

SYNTHESIS OF  $\sigma$ -PHENYLETHYNYLPENTACARBONYL  
DERIVATIVES OF MANGANESE AND RHENIUM

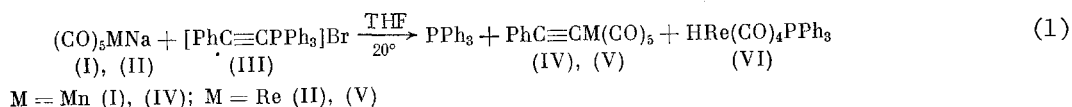
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Two methods which have previously been proposed for the synthesis of  $\sigma$ -ethynyl derivatives of metal carbonyls are the interaction of metallocarbonyl anions (MCA) with halogenacetylenes or with mixed ethynylphosphonium salts. For synthesizing derivatives of metals in the chromium subgroup, with the general formula  $\eta^5\text{-C}_5\text{H}_5(\text{CO})_5\text{M}\equiv\text{CC}_6\text{H}_5$ , these two methods supplement each other since the former is suitable when  $\text{M}=\text{Cr}$  and the latter when  $\text{M}=\text{Mo}$  or  $\text{W}$ . The application of these methods to other sufficiently nucleophilic MCA will help to fill certain gaps in the chemistry of ethynyl derivatives of metal carbonyls. In particular, manganese and rhenium pentacarbonyl anions would appear to be suitable for such reactions, since in the order of MCA nucleophilicity [3], they are adjacent to  $\text{C}_5\text{H}_5(\text{CO})_5\text{M}^-$  ( $\text{M}=\text{Cr}, \text{Mo}, \text{W}$ ). In our present work we have studied the reactions of  $(\text{CO})_5\text{M}^-$  ( $\text{M}=\text{Mn}, \text{Re}$ ) with ethynyltriphenylphosphonium bromide and phenylchloroacetylene.

Ethynyl derivatives of group VIIA metal carbonyls have received little attention. The compounds  $\text{PhC}\equiv\text{CRe}(\text{CO})_5$  and  $\text{C}_6\text{F}_5\text{C}\equiv\text{CM}(\text{CO})_5$  ( $\text{M}=\text{Mn}, \text{Re}$ ) have been synthesized by reactions of  $(\text{CO})_5\text{M}\text{Hal}$  with the Li-organic compounds  $\text{RC}\equiv\text{CLi}$  ( $\text{R}=\text{C}_6\text{H}_5$  or  $\text{C}_6\text{F}_5$ ), but the products were formed with very low yields and their structure was established only by IR spectroscopy and mass spectrometry [4]. To synthesize compounds of the type  $\text{RC}\equiv\text{CM}(\text{CO})_5$ , we did not use the method which usually gives good results, i.e., the decarbonylation of the corresponding acyl derivatives.

We found that under mild conditions (in THF at  $20^\circ\text{C}$ ), the Mn and Re pentacarbonyl anions react with  $[\text{PhC}\equiv\text{CPh}_3]\text{Br}$



The principal reaction products are triphenylphosphine (with an almost quantitative yield) and manganese(IV) or rhenium (V) pentacarbonyl-( $\sigma$ -phenylethynyl) (31% and 60%, respectively). When II reacts with III, in addition to (V) a crystalline substance (VI) is formed which is light yellow in color, has a composition  $\text{C}_{22}\text{H}_{16}\text{PReO}_4$ , and an mp of  $155$  to  $157^\circ$ . The structure  $\text{cis-HRe}(\text{CO})_4\text{PPh}_3$  has been assigned to this compound on the basis of an analysis of elements, and mass and IR spectral data. To establish the structure of (VI) unequivocally, the substance was prepared by direct synthesis from  $(\text{CO})_5\text{ReH}$  and  $\text{PPh}_3$  by a modified procedure [5]. The compound thus obtained proved to be identical with (VI) according to its IR spectrum and melting point.

