

2. F. Freeman, *Chem. Rev.*, 1975, **75**, 439.
3. F. G. Traylor, *Accounts Chem. Res.*, 1969, **2**, 152.
4. A. Factor and F. G. Traylor, *J. Org. Chem.*, 1968, **33**, 2607.
5. R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *J. Am. Chem. Soc.*, 1967, **89**, 880.
6. H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 1959, 227.
7. M. R. Johnson and B. Bickborn, *J. Chem. Soc., Chem. Commun.*, 1968, 1073.
8. P. Chamberlain and G. H. Whittham, *J. Chem. Soc. (B)*, 1970, 1382.
9. N. S. Zefirov and L. S. Gurvich, *J. Organometal. Chem.*, 1974, **81**, 309.
10. V. R. Kartashov, E. V. Skorobogatov, N. V. Malisova, Yu. K. Grishin, D. V. Bazhenov, and N. S. Zefirov, *Zh. Org. Khim.*, 1991, **27**, 2490 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
11. V. R. Kartashov, E. V. Skorobogatov, T. N. Sokolova, O. V. Vasil'eva, N. V. Malisova, Yu. K. Grishin, D. V. Bazhenov, and N. S. Zefirov, *Zh. Org. Khim.*, 1991, **27**, 1240 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
12. W. C. Baird and M. Ruza, *J. Org. Chem.*, 1968, **33**, 4105.
13. V. I. Sokolov, V. V. Bashilov, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, 1969, **188**, 127 [*Dokl. Chem.*, 1969, **188** (Engl. Transl.)].
14. V. I. Sokolov, V. V. Bashilov, P. V. Petrovskii, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, 1973, **213**, 1103 [*Dokl. Chem.*, 1973, **213** (Engl. Transl.)].
15. V. I. Sokolov and V. V. Bashilov, *J. Organometal. Chem.*, 1978, **162**, 271.
16. V. R. Kartashov, T. N. Sokolova, I. V. Timoffev, Yu. K. Grishin, D. V. Bazhenov, and N. S. Zefirov, *Zh. Org. Khim.*, 1991, **27**, 2077 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
17. A. Bax and R. Freeman, *J. Magn. Reson.*, 1981, **44**, 542.
18. R. Freeman and G. Bodenhausen, *J. Am. Chem. Soc.*, 1978, **100**, 320.
19. J. K. Sanders, *Progr. NMR Spectrosc.*, 1982, **15**, 353.
20. Yu. K. Grishin, D. V. Bazhenov, V. A. Roznyatovskii, M. A. Kazakova, V. R. Kartashov, and Yu. A. Ustynyuk, *Metalloorgan. Khim.*, 1988, **1**, 337 [*J. Inorg. Chem. USSR*, 1988, **1** (Engl. Transl.)].
21. F. Sasaki, K. Kanematsu, A. Kondo, and Yo. Noshitani, *J. Org. Chem.*, 1974, **39**, 3569.

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A radical mechanism of the reaction of molybdenum carbonyl complexes with bis(triethylgermyl)mercury

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The reaction of $[\text{Cp}(\text{CO})_3\text{Mo}]_2$ with $(\text{Et}_3\text{Ge})_2\text{Hg}$ occurs in toluene and THF by a radical mechanism. The interaction between $[\text{Cp}(\text{CO})_3\text{Mo}]_2\text{Hg}$ and $(\text{Et}_3\text{Ge})_2\text{Hg}$ has a radical character only in THF. The formation of $\text{Cp}(\text{CO})_3\text{MoH}$ at the first stage of these reactions substantially affects the further course of the process.

Key words: molybdenum, complex; reaction mechanism.

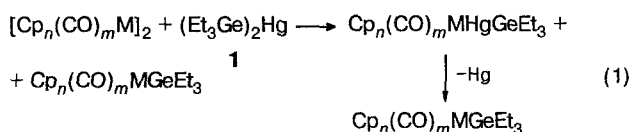
The rate constants for the reactions of dimeric carbonyl complexes of transition metals of the type $[\text{Cp}_n(\text{CO})_m\text{M}]_2$, where $\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Re}, \text{Mo}$; $n = 0, 1$; $m = 2 \div 5$, with bis(triethylgermyl)mercury agree well with their polarographic reduction potentials $E_{1/2}^{\text{red}}$ (ref. 1). The existence of a correlation between $\log k$ and $E_{1/2}^{\text{red}}$ and the literature data (refs. 2–4) suggest the radical mechanism of the reactions under consideration. The possibility of the occurrence of the radical mechanism has been studied using the reaction of molybde-

num carbonyl complexes with bis(triethylgermyl)mercury as an example.

