Organometallic Chemistry

Solid-state photochemical ligand exchange in the cymantrene series

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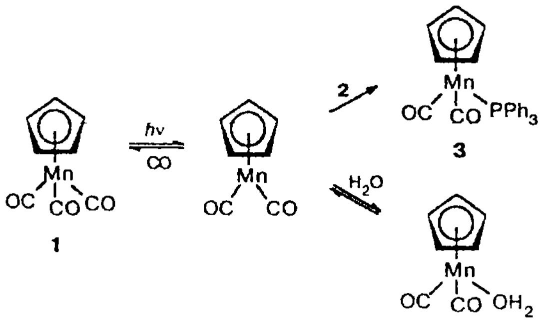
Solid-state photochemical ligand exchange in silica gel-supported π-complexes of transition metals has been demonstrated for the first time for cymantrene compounds. The method suggested allows the synthesis of monophosphine complexes to be carried out on preparative and analytical scales.

Key words: solid-state reactions, cymantrene, ligand exchange, photochemistry.

Many reactions of organic compounds for which solvents are conventionally used can successfully be carried out in the solid state. Reactions of solid reagents in the absence of a solvent are often more efficient and selective than those in solutions.[1–5] Although solid-state reactions of coordination compounds of transition metals have been known a long time, they cover mainly thermal and photochemical decomposition of these complexes.[6–8] The first studies devoted to the solid-state synthesis of organoelement compounds have appeared only recently.[9–12] In this work, we demonstrated for the first time the possibility of solid-state photochemical ligand exchange reactions in π-complexes of transition metals.

Irradiation of a quartz plate-supported mixture of cymantrene (**1**) and triphenylphosphine (**2**) powders with a mercury lamp results in a change in its color from pale yellow to dark orange and the appearance of ν(CO) bands at 1870 and 1940 cm^{-1} in the IR spectrum. The bands indicate the formation of the monophosphine complex $C_5H_5Mn(CO)_2PPh_3$ (**3**)[13] (Scheme 1). The formation of this compound is also confirmed by the ^1H and ^{31}P NMR spectra of solutions of the reaction mixture, according to which the yield of complex **3** amounts to 10—15% after 30-min irradiation. This result indicates the possibility of solid-state ligand exchange during photolysis of compound **1** and its derivatives.

Scheme 1



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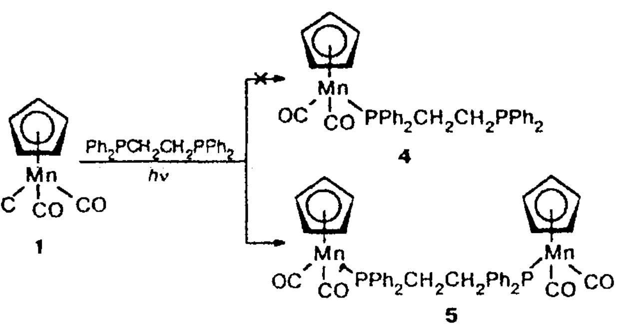
Further study was carried out using a standard photoreactor with a lamp for inner immersion in aqueous suspensions of reagents.

Irradiation of a suspension of powders **1** and **2** in water for 1 h results in the formation of complex **3** in a yield of <5%, and most of compound **1** remains unchanged after the reaction. During the reaction, the aqueous phase becomes crimson-red (EAS: λ_{max} = 390 nm), which indicates, most likely, that it contains the $C_5H_5Mn(CO)_2(H_2O)$ complex. In the latter, by analogy with THF and other oxygen-containing solvents,[14] a water molecule plays the role of the *O*-coordinated ligand (see Scheme 1).

In this case, a low conversion of the reagents is due, most likely, to their different hydrophobicities, because of which compounds **1** and **2** are in different parts of the reactor and cannot contact each other. To achieve a more efficient spatial contact between the reagents, in the experiments described hereinafter, the ligand exchange was performed by photolysis of a SiO_2-adsorbed suspension of a mixture of compounds **1** and **2** in water.

