According to ESR spectra, radicals similar to **1** are also formed in the reactions of $CpMn(CO)_2(THF)$ with the thioesters $P(OMe)(SEt)_2$, $PPh(SEt)_2$, and $PH(t\text{-}Bu)(SEt)$, as well as with tributylthiostannane Bu_3SnSPh. The homolytic cleavage of a sulfur—element bond on interaction with $CpMn(CO)_2(THF)$ is likely of rather general nature.

Synthesis of complex 1 (R = Ph). A solution of cymantrene (CTM) (2—4 mmol) in 80 mL of freshly distilled THF was irradiated with UV light under argon in a quartz reactor (2 h at −5°C). To the resulting crimson-colored $CpMn(CO)_2(THF)$ solution was added ~0.8 equiv. of thiophosphite $P(SPh)_3$. The solution was slowly warmed up to 20°C and exposed for 12—14 h at this temperature without irradiation. After removal of THF in a vacuum, a black or dark-blue residue was chromatographed on a silica gel column. Unreacted CTM and complex **2** were eluted with hexane, and complex **1a**, which is stable in the absence of oxygen, was eluted with THF. The latter complex was purified by recrystallization from hexane at −80°C. The yield of **1a** was equal to 50 %, mp 99—100°C (cf. Refs.[1,2]). IR (hexane), ν (cm^{-1}): 1933, 1999 (CO). ESR spectrum: sextet, $g = 2.0326$, $a_{Mn} = 54$ Oe. MS (EI, 70 eV), m/z (I_{rel}, %): 285 $[M]^+$ (7.5), 229 $[M-2CO]^+$ (100), 164 $[MnSPh]^+$ (21), 120 $[CpMn]^+$ (44), 109 $[SPh]^+$ (15), 65 $[Cp]^+$ (12), 55 $[Mn]^+$ (65). Complex **1a** can also be isolated from the reaction mixture by successive treatment with $NaBH_4$/Me_4NBr. The ESR spectra of the other radicals **1** exhibit sextets with $a_{Mn} = 50\div55$ Oe. It is interesting to note that the value of the hyperfine coupling constant with the ^{55}Mn nucleus in complexes **1** is intermediate between the ranges of hyperfine coupling constants with the Mn nuclei in coordination compounds of Mn^{2+} (a_{Mn} 100—120 Oe) and in radical complexes of manganese where the unpaired electron is localized mainly on an atom in one of the ligands (a_{Mn} is less than 20 Oe).[5]

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Vilsmeier formylation of aromatic organomercury compounds

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The reactivity of the C—Hg bond in aromatic derivatives of mercury is responsible for the occurrence of various processes of nucleophilic substitution in these compounds. However, the behavior of organomercury compounds (in contrast to organostannanes[1]) in the Vilsmeier—Haack reaction has not been studied. There is but a single reference that upon the action of the Vilsmeier reagent on a mercurated divinylbenzene — polystyrene copolymer, a C=O absorption band appears in the IR spectrum.[2]

We have found that aromatic organomercury compounds react with DMFA and $POCl_3$ to give aldehydes. The reactivities of the compounds studied, arylmercuric chlorides and diarylmercury, are comparable; in the case of R_2Hg, both aryl fragments take part in the reaction. The yields of aldehydes are within 45—85 %; they increase with increases in the electron-donor ability of the substituents in the benzene ring.

The positions of the substituents in the reaction products suggest that the reaction proceeds stereo-

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$$\mathrm{RHgCl\ (0.5\ R_2Hg)} + \mathrm{HC(O)NMe_2} \xrightarrow[\mathrm{H_2O}]{\mathrm{POCl_3, 70°C}} \mathrm{RCHO}$$

R (in RHgCl) = Ph (45 %, 5 h), p-MeC_6H_4 (65 %, 4 h), p-$MeOC_6H_4$ (73 %, 4 h), o-$MeOC_6H_4$ (70 %, 4 h)
R (in R_2Hg) = p-EtC_6H_4 (65 %, 5 h), p-(t-Bu)C_6H_4 (70 %, 5 h), p-$Et_2NC_6H_4$ (85 %, 1 h)

selectively as *ipso*-substitution of the mercury residue by the formyl group.

A typical experiment was carried out as follows. $POCl_3$ (3 mmol), DMFA (1 mL), and 1 mmol of RHgCl (or 0.5 mmol of R_2Hg) were mixed under argon. The reaction mixture was stirred for 4—5 h at 70°C and then hydrolyzed with 3 mL of ice water. Then the pH was brought to 6 by adding 10 % aqueous NaOH. The aqueous layer was extracted with ether. The ethereal extract was washed with water and dried with Na_2SO_4. The aldehydes obtained were characterized as 2,4-dinitrophenylhydrazones; their constants were in agreement with the literature data.

Thus, by employing organomercury compounds, the Vilsmeier—Haack reaction can be carried out with arenes, which either were previously considered to be inert or reacted under severe conditions and in low yields. The reaction of organomercury compounds that we studied can be now used for the selective introduction of a formyl group into aromatic compounds.

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Palladium-catalyzed reaction of phenylacetylene with aryl iodides in aqueous medium

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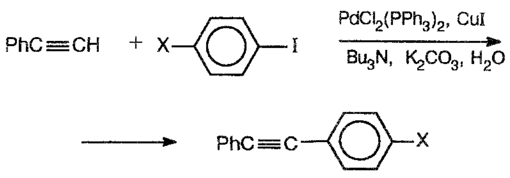
The cross-coupling of terminal acetylenes with aryl halides is usually carried out in organic solvents (Et_2NH, benzene, chloroform, dimethylformamide) in the presence of an amine, CuI, and palladium complexes.[1,2]

We have found that phenylacetylene readily undergoes cross-coupling with aryl iodides in aqueous K_2CO_3 in the presence of 1 mol. % $PdCl_2(PPh_3)_2$, 2 mol. % CuI, and 10 mol. % Bu_3N. The reaction proceeds at 20—40°C and is completed within 1.5—2 h to give substituted tolans in high yields (92—98 %).

If Bu_3N is replaced by Et_3N, the yield of the cross-coupling product decreases, and the process becomes more lengthy.

General procedure. To a mixture of PhC≡CH (1.3 mmol), p-$NO_2C_6H_4I$ (1 mmol), $PdCl_2(PPh_3)_2$ ($1 \cdot 10^{-2}$ mmol), CuI ($2 \cdot 10^{-2}$ mmol), K_2CO_3 (1.3 mmol), and 2 mL of water was added 0.1 mmol of Bu_3N under argon. The reaction mixture was stirred for 1.5 h at room temperature and extracted with ether. The ethereal solution was dried with Na_2SO_4 and evaporated to give 0.204 g (92 %) of p-nitrotolan, mp 119°C (see Ref.[3]). The following compounds were pre-



X = H, NO_2, CN, MeCO

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