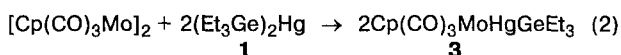
Results and Discussion

The reaction of transition metal carbonyl complexes with bis(triethylgermyl)mercury(1) yields $\text{Cp}_n(\text{CO})_m\text{MHgGeEt}_3$ at the first stage. It is suggested that the accumulation of the final product,

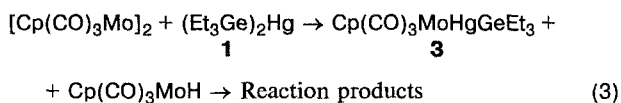
$\text{Cp}_n(\text{CO})_m\text{MGeEt}_3$, occurs simultaneously, *i.e.*, the reaction proceeds according to a scheme that requires equimolar amounts of the reactants:



However, IR spectroscopic monitoring of the reaction of $[\text{Cp}(\text{CO})_3\text{Mo}]_2$ with excess compound **1** revealed that the formation of $\text{Cp}(\text{CO})_3\text{MoGeEt}_3$ (**2**) does not occur synchronously with, and to the same extent as, $\text{Cp}(\text{CO})_3\text{MoHgGeEt}_3$ (**3**). Compound **3** proved to be the only product of the first stage of the reaction, while compound **2** only formed upon its demercuration. Further transformations of the $\text{Cp}(\text{CO})_3\text{Mo}^-$ and Et_3Ge^+ moieties remained obscure. At the same time, our kinetic data for the reaction of $[\text{Cp}(\text{CO})_3\text{Mo}]_2$ with **1** show that 2 moles of compound **3** are formed per 1 mole of the dimer converted:



When this reaction is carried out in toluene or THF at a 1:1 molar ratio between the reactants, $\text{Cp}(\text{CO})_3\text{MoH}$ ($\nu(\text{CO})$ 1940 and 2028 cm^{-1}) is evolved at the first stage simultaneously with compound **3**. Compound **2**, $[\text{Cp}(\text{CO})_3\text{Mo}]_2\text{Hg}$, $[\text{Cp}(\text{CO})_3\text{Mo}]_2$, Et_3GeH , and $(\text{Et}_3\text{Ge})_2$ were detected in the reaction products.



The character of the resulting compounds implies a radical mechanism for the reaction. The interaction of $[\text{Cp}(\text{CO})_3\text{Mo}]_2$ with $(\text{Et}_3\text{Ge})_2\text{Hg}$ at a molar ratio of 1:1 in toluene or THF can be represented by Scheme 1.

The initial electron transfer probably leads to the formation of the organometallic radical anion and the organomercury radical cation, the fragmentation of which is followed by the fast recombination of the charged particles and the interaction of the radicals with each other and with the solvent. It is possible that the scheme suggested does not include all the reactions occurring, but it illustrates the formation of the products of reaction (3).

We confirmed experimentally the possibility of the synthesis of $[\text{Cp}(\text{CO})_3\text{Mo}]_2\text{Hg}$ by an exchange reaction of molybdenum hydride with $\text{Cp}(\text{CO})_3\text{MoHgGeEt}_3$ according to Eq. (5) (see Scheme 1). The second path of the formation of $[\text{Cp}(\text{CO})_3\text{Mo}]_2\text{Hg}$, by symmetrization of $\text{Cp}(\text{CO})_3\text{MoHgGeEt}_3$, also cannot be ruled out.

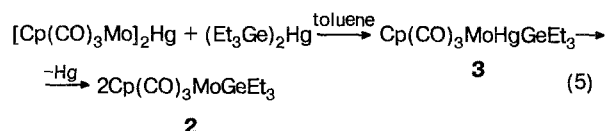


The reaction of $[\text{Cp}(\text{CO})_3\text{Mo}]_2\text{Hg}$ with compound **1** in toluene, unlike that of $[\text{Cp}(\text{CO})_3\text{Mo}]_2$, does not yield

