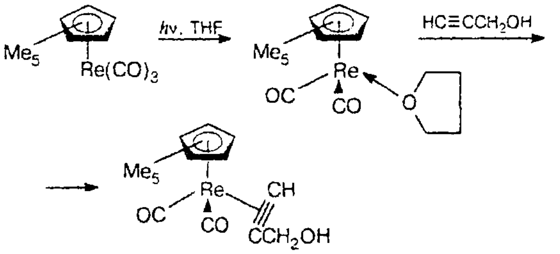
11

The structure of compound **11** was confirmed by the IR and ^{1}H NMR spectra, whose parameters were very close to those observed for complex **1a**. It is most likely that the coordinated triple bond is hydrogenated under conditions of the one-stage reaction. This can be explained by the attack of a proton at the coordinated triple bond with intermediate generation of the vinyl cation, which then adds the hydride ion to form coordinated allyl alcohol that is easily transformed into stable allyl complex **10**. Tungsten hydride complexes that are formed in parallel reactions and result in a considerable amount of decomposition products can serve as the source of the hydride ion. This possibility of transformation of the triple bond into the double bond in the coordination sphere of the transition metal has been shown by us for chelate chromium complexes.[16] When the reaction is performed in stages, *i.e.*, in the absence of an acid under UV irradiation, the presence of virtual donors of the hydride ion is ruled out, which results in only a single possibility of stabilization — through the formation of propargyl complex **11**. The absence of the hydroxyallyl complex in the reaction products can be related to a lower reactivity of the tungsten vinyl complex, as compared to similar chromium and molybdenum compounds, and to the predominant addition of the hydride ion, which is a stronger nucleophile than water.

The material considered agrees with the known statement on increase in the stability of cationic complexes with increase in the basicity of the metal, which increases both on going from lighter to heavier metals in the same subgroup with the same ligand environment and for the same metal at a higher donating ability of the ligands. Therefore, along with increasing the basicity of the metal, we also attempted to vary the donating ability of the ligands. An increase in the basicity of the metal led to a qualitative change in the result in the series of arenemetaltricarbonyl derivatives of Group VI metals (Cr < Mo < W). However, in the series of cyclopentadienyltricarbonyl derivatives of Group VII metals, this transition is insufficient for stabilization of the propargyl ligand. In the case of rhenium, stabilization is possible only when the pentamethyl-substituted cyclopentadienyl ligand is used. However, only the starting complex decomposes under conditions of the direct "one-stage" reaction. Since the synthesis and isolation of the cyclopentadienyl- and pentamethylcyclopentadienylrheniumdicarbonyl complexes with terminal acetylenes through tetrahydrofuran derivatives has previously been reported,[17] we attempted to prepare a similar derivative in the reaction with propargyl alcohol. As a result, we succeeded in isolating complex **12** in the individual state (Scheme 8), although in a low yield.[5]

The structure of compound **12** was confirmed by the IR and ^{1}H NMR spectra, whose parameters are close to those described previously.[17] A temperature dependence appears in the ^{1}H NMR spectrum of complex **12**. For example, a well resolved spectrum containing a triplet at 5.28 ppm and a doublet at 4.71 ppm (J = 2.1 Hz) is observed at 25 °C in deuteronitromethane, which indicates the coordination of propargyl alcohol at the triple bond. The doublet is broadened on cooling, and at a temperature lower than −15 °C, the decoalescence of

Scheme 8

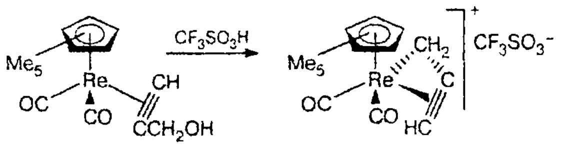


12

the signal with its transformation into the AB system with J_{AB} = 16.0 Hz is observed. This indicates restricted rotation of the acetylene ligand about the metal—ligand bond. The value of the free energy of rotation $\Delta G^{\#}$ = 12.3 kcal mol^{-1} was determined from these experiments.*

The addition of trifluoromethanesulfonic acid results in a substantial change in the spectral region of the C_3H_3 fragment. A similar picture was observed for η^3-propargyl complexes of molybdenum **8a—c** and tungsten **11**. This indicates the formation of cationic propargyl complex **13** (Scheme 9).

Scheme 9

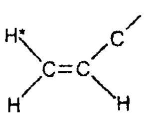


12 **13**

Thus, the compounds synthesized are representatives of a new class of complexes, mononuclear complexes with three-electron η^3-propargyl ligands. We attempted to characterize these complexes as entirely as possible and study their structure by different physical and physicochemical methods. They are generally close to the well studied η^3-allyl complexes; hence, we compared first of all these two types of compounds.

