immobilized Ru tetrasulfate as a catalyst resulted in a fourfold decrease in the hydrodehalogenation rate in air and a twofold decrease in the extent of conversion. In the presence of the catalytic system based on $RuCl_3$, the reaction rate in air remained unchanged. A decrease in the rate was observed only when air was bubbled through the reaction mixture. Immobilized Ru tetraacetate appeared to be most stable toward oxygen: the rate and extent of conversion scarcely differed from those in Ar even when air was bubbled through the reaction mixture.

References

1. B. James, *Homogeneous Hydrogenation,* Wiley, New York, 1973.
2. V. I. Isaeva, Zh. Dych, L. I. Lapher, V. I. Yakerson, and V. Z. Sharf, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 65 [*Bull. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 49 (Engl. Transl.)].

Received March 1, 1993

Novel methods for the synthesis of the sulfur-containing organomanganese radicals $[CpMn(CO)_2SR]^{\bullet}$

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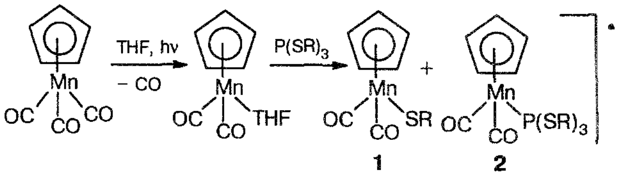
The sulfur-containing organomanganese radicals $[CpMn(CO)_2SR]^{\bullet}$ (**1**), which form upon the oxidation[1] of the cymantrene derivatives $CpMn(CO)_2S(H)R$ by atmospheric oxygen and in the reactions of $CpMn(CO)_2(THF)$ with disulfides[2] and triphenyltrithiostibine,[3] are rather rare organometallic paramagnetic complexes that are stable under normal conditions.

Recently we have shown[4] that thioesters of P(III) acids react with $CpMn(CO)_2(THF)$ to give strong complexes (**2**) with coordination by means of the phosphorus atom. A more detailed investigation of this reaction revealed that the formation of sulfur-containing organomanganese free radicals which can be detected by IR and ESR spectroscopy in a reaction mixture always accompanies the formation of **2**. The formation of **1** is obviously due to the homolytic cleavage of a P—S bond in the thiophosphites.



R = Ph, Me, Et, *i*-Pr

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, p. 614, March, 1993.

1066-5285/93/4203-0583$12.50

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*-Bu)(SEt), as well as with tributylthiostannane Bu$_3$SnSPh. 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$_4$NBr. The ESR spectra of the other radicals **1** exhibit sextets with a_{Mn} = 50÷55 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]

References

1. A. Winter, G. Huttner, M. Gottlieb, and I. Jibril, *J. Organomet. Chem.*, 1985, **286**, 317.
2. P. Lau, H. Braunwarth, G. Huttner, D. Gunauer, K. Evertz, W. Imhof, Ch. Emmerich, and L. Zsolnai, *Organometallics*, 1991, **10**, 3861.
3. A. Lombard, G. Huttner, and K. Evertz, *J. Organomet. Chem.*, 1988, **350**, 243.
4. A. G. Ginzburg, I. Yu. Gorshunov, O. G. Sinyashin, and V. I. Sokolov, *Metalloorg. Khim.*, 1992, **5**, 1094 [*J. Organomet. Chem. USSR*, 1992, **5** (Engl. Transl.)].
5. A. R. Forrester, *Numerical Data and Functional Relationships in Science and Technology*, Landolt-Bornstein, 1989, **17**, Part 2, 5.

Received March 5, 1993

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$_2$Hg, 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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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, p. 615, March, 1993.

1066-5285/93/4203-0584$12.50