Scheme 1

1. $[\text{Cp}(\text{CO})_3\text{Mo}]_2 + (\text{Et}_3\text{Ge})_2\text{Hg} \rightarrow [\text{Cp}(\text{CO})_3\text{Mo}]_2^{\cdot-} + (\text{Et}_3\text{Ge})_2\text{Hg}^{\cdot+}$
 $[\text{Cp}(\text{CO})_3\text{Mo}]_2^{\cdot-} \rightarrow \text{Cp}(\text{CO})_3\text{Mo}^{\cdot-} + \text{Cp}(\text{CO})_3\text{Mo}^{\cdot-}$
 $(\text{Et}_3\text{Ge})_2\text{Hg}^{\cdot+} \rightarrow \text{Et}_3\text{Ge}^{\cdot+} + \text{Et}_3\text{GeHg}^{\cdot+}$
2. $\text{Cp}(\text{CO})_3\text{Mo}^{\cdot-} + \text{SH} \rightarrow \text{Cp}(\text{CO})_3\text{MoH} + \text{S}^{\cdot-}$
 $\text{Cp}(\text{CO})_3\text{MoH} + \cdot\text{GeEt}_3 \rightarrow \text{Cp}(\text{CO})_3\text{Mo}^{\cdot-} + \text{Et}_3\text{GeH}$
 $2\text{Cp}(\text{CO})_3\text{Mo}^{\cdot-} \rightarrow [\text{Cp}(\text{CO})_3\text{Mo}]_2$
3. $2\text{Et}_3\text{Ge}^{\cdot-} \rightarrow (\text{Et}_3\text{Ge})_2$
4. $\text{Cp}(\text{CO})_3\text{Mo}^{\cdot-} + \text{Et}_3\text{GeHg}^{\cdot+} \rightarrow \text{Cp}(\text{CO})_3\text{MoHgGeEt}_3$
 $\text{Cp}(\text{CO})_3\text{MoHgGeEt}_3 \xrightarrow{-\text{Hg}} \text{Cp}(\text{CO})_3\text{MoGeEt}_3$
5. $\text{Cp}(\text{CO})_3\text{MoH} + \text{Cp}(\text{CO})_3\text{MoHgGeEt}_3 \rightarrow [\text{Cp}(\text{CO})_3\text{Mo}]_2\text{Hg} + \text{Et}_3\text{GeH}$

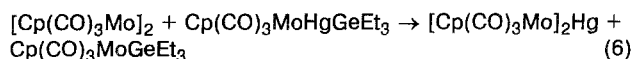
a large amount of radical products (~12 %) and gives compound **2** as the main product.



The reaction of $[\text{Cp}(\text{CO})_3\text{Mo}]_2\text{Hg}$ with **1** in THF occurs according to Eq. (3) and affords approximately equal amounts of $\text{Cp}(\text{CO})_3\text{MoHgGeEt}_3$ and $\text{Cp}(\text{CO})_3\text{MoH}$ at the first stage. Thus, the reactions of $[\text{Cp}(\text{CO})_3\text{Mo}]_2$ and $[\text{Cp}(\text{CO})_3\text{Mo}]_2\text{Hg}$ with $(\text{Et}_3\text{Ge})_2\text{Hg}$ in THF occur by the same radical mechanism. The formation of the same products at the first stage of these reactions leads to identical final products as well.

The character of the final products is determined by the capability of $\text{Cp}(\text{CO})_3\text{MoHgGeEt}_3$ and $\text{Cp}(\text{CO})_3\text{MoH}$ produced at the first stage of the reaction to undergo further transformations. Recall that complex $\text{Cp}(\text{CO})_3\text{MoHgGeEt}_3$ is thermally unstable and decomposes on storage in solution at 20 °C within several hours to give mercury and predominantly $\text{Cp}(\text{CO})_3\text{MoGeEt}_3$. Therefore, when reactions (3) and (5) are carried out with an excess of **1** in toluene, the prevailing route is demercuration of $\text{Cp}(\text{CO})_3\text{MoHgGeEt}_3$ to yield $\text{Cp}(\text{CO})_3\text{MoGeEt}_3$, which shifts equilibrium (4) toward the formation of $[\text{Cp}(\text{CO})_3\text{Mo}]_2\text{Hg}$. In the absence of an excess of **1**, symmetrization occurs synchronously with demercuration. Two transformation routes giving symmetrical products are possible: interaction of **3** with the dimer (reaction 6) and with molybdenum hydride (reaction

(5), see Scheme 1) to give the products of complete substitution.