The composition of products formed in reaction (1) agrees with an oxidation-reduction mechanism leading to the formation of a radical pair  $\{(\text{CO})_5\text{M}^\cdot, \cdot\text{PPh}_3(\text{C}\equiv\text{CPh})\}$  or to pentacoordinated phosphorane  $(\text{CO})_5\text{M}-\text{PPh}_3(\text{C}\equiv\text{CPh})$  as an intermediate compound.

We have previously shown that when  $\text{PhC}\equiv\text{CHal}$  reacts with  $\text{CpW}(\text{CO})_3\text{K}$ , the yield of  $\text{Cp}(\text{CO})_3\text{-WC}\equiv\text{CPh}$  depends on the halide, decreasing in the order  $\text{Cl} > \text{Br} > \text{I}$ , whereas the ease of reaction and the yield of  $\text{Cp}(\text{CO})_3\text{W}\text{Hal}$  increase in the reverse sequence:  $\text{I} > \text{Br} > \text{Cl}$  [2]. In the present work we have studied the reaction between anions (I) or (II) and  $\text{PhC}\equiv\text{CCl}$  (VII) in THF at  $40$  to  $60^\circ$  for a reaction time of 2 to 4 h. Under these conditions the  $\sigma$ -phenylethynyl compounds (IV) and (V) are obtained in low yields and in addition a whole series of colored unidentified products are formed. Apparently the reaction between (VII) and Mn or Re pentacarbonyl anions has a more complex mechanism than the analogous reaction involving the  $\text{CpW}(\text{CO})_3^-$  anion.

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TABLE 1. Chemical Shifts of NMR  $^{13}\text{C}$  (ppm) in  $\text{X}-\text{C}_\alpha\equiv\text{C}_\beta-\text{C}_6\text{H}_5$

X	Temp. of meas. °C	CO	$\text{C}_\alpha$	$\text{C}_\beta$	$\text{C}^1$	$\text{C}^2$	$\text{C}^{3,6}$	$\text{C}^{3,5}$
$\text{Mn}(\text{CO})_5$	20	207,4 207,5	90,5	116,9	127,4	128,3	131,5	126,4
$\text{Mn}(\text{CO})_5$	-70	206,6	91,6	115,8	126,0	128,0	130,4	126,0
$\text{Re}(\text{CO})_5$	20	179,9 179,1	80,4	112,7	127,2	128,2	131,6	126,3
H	20	—	77,8	84,0	122,7	128,9	128,6	128,9

Thus the interaction of MCA with  $[\text{PhC}\equiv\text{CPh}_3]\text{Br}$  leads to the formation of the corresponding  $\sigma$ -phenylethynyl compounds not only of Mo and W [1, 2], but also Mn and Re.

Compounds (IV) and (V) are crystalline substances, pale cream (IV) or pale yellow (V) in color, stable in air in the solid form, and slowly decomposing in solution. The structures of the compounds obtained were confirmed by IR-, NMR $^{13}\text{C}$ -, and mass spectral data, and by element analysis. Signals of the  $\alpha$ - and  $\beta$ -acetylene carbon nuclei in the NMR  $^{13}\text{C}$  spectrum of compounds (IV) and (V) (Table 1) are displaced towards the weak field in comparison with the analogous signals in phenylacetylene, this shift being more significant for signals of  $\text{C}_\beta$ -atoms. Signals from  $\alpha$ -carbon atoms are broadened because of the interaction with the metal atom nucleus which has a quadrupole moment and thus makes their identification more reliable. In the spectrum of complex (V) at 20°C in  $\text{CH}_2\text{Cl}_2$ , the cis- and trans-groups of CO show two signals at 179.07 and 179.88 ppm with an integral intensity ratio of 4:1. In the case of the Mn analog (IV) at 20°C, all carbonyl groups display a single broadened signal at 207.11 ppm, which when the temperature decreases to -70°, splits into two signals with chemical shifts (CS) 207.5 and 206.6 ppm, and, as in the spectrum of complex (V), a less intensive signal from the nucleus of the carbonyl C atom in the trans position is observed in the weaker field.