Under these conditions, the photolysis of the mixture of reagents allowed phosphine complex **3** to be isolated in 46% yield after 30 min with an 80% conversion of compound **1**. A crimson coloring of the aqueous phase is not observed, *i.e.*, the reaction occurs completely in the solid phase on the SiO_2 surface. The CO ligand is also efficiently substituted in molecule **1** during irradiation of its mixture with 1,2-bis(diphenylphosphino)ethane in a 1 : 1 ratio. Although in this case, the formation of mononuclear complex **4** can be expected in the solid-state synthesis, bridged complex **5** (Scheme 2) is the main reaction product, whose yield after 1-h irradiation amounts to 29%. At the same time, in the conventional method of ligand substitution, photolysis of the reagents in a solution,[15] the yield of this compound after 18 h is 21%.

Scheme 2



When diphenylphosphinocymantrene (**6**) is irradiated in the absence of compound **2**, the reaction proceeds nonselectively and results in a complex mixture of mono- and binuclear phosphine complexes, whose formation has previously been observed for this reaction in the liquid phase.[16] However, mainly complex **7** is formed in 53% yield upon simultaneous photolysis of compounds **6** and **2** in the solid state (Scheme 3).

Scheme 3

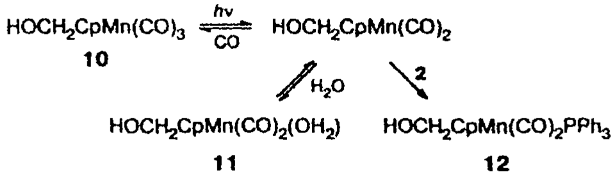
$$\underset{\mathbf{6,\ 8}}{\mathrm{XCpMn(CO)_3}} \xrightarrow[2]{h\nu} \underset{\mathbf{7,\ 9}}{\mathrm{XCpMn(CO)_2PPh_3}}$$

X = Ph_2P (**6**, **7**), Me (**8**, **9**)

The described variant of photochemical ligand exchange using silica gel as the support allows reactions to be performed in the absence of a solvent with both solid and liquid reagents. In fact, (triphenylphosphine)(dicarbonyl)methylcyclopentadienylmanganese (**9**) is formed in 60% yield upon 40-min photolysis of a silica gel-supported mixture of compound **2** with liquid methylcymantrene (**8**). The yield of compound **9** after 15-h photosubstitution in a solution is 44%.[17]

By contrast to the examples considered above, irradiation of a silica gel-supported suspension of a mixture of hydroxymethylcymantrene (**10**)[18] with PPh_3 in water results in an intense crimson coloring of the aqueous phase, which is also related, most likely, to the formation of aqua-complex **11** (Scheme 4). The yield of the product of ligand exchange (**12**) is very low (<5%).

Scheme 4



Although cymantrene and its derivatives, as well as phosphines, are poorly water-soluble, as a rule, the reaction course in the case of alcohol **10** invoked us to estimate the solubility of compounds used in water by EAS. Under photoreaction conditions, all compounds except for **10** form solutions with concentrations not higher than 10^{-5}—10^{-4} mol L^{-1}. The value obtained agrees well, in particular, with the known value of solubility of methylcymantrene in water (29 mg L^{-1}).[19] By contrast, the concentration of alcohol **10** in water is at a level of 10^{-3} mol L^{-1} and does not decrease when silica gel is added. Thus, a low yield of the substitution product formed during the photolysis of compound **10** is probably associated with its high solubility in water and decomposition during irradiation in solution in the absence of phosphine. To confirm the structure of alcohol **12**, which has not been described previously, we attempted to synthesize it by the conventional method of photolysis of a mixture of compounds **10** and **2** in benzene in the presence of THF. The reaction in solution is also accompanied by considerable decomposition of the starting compound, due to which the yield of alcohol **12** does not exceed 5—10%. Thus, a low yield of this compound during ligand substitution is associated not only with a high solubility of alcohol **10** in water but also with a low ability of this compound to undergo ligand exchange with triphenylphosphine.