The IR spectra of complexes **8**, **11**, and **13** contain two absorption bands in the carbonyl stretching region. As compared with those in the spectra of the neutral complexes close in structure, these bands are shifted toward higher frequencies. For example, for rhenium complex **13**, $\Delta\nu$ = 90—100 cm^{-1}. The presence of only one pair of bands indicates the absence of *endo/exo*-isomerism, as mentioned[2] for the Mo, W, and Re allyl complexes. This can also indicate a substantial difference in the structure of the allyl and propargyl complexes. As follows from the IR spectra, in electron-donating properties the propargyl ligand is close to the *exo*-allyl ligand.

^{1}H NMR spectra are more characteristic for propagyl complexes. Signals of protons of CH_2 groups are the AB system (δ 4.02—4.07 and 3.27—3.96, J_{AB} = 10.7—10.8 Hz, $^4J_{HH}$ = 2.2—2.5 Hz), and those of protons of ≡CH are a triplet (δ 5.5—5.7) or, more exactly, a doublet of doublets with close spin-spin coupling constants ($^4J_1 \approx {}^4J_2$ = 2.2—2.5 Hz). It is noteworthy that for complexes **8a** and **9**, the chemical shifts are very close, whereas on going from **8a** to **8b** and further to **8c**, some increase occurs in shielding of all protons of the C_3H_3 ligand, especially one (upfield) component of the CH_2 group (the difference in chemical shifts of the AB component increases: for complexes **8a** and **9**, 0.11—0.16 ppm; for **8b**, 0.45 ppm; and for **8c**, 0.71 ppm). This can indicate the arrangement of one of the protons of the CH_2 group near methyl substituents of the ring. We have previously observed a similar effect for chromium areneolefinic chelates[18] when a noticeable increase in shielding of one of the protons of the π-bound vinyl group was also observed upon introduction of methyl substituents in the arene ligand in the immediate vicinity of the H* atom with parallel arrangement of the olefinic and arene ligands in the molecule.



In the ^{1}H NMR spectrum of rhenium complex **13**, the chemical shifts and especially the coupling constants for the C_3H_3 ligand are sufficiently close to the parameters in the spectra of similar Mo and W complexes, although the signals, as a whole, are somewhat shifted downfield.

In the ^{13}C NMR spectra of complexes **8a,c**, the propargyl ligand appears as three signals. A doublet at 70—75 ppm ($^1J_{CH} \approx$ 243—246 Hz) corresponds to the carbon atom of methine. The central carbon atom also appears as a doublet in the region of 67—70 ppm ($^2J_{CH} \approx$ 26—29 Hz), whereas the signal of the carbon atom of the methylene group lies in the region of 33—40 ppm ($^1J_{CH}$ = 167 Hz). The signals of arene protons and Me groups in the ^{1}H NMR spectra and the signals of carbon atoms in the ^{13}C NMR spectra are arranged ~~in the regions that are characteristic of them, but are~~ somewhat shifted downfield, which agrees with the presence of the positive charge. According to this, an upfield shift of the signals of the carbon atoms of the carbonyl groups is observed in the ^{13}C NMR spectra. The carbonyl groups are nonequivalent, which indicates the absence of symmetry in molecules **8a,c**.

The data of NMR spectroscopy suggest that the CH_2 groups are sufficiently strongly bonded with the metal atom. This is favored by the upfield shift of the signals of protons of this group in the ^{1}H NMR spectra and of car-

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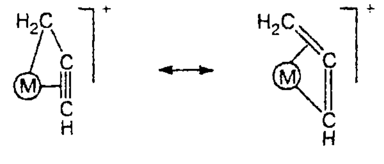
* The synthesis of complex **12** by a similar method has recently been reported.[7] It has been characterized by the ^{1}H NMR and IR spectra, whose parameters virtually coincide with those obtained by us, and also with ^{13}C NMR spectra and XRD data. The temperature dependence was also explained by retarded rotation (J_{AB} = 16 Hz, $\Delta G^{\#}$ = 12.2 kcal mol^{-1}).

bon atoms in the ^{13}C NMR spectra. For example, for the rhenium complexes, on going from **12** to **13**, the signals of protons of the CH_2 groups are shifted upfield by 0.47 ppm (δ ~4.24), even despite the presence of the positive charge on cation **13**. In the case of molybdenum **8a—c** and tungsten complexes **11**, these signals are present in a stronger field (δ ~3.6—4.0). A similar situation is observed for the ^{13}C NMR spectra: the upfield shift is 20—30 ppm as compared, for example, with the $\delta(CH_2)$ value for chelate chromium areneacetylene complexes.[5]