In contrast with  $(\text{CO})_5\text{MnPh}$  and  $(\text{CO})_5\text{MnCH}_3$ , which react readily with phosphines and phosphites at  $\sim 20^\circ$  in different solvents [6], the phenylethynyl derivatives (IV) and (V) obtained by us showed no tendency for such conversions. Thus when (IV) or (V) were boiled with  $\text{PPh}_3$  in THF or hexane for 12 h, no substitution products were detected and only the original compounds were isolated.

#### EXPERIMENTAL

All operations were carried out in an atmosphere of purified argon. For chromatography we used silica gel (SG), grade L 100/160  $\mu$  (Czechoslovakia). The IR spectra were taken in cyclohexane solution on a UR-20 spectrometer, mass spectra on an MS-30 mass spectrometer, and NMR  $^{13}\text{C}$ - $\{^1\text{H}\}$  on a Bruker NX-90 spectrometer (22, 635 MHz) in a Fourier transform regime; as internal standard we used the signal from the  $\text{CH}_2\text{Cl}_2$  solvent (54.0 ppm).  $[\text{PhC}\equiv\text{CPh}_3]\text{Br}$  was prepared according to [7] and  $\text{PhC}\equiv\text{CCl}$  according to [8].

1. Reaction between  $\text{NaMn}(\text{CO})_5$  (I) and (III). To the filtered solution of (I), obtained by reducing  $\text{Mn}_2(\text{CO})_{10}$  (1.95 g) (5 mmoles) with 1% Na amalgam (1.15 g) in THF (100 ml), under conditions of stirring and cooling to  $-30^\circ$ , we added (III) (4.43 g) (10 mmoles). The mixture was gradually heated to  $\sim 20^\circ$ . The reaction course was followed from IR spectra of the reaction mixture. At  $\sim 20^\circ$  the original anion was no longer present in the mixture. The solvent was evaporated in vacuo by an aspirator. The residue was chromatographed on an SG column, eluted first with petroleum ether, then with petroleum-benzene mixtures (3:1, 1:1, 1:3), and finally with pure benzene. After removal of solvent, fractions were analyzed by TLC and IR spectroscopy in comparison with known samples. Fractions containing  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{PPh}_3$  were discarded; those which, according to IR spectra, contained (IV) were dissolved in hexane. The solution was concentrated and cooled. Bright cream-colored crystals of (IV) separated (0.91 g, 31%) with mp 79 to  $80^\circ$ . IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 2015, 2045, 2145 ( $\text{C}\equiv\text{O}$ ), 2120 ( $\text{C}\equiv\text{C}$ ). Mass spectrum: 296 ( $\text{M}^+$ ), 240 ( $\text{M} - 2\text{CO}$ ) $^+$ , 212 ( $\text{M} - 3\text{CO}$ ) $^+$ , 184 ( $\text{M} - 4\text{CO}$ ) $^+$ , 156 ( $\text{M} - 5\text{CO}$ ) $^+$ , 102 ( $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$ ). Found: C 52.91; H 2.01; Mn 18.31%.  $\text{C}_{13}\text{H}_5\text{MnO}_5$ . Calculated: C 52.73; H 1.70; Mn 18.55%.