All solid-state reactions described above were carried out with microquantities of substances during irradiation of the compounds on Silufol plates followed by chromatography of the reaction products. The results of these experiments, as well as the photolysis of a mixture of reagents **1** and **2** on the quartz support, show that water used in the solid-state photolysis is not the medium in which ligand exchange occurs. Nevertheless, the role of water in stabilization of intermediate dicarbonyl complexes on the SiO_2 surface can be sufficiently important. At the same time, our experiments on silica gel plates provide for fast preparation of compounds in minor amounts by a simple method and for verification of the possibility and direction of solid-state photochemical reactions.

Thus, we showed the possibility of solid-state photochemical reactions of CO ligand exchange in π-complexes of the cymantrene series. In several cases, this method is more efficient than photolysis in solution and can be especially useful when the compounds used are poorly soluble.

Experimental

^1H and ^{31}P NMR spectra were recorded on a Bruker WP-200 SY spectrometer in $CDCl_3$ using Me_4Si as the internal standard. Mass spectra (EI, 70 eV) were recorded on a Kratos MS-890 instrument. Electronic absorption and IR spectra were recorded on Specord UV-VIS and UR-20 instruments, respectively. Photoreactions were carried out using a TQ 150 (Normag) immersion high-pressure mercury lamp.

Compounds **3**, **5**—**7**, **9**, and **10** were obtained by the known procedures.[13—17] Phosphines and compounds **1** and **8** are commercially available and were purified by standard methods.

Solid-state ligand exchange reactions (general procedure). SiO_2 (100—400 μm) (2—3 mL) was added to a solution of the complex (1 mmol) and phosphine (1 mmol) in benzene (50 mL), and the solvent was removed on a rotary evaporator at 20 Torr. The sample obtained was additionally exposed to air at 25 °C for 24 h and placed in a standard Pyrex photoreactor with an inlet of inert gas and a cooling jacket between the lamp and reaction zone. A suspension of reagents in 200 mL of distilled water was irradiated in a nitrogen flow at 20 °C for 45—80 min with intense stirring on a magnetic stirrer. Then the solid phase was filtered off, dried, and placed in a column (2×10 cm) packed with silica gel. The reaction products were isolated by elution with gradual changing of the solvent from hexane to $CHCl_3$ and monitoring of the composition of fractions by TLC on Silufol plates. The structures of products were confirmed by the determination of their melting points and comparison of their IR and NMR spectra with those of authentic samples.

Irradiation on quartz plates. A mixture of compounds **1** (20 mg) and **2** (26 mg) supported as a thin layer on the surface of a 7×7-cm quartz plate was irradiated from a distance of 25 cm for 30 min. Then the reaction products were washed off with benzene, and complex **3** was isolated in 9% yield (4 mg) by preparative TLC on Silufol plates using a hexane—benzene mixture as the eluent.

Ligand substitution reactions on Silufol plates (general procedure). Solutions of mixtures of reagents were supported as spots on the starting line of the chromatographic plate and, after drying, irradiated with a Hg lamp from a distance of 25 cm for 10 min. Then spots of the starting mixture and reference compounds were supported on the plate and chromatographed in hexane—$CHCl_3$ systems.

Hydroxymethylcyclopentadienyl(dicarbonyl)(triphenylphosphine)manganese (12). A solution of compound **8** (234 mg, 1 mmol) and compound **2** (316 mg, 1.2 mmol) in benzene (150 mL) and THF (20 mL) was irradiated in the photoreactor in an argon flow for 90 min at 15 °C. During the reaction, the solution became yellow, and a porous brown precipitate was formed. The reaction mixture was filtered, and the filtrate was evaporated to 2—3 mL and chromatographed on a column packed with SiO_2 (100—200 mm, $CHCl_3$ as the eluent), collecting fractions with R_f 0.1. Complex **12** with m.p. 215—216 °C was isolated in 4% yield (19 mg) after recrystallization from hexane. MS (EI), *m/z*: 468 [M^+], 412 [M^+ − 2 CO], 334 [M^+ − 2 CO − PhH], 262 [PPh_3]. IR (CH_2Cl_2), ν/cm^{-1}: 1938, 1870. ^1H NMR ($CDCl_3$), δ: 2.08 (br.s, 1 H, OH); 3.94 (s, 2 H, CH_2); 4.19 (m, 2 H, Cp); 4.40 (m, 2 H, Cp); 7.1—7.5 (m, 15 H, Ph).

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