A similar tendency is observed in the case of the cationic manganese allyl complex $CpMn(CO)_2(\eta^3-C_3H_5)BF_4$,[2] for which the signals corresponding to the methylene group are also shifted upfield as compared to similar signals of its precursor $CpMn(CO)_2(\eta^2-CH_2{=}CHCH_2OH)$. At the same time, protons of the CH_2 groups in the propargyl complexes of Mo (**8a—c**), W (**11**), and Re (**13**) are less shielded than protons of CH_2 of the unsubstituted allyl ligand (δ 2.76) in the molybdenum allyl complex $1,3,5-Me_3C_6H_3Mo(CO)_2(\eta^3-C_3H_5)BF_4$. However, the signals of carbon atoms of the CH_2 group of compounds **8a,c** are more shielded than the carbon atoms of the CH_2 group of the unsubstituted allyl ligand.[2] It is noteworthy that in the case of primary metallocenylcarbenium ions for the whole triad (Fe, Ru, Os), the signals of the CH_2 groups in the NMR spectra (both ^1H and ^{13}C) are shifted downfield as compared to those of the corresponding carbinol,[19] and their shifts for protons are 1.18 (Fe), 0.66 (Ru), and 0.33 ppm (Os), whereas for carbon atoms, they are 49.2 (Fe), 33.2 (Ru), and 13.9 ppm (Os).

In addition, the shape of the signals of the CH_2 group (AB system) and coupling constants (J_{AB}) also indicate indirectly the presence of a sufficiently strong bond of this group with the metal. The coupling constant (J_{AB} = 11 Hz) is much closer to that for the aliphatic CH_2 group (for **12**, J_{AB} = 16 Hz), whereas the geminal constant for the CH_2 groups of the carboranyl analog $CpRe(CO)_3$ [20] and allyl complexes is close to zero and ranges within 0—3 Hz. At the same time, the $^1J_{^{13}C-H}$ coupling constant for complexes **8a,c** is 167 Hz, which is close to the corresponding values of $^1J_{^{13}C-H}$ for metallocenylcarbenium ions and allyl complexes. The signals of two other carbon atoms of the propargyl fragment of complexes **8a,c** are in the region characteristic of coordinated acetylenes, which indicates, along with the large coupling constant ($^1J_{CH}$ = 243—246 Hz),[*] a considerably acetylenic character of this fragment. However, the structure of these complexes, as a whole, can be more correctly presented as two mesomeric structures **14** and **15** with a predominant contribution of form **14**. The contribution of form **15** with the allenyl ligand takes place, most likely, with a much lower weight, because in this case, the geminal constant of protons of the CH_2 group should be close to zero (0—3 Hz), and the $^1J_{CH}$ value for the sp^2-hybridized carbon atom of the CH group should be substantially lower (within 160—170 Hz).


14 **15**

And finally, the most important information on the structure of the propargyl complexes was obtained from the XRD data[*] of molybdenum pentamethylbenzene complex **8b**.[4] In molecule **8b**, as in the molybdenum π-allyl complexes, all three carbon atoms are localized at bonding distances from the Mo atom (2.282—2.340 Å). However, unlike the allyl complexes, in which the central carbon atom is noticeably (by ~0.7 Å) shifted from the plane that passes through the metal atom and terminal carbon atoms of the allyl ligand, the Mo atom and three C atoms of the propargyl ligand in complex **8b** are localized almost in the same plane (their deviations from this plane do not exceed 0.014 Å).

All data of ^1H and ^{13}C NMR spectroscopy obtained for propargyl complexes of molybdenum and tungsten of the type $(C_6Me_nH_{6-n})M(CO)_2(CH_2CCH)BF_4$ and rhenium $C_5Me_5Re(CO)_2(CH_2CCH)BF_4$ indicate that the symmetry plane is absent in the molecule, which distinguishes them from similar complexes with the unsubstituted allyl ligand. This is indicated, for example, by two signals corresponding to two nonequivalent CO groups in the ^{13}C NMR spectra of the propargyl complexes. For the molybdenum, rhenium, and manganese allyl complexes, we observed the dynamic process related to the "rotation" of the η^3-allyl ligand (*exo*/*endo*-isomerism) with a coalescence temperature from 0 to ~20 °C. An attempt to heat solutions of the $(1,3,5-Me_3C_6H_3)Mo(CO)_2(CH_2CCH)BF_4$ (**8a**) or $(C_6Me_6)Mo(CO)_2(CH_2CCH)BF_4$ (**8c**) complexes did not result in a temperature dependence in the NMR spectra at temperatures below 100 °C. Based on these data, a conclusion about stoichiometric rigidity of the propargyl complexes could be drawn. At the same time, a temperature dependence could be absent because of the absence of appropriate enantiotopic indicator groups.

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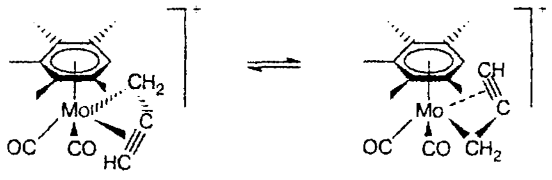
[*] The ^1H and ^{13}C NMR spectroscopy data for the analog of complex **13** with the BF_4 anion have recently been published.[7] Their parameters are close to those obtained by us for the ^1H NMR spectrum of compound **13** and for the ^{13}C NMR spectra of complexes **8a,c**. For example, $^1J_{\equiv CH}$ = 232 Hz, $^1J_{CH_2}$ = 170 Hz. Another complex with the unsubstituted C_3H_3 ligand was described[12,13] for platinum $[(PPh_3)_2Pt(C_3H_3)]BF_4$; $^1J_{\equiv CH}$ = 246 Hz, $^1J_{CH_2}$ = 171 Hz.