2. Reaction between  $\text{NaRe}(\text{CO})_5$  (II) and (III). An analogous experiment was carried out starting from  $\text{Re}_2(\text{CO})_{10}$  (3.26 g) (5 mmoles) and (III) (4.4 g) (10 mmoles). Isolated by

column chromatography were:  $\text{Ph}_3\text{P}$  (1.66 g) (64%) and (V) (2.55 g) (60%), mp  $110^\circ$  (with decomp.) (hexane). IR spectra ( $\nu$ ,  $\text{cm}^{-1}$ ): 2000, 2045, 2150 ( $\text{C}\equiv\text{O}$ ), 2120 ( $\text{C}\equiv\text{C}$ ). Mass spectra: 428 ( $\text{M}^+$ ), 400 ( $\text{M} - \text{CO}$ ) $^+$ , 344 ( $\text{M} - 3\text{CO}$ ) $^+$ , 316 ( $\text{M} - 4\text{CO}$ ) $^+$ , 288 ( $\text{M} - 5\text{CO}$ ) $^+$ . Found: C 37.20; H 1.36; Re 43.26%.  $\text{C}_{13}\text{H}_5\text{ReO}_5$ . Calculated: C 36.52; H 1.18; Re 43.58%. 0.7 g ( $\sim 10\%$ ) (VI), mp 155 to  $157^\circ$  (benzene—heptane). IR spectra ( $\nu$ ,  $\text{cm}^{-1}$ ): 1966, 1980, 1995, 2085 ( $\text{C}\equiv\text{O}$ ) (m. [5]). Mass spectrum: 562 ( $\text{M}^+$ ), 561 ( $\text{Ph}_3\text{PRe}(\text{CO})_4$ ) $^+$ , 533 ( $\text{M} - \text{HCO}$ ) $^+$ . Found: C 47.12; H 2.95; Re 28.71; P 5.47%.  $\text{C}_{22}\text{H}_{16}\text{O}_4\text{PRE}$ . Calculated: C 47.04; H 2.87; Re 33.17; P 5.51%.

3. Synthesis of  $\text{HRe}(\text{CO})_4\text{PPh}_3$ . To the filtered solution of (II), obtained by reducing  $\text{Re}_2(\text{CO})_{10}$  (1.25 g) (1.7 mmoles) with 1% Na amalgam (0.4 g) in THF (20 ml), we added  $\text{Ph}_3\text{P}$  (0.87 g) (3.4 mmoles) and while mixing added dropwise a solution of 0.17 ml  $\text{H}_3\text{PO}_4$  in 2 ml THF. After 1 h the original anion was absent from the reaction mixture. After the mixture had been treated as in experiment 1 we isolated  $\text{Re}_2(\text{CO})_{10}$  (0.09 g) and  $\text{HRe}(\text{CO})_4\text{PPh}_3$  (0.2 g) ( $\sim 10\%$ ), mp 151 to  $154^\circ$  (benzene—heptane) (the IR spectrum was identical to that of (VI) and to that in [5]).

4. Reaction between  $\text{NaMn}(\text{CO})_5$  (I) and (VII). To the filtered solution of (I), obtained by reduction of  $\text{Mn}_2(\text{CO})_{10}$  (1 g) (2.5 mmoles) with 1% Na amalgam (0.6 g) in THF (30 ml), under conditions of stirring and cooling to  $-70^\circ$ , we added (VII) (0.7 g) (5 mmoles). After room temperature had been reached, the reaction (followed by the IR spectrum of the mixture) did not take place. The reaction mixture was heated for 4 h at 40 to  $50^\circ$ . By column chromatography we isolated  $\text{Mn}_2(\text{CO})_{10}$  (0.11 g), (IV) (0.05 g) ( $\sim 2\%$ ), and some unidentified colored products.

5. Reaction between  $\text{NaRe}(\text{CO})_5$  and (VII). As in experiment 4, from  $\text{Re}_2(\text{CO})_{10}$  (1.3 g) and (VII) (0.54 g), when heated for 1 h at 40 to  $50^\circ$ , we isolated  $\text{Re}_2(\text{CO})_{10}$  and (V) (IR spectrometry).

#### CONCLUSIONS

1. Manganese and rhenium pentacarbonyls interacted with phenylethynyltriphenylphosphonium bromide to give their  $\sigma$ -phenylethynyl derivatives.
2. The reaction between manganese or rhenium pentacarbonyls and phenylchloroacetylene takes place under more drastic conditions and the product yields are insignificant.

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