Thus, the reaction of $[\text{Cp}(\text{CO})_3\text{Mo}]_2$ with $(\text{Et}_3\text{Ge})_2\text{Hg}$ occurs by a radical mechanism in both THF and toluene, whereas the reaction of $[\text{Cp}(\text{CO})_3\text{Mo}_2]\text{Hg}$ has a radical character only in THF. The formation of $\text{Cp}(\text{CO})_3\text{MoH}$ at the first stage of these reactions exerts a substantial effect on the further course of the reaction. The data obtained allow one to suggest that the possibility of radical processes in the reactions of carbonyl complexes of other transition metals (Mn, Fe, Co, Re) with organodimetallic mercury derivatives also cannot be ruled out.

Experimental

Five products were isolated from the reaction mixture after the reaction of $[\text{Cp}(\text{CO})_3\text{Mo}]_2$ with $(\text{Et}_3\text{Ge})_2\text{Hg}$ (1): $\text{Cp}(\text{CO})_3\text{MoGeEt}_3$ (2), $[\text{Cp}(\text{CO})_3\text{Mo}]_2\text{Hg}$, $[\text{Cp}(\text{CO})_3\text{Mo}]_2$, Et_3GeH , and $(\text{Et}_3\text{Ge})_2$. Digermane was identified by chroma-

tography, the other four products and the intermediate compounds, $\text{Cp}(\text{CO})_3\text{MoHgGeEt}_3$ (3) and $\text{Cp}(\text{CO})_3\text{MoH}$ were identified on the basis of their IR spectra recorded on a UR-20 spectrophotometer. IR (toluene), $\nu(\text{CO})/\text{cm}^{-1}$: $[\text{Cp}(\text{CO})_3\text{Mo}]_2$ — 1915, 1960, 2018; $[\text{Cp}(\text{CO})_3\text{Mo}]_2\text{Hg}$ — 1893, 1993, 2000; $\text{Cp}(\text{CO})_3\text{MoHgGeEt}_3$ — 1873, 1900, 1976; $\text{Cp}(\text{CO})_3\text{MoGeEt}_3$ — 1905, 1925, 1995; $\text{Cp}(\text{CO})_3\text{MoH}$ — 1940, 2028. The Ge—H stretching vibration in triethylgermane is observed at 2008 cm^{-1} .

References

1. G. A. Abakumov, A. N. Tatarnikov, E. N. Gladyshev, S. Ya. Khorshev, and M. I. Sykhrannova, *Abs. pap. of V All-Union conference on organometallic chemistry*, Riga, 1991, 202 (in Russian).
2. C. L. Word and J. K. Kochi, *J. Am. Chem. Soc.*, 1979, **101**, 5593.
3. S. Furuzumi, J. K. Kochi, and C. L. Word, *J. Am. Chem. Soc.*, 1980, **102**, 2928.
4. R. J. Klinger and J. K. Kochi, *J. Am. Chem. Soc.*, 1981, **103**, 5839; *Ibid.*, 1982, **104**, 4186.
5. G. A. Abakumov, A. N. Tatarnikov, M. I. Sykhrannova, S. Ya. Khorshev, and E. N. Gladyshev, *Metalloorgan. Khim.*, 1992, **5**, 941 [*J. Organomet. USSR*, 1992, **5** (Engl. Transl.)].

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Isomerism in metal complexes of 1,3,5-diazaphosphorinanes. Synthesis, crystal and molecular structure of conformers of *cis*-bis(1,3,5-triphenyl-1,3,5-triazaphosphorinane)dichloroplatinum(II)

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The crystal and molecular structures were determined for two individual conformers of *cis*-bis(1,3,5-triphenyl-1,3,5-diazaphosphorinane)dichloroplatinum(II) differing in the rotation of the heterocyclic ligand planes around the P—Pt bond and in the orientation of the substituents at the phosphorus atoms in the ligands.

Key words: metal complexes of 1,3,5-diazaphosphorinanes, isomerism, synthesis, crystal and molecular structure.

Heterocyclic phosphines used as ligands are remarkable for the fact that they can occur in solution as a mixture of a limited number of stable conformers differing in their steric and electronic properties.

1,3,5-Diazaphosphorinanes exist in solution preferentially in the chair conformation with triequatorial orientation of the substituents at the heteroatoms.¹ In metal complexes, conformational mobility of the ligands