[*] The X-ray structural study was carried out by A. I. Yanovsky and Yu. T. Struchkov (deceased) (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences).

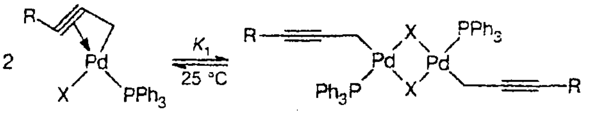
As is known, the lower the difference between chemical shifts of enantiotopic groups, the lower the coalescence temperature. Therefore, for a signal with a high difference in chemical shifts of these groups, the coalescence point can not be achieved, for example, because of decomposition of the complex. In fact, in the ^{1}H NMR spectrum of the $(C_6Me_5H)Mo(CO)_2(CH_2CCH)BF_4$ complex (**8b**) at room temperature, all Me groups are nonequivalent, and their chemical shifts differ insignificantly; however, an increase in temperature results in broadening and coalescence of signals, first of *m*- and then of *o*-methyl groups. It has been found in studying the temperature dependence of the ^{1}H NMR spectrum of complex **8b** in CD_3NO_2 that at −20 °C it contains five narrow signals with δ 2.193 (Me_m), 2.204 (Me_o), 2.246 (Me_p), 2.257 (Me_m), and 2.410 (Me_o) in the region characteristic of protons of Me groups. When the temperature increases to 20 °C, all signals remain narrow, although a slight temperature drift is observed, which results, in particular, in overlapping of the signals of the *p*- and closest to it *m*-methyl groups. At temperatures higher than 20 °C, the signals of the *m*- and *o*-methyl groups are noticeably broadened, and the width of the signal of the *p*-methyl group remains almost unchanged. At 50 °C, coalescence of *m*-methyl groups is observed (δ 2.24), and at 65 °C, *o*-methyl groups undergo coalescence (δ 2.34). Further increase in the temperature results in a continuous narrowing of signals of *m*- and *o*-methyl groups, due to which the spectrum contains three signals of methyl groups δ 2.27 (Me_m, $\Delta\nu_{1/2}$ = 1.2 Hz), 2.32 (Me_p, $\Delta\nu_{1/2}$ = 1.1 Hz), and 2.35 (Me_o, $\Delta\nu_{1/2}$ = 2.4 Hz) in a ratio of 2 : 1 : 2. The described temperature changes in the spectrum can be explained by pseudo-rotation of the propargyl ligand.



8b′ **8b″**

Based on the data obtained, we calculated the activation parameters of this process: $\Delta H^{\neq}$ = 10.1±0.5 kcal mol^{-1}, $\Delta S^{\neq}$ = −21.2±1.6 eu, $\Delta G^{\neq}_{298}$ = 16.4 kcal mol^{-1}, and E_a = −10.8±0.5 kcal mol^{-1}. The mechanism of mutual transformation of the propargyl ligand **8b′** $\rightleftharpoons$ **8b″** was not studied specially, but it can be assumed that at the first stage the triple bond is eliminated from the metal atom in cation **8b′** (including under the action of the solvent) followed by turning about the σ-Mo—CH_2 bond in the η^1-propargyl ligand and further coordination of the triple bond to the opposite side (**8b″**). The fundamental possibility of η^3—η^1-transformation of the propargyl ligand has been shown in the already mentioned reactions of the platinum[11] and palladium[21] complexes with nucleophiles and by the existence of equilibrium for the neutral palladium propargyl complexes[21] (Scheme 10).

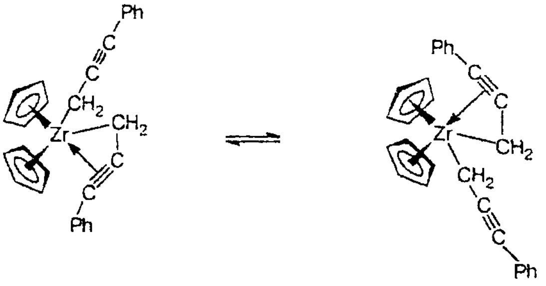
Scheme 10



R = Bu^t, SiMe$_3$, SiMe$_2$Bu^t, SiPr^i; X = Cl, Br, I

The dynamic behavior of the propargyl ligand is also illustrated by the exchange related to a change in the type of coordination $\eta^3 \rightarrow \eta^1$ for one ligand accompanied by synchronous $\eta^1 \rightarrow \eta^3$ transformation of the second ligand in the zirconium complex containing two propargyl ligands with different types of coordination[22] (Scheme 11).

Scheme 11



This complex exhibits a temperature dependence in the ^{1}H NMR spectrum. At 240 K, the signal of the CH_2 group is broadened (δ 2.80), and at 180 K, it is split into two broad signals with equal intensities (δ 3.3 and 1.9). It is noteworthy that a similar process was also observed for complexes simultaneously containing σ- and π-allyl ligands.[23] At the same time, complexes of the $(\eta^3\text{-All})Pd(Hal)(PR_3)$ type do not tend to dimerization accompanied by $\eta^3 \rightarrow \eta^1$ transformation of the allyl ligand, which is observed in the case of propargyl analogs.[21] This difference in behavior is evidently related to a higher strength of the bond of the η^3-allyl ligand as compared to that of the η^3-propargyl ligand. The type of dynamic behavior found by us for the η^3-propargyl complexes has not been observed for the η^3-allyl complexes, although it could be detected, for example, for derivatives with a substituent in position 1 of the allyl ligand or in the *endo*-form.

Thus, Mo, W, and Re complexes of the new type with the $3\bar{e}$-η^3-propargyl ligand were obtained, and their structure and dynamic behavior were studied.

Experimental

All procedures on synthesis of the compounds described were carried out in an argon atmosphere using anhydrous solvents. A DRL-125 immersion lamp was used for UV irradiation. IR spectra were recorded in solutions on a Specord IR-75 spectrophotometer, ^{1}H NMR spectra were recorded on a Bruker WP-200 SY spectrometer (200.13 MHz), and ^{13}C and ^{31}P NMR spectra were recorded on Bruker WP-60 (15.08 MHz) and Bruker WP-200 SY (50.31 MHz) spectrometers, respectively.

(η^6-Arene)dicarbonyl(η^3-propynyl)molybdenum tetrafluoroborates (general procedure). A solution of arenemolybdenumtricarbonyl (1.5 mmol), propargyl alcohol (0.24 mL, 0.22 g, 4 mmol), and $HBF_4 \cdot OEt_2$ (0.23 mL, 0.17 g, 2 mmol) in ether (170 mL) was UV-irradiated (with IR monitoring of the reaction in the region of 2000 cm^{-1}) for 20—30 min until the initial substance disappeared. The precipitate that formed was filtered off and dried in a strong argon flow. Analytically pure samples were isolated by multiple precipitation with ether from $MeNO_2$. Complexes **8a** (yield 95%), **8b** (yield 80%), and **8c** (yield 86%) were obtained. IR ($MeNO_2$), ν/cm^{-1}: complex **8a**, 1927, 1977; complex **8b**, 1918, 1990; complex **8c**, 1917, 1989. ^{1}H NMR (CD_3NO_2), δ: complex **8a**, 2.25 (s, 9 H, CH_3—Ar); 3.90, 4.06 (AB system, 2 H, $-CH_2-C\equiv$, J_1 = 2.3 Hz, J_2 = 2.5 Hz, J_{aver} = 2.4 Hz. J_{AB} = 10.7 Hz); 5.72 (t, 1 H, $\equiv C-H$, J = 2.4 Hz); 6.65 (s, 3 H, ArH); complex **8b**, 2.21, 2.24, 2.26, 2.26, 2.40 (all s, 15 H, CH_3—Ar); 3.39, 3.99 (AB system, 2 H, $-CH_2-C\equiv$, $J_1 = J_2$ = 2.3 Hz, J_{AB} = 11.0 Hz); 5.54 (t, 1 H, $\equiv C-H$, J = 2.3 Hz); 6.86 (s, 1 H, ArH) (283 K); complex **8c**, 2.41 (s, 18 H, CH_3—Ar); 3.90, 4.06 (AB system, 2 H, $-CH_2-C\equiv$, J_1 = 2.2 Hz, J_2 = 2.5 Hz, J_{aver} = 2.3 Hz. J_{AB} = 10.8 Hz); 5.54 (t, 1 H, $\equiv C-H$, J = 2.3 Hz). ^{13}C NMR ($MeNO_2$), δ: complex **8a**, 19.9 (q, CH_3—Ar, J_{C-H} = 130.9 Hz); 33.4 (t, $-CH_2-$, J_{C-H} = 167 Hz); 66.6 (d, C≡, J_{C-H} = 26 Hz); 70.4 (d, $\equiv C-H$, J_{C-H} = 246 Hz); 110.8 (d, C_{Ar}—H, J_{C-H} = 177.2 Hz); 126.9 (s, $C_{Ar}-CH_3$); 228.9, 235.4 (both s, CO); complex **8c**, 17.5 (q, CH_3—Ar, J_{C-H} = 130.1 Hz); 39.6 (t, $-CH_2-$, J_{C-H} = 166.6 Hz); 69.9 (d, C≡, J_{C-H} = 28.6 Hz); 74.5 (d, $\equiv C-H$, J_{C-H} = 242.8 Hz); 123.7 (s, $C_{Ar}-CH_3$); 230.9, 237.32 (both s, CO).

(η^3-2-Hydroxyallyl)dicarbonyl(η^6-hexamethylbenzene)molybdenum tetrafluoroborate (9). A mixture of compounds **8c** and **9** (0.08 g) was obtained similarly from tricarbonyl(η^6-hexamethylbenzene)molybdenum (0.15 g, 0.44 mmol), propargyl alcohol (0.21 mL, 0.2 g, 3.5 mmol), and 48% aqueous HBF_4 (0.13 g, 1.76 mmol, d = 1.3 g cm^{-3}) in ether (170 mL), the ratio **8c** : **9** = 73 : 27 (according to the ^{1}H NMR spectra). ^{1}H NMR (CD_3NO_2), δ: 1.37 (dd, 2 H, H_{anti}, J_1 = 2.2 Hz, J_2 = 1.2 Hz); 2.39 (s, 18 H, CH_3—Ar); 3.72 (dd, 2 H, H_{syn}, J_1 = 2.2 Hz, J_2 = 1.1 Hz); 5.42 (m, 1 H, OH).

(η^3-Allyl)dicarbonyl(η^6-mesitylene)tungsten tetrafluoroborate (10). Complex **10** (0.03 g, 32.8%) was obtained similarly from tricarbonyl(η^6-mesitylene)tungsten (0.19 g, 0.5 mmol), propargyl alcohol (0.24 mL, 0.22 g, 4 mmol), and $HBF_4 \cdot OEt_2$ (0.28 mL, 0.17 g, 2 mmol) in ether (170 mL) under irradiation for 3 h. IR ($MeNO_2$), ν/cm^{-1}: 1951, 2005 (CO). Ref. 2: IR ($MeNO_2$), ν/cm^{-1}: 1956, 2009 (CO).

Dicarbonyl(η^6-mesitylene)(η^3-propynyl)tungsten tetrafluoroborate (11). A solution of tricarbonyl(η^6-mesitylene)tungsten (0.19 g, 0.5 mmol) and propargyl alcohol (0.24 mL, 0.22 g, 4 mmol) was UV-irradiated for 40 min (IR monitoring of the reaction in the region of 2000 cm^{-1}) until the starting complex disappeared. $HBF_4 \cdot OEt_2$ (0.23 mL, 0.17 g, 2 mmol) was added to the reaction mixture. The precipitate that formed was filtered off and dried in a strong argon flow. Complex **11** (0.05 g, 20%) was obtained. The analytically pure sample was isolated by multiple precipitation from $MeNO_2$ with ether. ^{1}H NMR (CD_3NO_2), δ: 2.30 (s, 9 H, CH_3—Ar); 3.96, 4.07 (AB system, 2 H, $-CH_2-$, J_{aver} = 2.3 Hz, J_{AB} = 10.6 Hz); 5.71 (t, 1 H, ≡CH, J = 2.4 Hz); 6.66 (s, 3 H, ArH).

Dicarbonyl(η^3-2-hydroxyallyl)(η^5-cyclopentadienyl)manganese tetrafluoroborate (3) and dicarbonyl[1-3-η-2-(prop-2-ynyloxy)propenyl](η^5-cyclopentadienyl)manganese tetrafluoroborate (4). *A* (without isolation of the complex with propargyl alcohol). Propargyl alcohol (0.22 g, 2 mmol) was added to a solution of $CpMn(CO)_3$ (0.21 g, 1 mmol) in ether (170 mL), and the mixture was UV-irradiated (IR monitoring of the reaction in the region of 2000 cm^{-1}) for 10 min until the initial complex disappeared. 48% aqueous HBF_4 (0.28 mL, 0.17 g, 2 mmol, d = 1.3 g cm^{-3}) was added to the reaction mixture. The ether was evaporated on a rotary evaporator to 1/8 of the initial volume, and the oily precipitate that formed was decanted and twice precipitated from $MeNO_2$ with ether. A mixture of complexes **3** and **4** (0.21 g) was obtained. IR ($MeNO_2$), ν/cm^{-1}: 2013, 2054 (CO). ^{1}H NMR ($(CD_3)_2CO$), δ: complex **3**, 3.55 (s, 2 H, H_{anti}); 4.34 (s, 2 H, H_{syn}); 5.75 (s, 5 H, C_5H_5); 9.23 (s, 1 H, OH); complex **4**, 3.26 (br.s, 1 H, $\equiv C-H$); 3.63 (d, 2 H, H_{anti}, J = 1.7 Hz); 4.56, 4.59 (both d, 4 H, 2 H_{syn}, CH_2, J = 1.8 Hz, J = 1.6 Hz); 5.81 (s, 5 H, C_5H_5).

B (with isolation of the intermediate cyclopentadienyldicarbonylmanganese complex **2** with propargyl alcohol). A solution of $CpMn(CO)_3$ (1 g, 4.7 mmol) in THF (70 mL) was UV-irradiated (IR monitoring of the reaction in the region of 2000 cm^{-1}) for 70 min. Propargyl alcohol (0.3 mL, 0.23 g, 5 mmol) was added to the reaction mixture, which was stirred for 3 h on a magnetic stirrer until the ratio (according to the IR spectrum) $CpMn(CO)_2(THF)$: **2** ≈ 1 : 2 was achieved. The reaction mixture was concentrated in the absence of air and chromatographed on a column with silica gel 40/100 μm. The fractions eluted with a petroleum ether—Et_2O (2 : 1) mixture were pooled, concentrated without air, and crystallized from an ether—heptane mixture in a Dewar flask with solid CO_2. The fraction was repeatedly chromatographed on a column with silica gel 40/100 μm with cooling with a solid CO_2—acetone mixture. A fraction eluted with a petroleum ether—Et_2O (2 : 1) mixture was gathered. The solvent was evaporated, and the residue was crystallized from an ether—heptane mixture in a Dewar flask with solid CO_2. Dicarbonyl(η^2-prop-2-ynol)(η^5-cyclopentadienyl)manganese (**2**) was obtained (0.2 g, 17.6%). IR (THF), ν/cm^{-1}: 1931, 1869.

48% aqueous HBF_4 (0.1 mL, 0.75 mmol, d = 1.3 g cm^{-3}) was added to a solution of complex **2** (0.11 g) in $MeNO_2$ (2 mL), and the mixture was stirred for 10 min on a magnetic stirrer. Ether (50 mL) was added to the mixture, and the precipitate that formed was filtered off and precipitated with ether from $MeNO_2$. Complex **3** (0.09 g, 56%) was obtained. IR ($MeNO_2$), ν/cm^{-1}: 2015, 2053 (CO). ^{1}H NMR ($(CD_3)_2CO$), δ: 3.57 (s, 2 H, H_{anti}); 4.36 (s, 2 H, H_{syn}); 5.77 (s, 5 H, C_5H_5); 9.44 (s, 1 H, OH).

Dicarbonyl(η^3-2-hydroxyallyl)(η^5-cyclopentadienyl)rhenium tetrafluoroborate (6) and dicarbonyl[1-3-η-2-(prop-2-ynyloxy)propenyl](η^5-cyclopentadienyl)rhenium tetrafluoroborate (7). *A* (without isolation of the intermediate complex with propargyl alcohol). A solution of $CpRe(CO)_3$ (0.17 g, 0.5 mmol) and propargyl alcohol (0.24 mL, 0.22 g, 4 mmol) in benzene (170 mL) was UV-irradiated (IR monitoring of the reaction in the region of 2000 cm^{-1}) for 1 h until the ratio initial substance : reaction product = 1 : 2 was achieved. $HBF_4 \cdot OEt_2$ (0.28 mL, 0.17 g, 2 mmol) was added to the reaction mixture. Stirring was continued for 1 h, and the precipitate that formed was decanted, dissolved in a minimum amount of $MeNO_2$, and precipitated with ether. The precipitate that formed was filtered off and dried in a strong argon flow. A mixture of complexes **6** and 7 (0.21 g) was obtained in a ratio of 1 : 1 (according to the data of ^{1}H NMR spectroscopy). IR ($MeNO_2$), ν/cm^{-1}: 1993, 2053 (CO). ^{1}H NMR (CD_3NO_2), δ: complex **6**, 3.59 (dd, 2 H, H_{anti}, J_1 = 1.4 Hz, J_2 = 4.1 Hz); 4.27 (dd, 2 H, H_{syn}, J_1 = 1.4 Hz, J_2 = 4.1 Hz); 6.11 (s, 5 H, C_5H_5); complex 7, 2.95 (t, 1 H, ≡CH, J = 2.4 Hz); 3.52 (dd, 2 H, H_{anti}, J_1 = 1 Hz, J_2 = 3.2 Hz); 4.14 (dd, 2 H, H_{syn}, J_1 = 1.1 Hz, J_2 = 3.2 Hz); 4.63 (d, 2 H, CH_2, J = 2.5 Hz); 6.06 (s, 5 H, C_5H_5).

Dicarbonyl(η^3-*propynyl*)(η^5-pentamethylcyclopentadienyl)-rhenium triflate (13) (with isolation of the intermediate complex with propargyl alcohol). A solution of tricarbonyl(η^5-pentamethylcyclopentadienyl)rhenium (0.8 g, 2 mmol) in THF was UV-irradiated (IR monitoring of the reaction in the region of 2000 cm^{-1}) for 6 h. Propargyl alcohol (0.48 mL, 0.44 g, 8 mmol) was added to the reaction mixture, which was stirred for 24 h. The reaction mixture was concentrated without contact with air and concentrated on a column with silica gel 40/100 μm. A fraction eluted with an ether—petroleum ether (1 : 2) mixture was gathered. The solvent was evaporated without air. Dicarbonyl(η^5-pentamethylcyclopentadienyl)(η^2-prop-2-ynol)rhenium (**12**) was obtained (0.01 g, 1.15%). IR ($CHCl_3$), ν/cm^{-1}: 1864, 1951 (CO). The substance was dissolved in CD_3NO_2 and filtered in a tube for recording NMR spectra. ^{1}H NMR (CD_3NO_2), δ: 2.01 (s, 15 H, CH_3—Cp); 4.71 (d, 2 H, CH_2—C≡, J = 2.1 Hz); 5.28 (t, 1 H, H—C≡, J = 2.1 Hz). After recording a preliminary ^{1}H NMR spectrum, 1 drop of CF_3SO_3H was added. The repeated detection of the ^{1}H NMR spectrum showed complex **13**. ^{1}H NMR (CD_3NO_2), δ: 2.15 (s, 15 H, CH_3—Cp); 3.72, 4.76 (AB system, 2 H, CH_2—C≡, J = 2.3 Hz, J_{AB} = 11 Hz); 6.02 (t, 1 H, HC≡, J = 2.3 Hz). IR (CD_3NO_2), ν/cm^{-1} (after isolation from the tube): 1966, 2038 (CO).

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References

1. A. N. Nesmeyanov, V. V. Krivykh, E. S. Il'minskaya, and M. I. Rybinskaya, *J. Organomet. Chem.*, 1981, **209**, 309.
2. V. V. Krivykh, O. V. Gusev, and M. I. Rybinskaya, *J. Organomet. Chem.*, 1989, **362**, 351.
3. B. B. Curves, E. S. Taits, P. V. Petrovskii, and M. I. Rybinskaya, *Metalloorg. Khim.*, 1989, **2**, 939 [*Organomet. Chem. USSR*, 1989, **2** (Engl. Transl.)].
4. V. V. Krivykh, E. S. Taits, P. V. Petrovskii, Yu. T. Struchkov, and A. I. Yanovsky, *Mendeleev Commun.*, 1991, 103.
5. E. S. Taits, Ph. D. (Chem.) Thesis, INEOS AN SSSR, Moscow, 1989, 66 pp. (in Russian).
6. C. P. Casey and C. S. Yi, *J. Am. Chem. Soc.*, 1992, **114**, 6597.
7. C. P. Casey, A. D. Selmeczy, J. R. Nash, C. S. Yi, R. D. Powell, and R. K. Hayashi, *J. Am. Chem. Soc.*, 1996, **118**, 6698.
8. A. D. Horton and A. G. Orpen, *Organometallics*, 1992, **11**, 8.
9. M. W. Baize, P. W. Blosser, V. Plantevin, D. G. Schimpff, J. C. Gallucci, and A. Woicicki, *Organometallics*, 1996, **15**, 164.
10. S. Ogoshi, K. Tsutsumi, and H. Kurosawa, *J. Organomet. Chem.*, 1995, **493**, C19.
11. P. W. Blosser, D. G. Schimpff, J. C. Gallucci, and A. Woicicki, *Organometallics*, 1993, **12**, 1993.
12. T.-M. Huang, J.-T. Chen, G.-H. Lee, and Y. Wang, *J. Am. Chem. Soc.*, 1993, **115**, 1170.
13. T. M. Huang, R.-H. Hsu, C.-S. Yang, J.-T. Chen, G.-H. Lee, and Y. Wang, *Organometallics*, 1994, **13**, 3657.
14. P. J. Stang, C. M. Crittel, and A. M. Arif, *Organometallics*, 1993, **12**, 4799.
15. N. E. Kolobova, L. L. Ivanov, Yu. A. Chernykh, and V. V. Derunov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1396 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31** (Engl. Transl.)].
16. V. V. Krivykh, E. S. Il'minskaya, and M. I. Rybinskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 1911 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32** (Engl. Transl.)].
17. H. G. Alt and H. E. Engelhardt, *J. Organomet. Chem.*, 1988, **342**, 235.
18. A. N. Nesmeyanov, V. V. Krivykh, P. V. Petrovskii, V. S. Kaganovich, and M. I. Rybinskaya, *J. Organomet. Chem.*, 1978, **162**, 323.
19. M. I. Rybinskaya, A. Z. Kreindlin, S. S. Fadeeva, and P. V. Petrovskii, *J. Organomet. Chem.*, 1988, **345**, 341.
20. L. I. Zakharkin, V. V. Kobak, V. A. Pisareva, V. A. Antonovich, V. A. Ol'shevskaya, A. I. Yanovsky, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1985, **297**, 77.
21. K. Tsutsumi, S. Ogoshi, S. Nishiguchi, and S. Kurosawa, *J. Am. Chem. Soc.*, 1998, **120**, 1938.
22. P. W. Blosser, J. C. Gallucci, and A. Wojcicki, *J. Am. Chem. Soc.*, 1993, **113**, 2994.
23. B. Henc, P. W. Jolly, R. Sabz, S. Stobbe, G. Wilke, R. Benn, R. Mynott, K. Seevogel, R. Goddard, and C. Krueger, *J. Organomet. Chem.*, 1980, **191**, 449.

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