NEW REACTION PATHWAYS OF ORGANOSILICON AND ORGANOGERMANIUM MERCURY DERIVATIVES WITH CYCLOPENTADIENYL AND CARBONYL COMPLEXES OF IRON, COBALT, AND NICKEL

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Our method for the preparation of organobimetallic compounds with a Ge-M group (M = Fe, Co, N) is based on the reaction of bis(triethylgermyl)mercury (I) with half-sandwich complexes of Ni and Fe, π -CpFe(CO)₂X, π -CpNi(PPh₃)Cl, and their dimers, $[\pi$ -CpFe(CO)₂]₂ and $[\pi$ -CpNi(CO)]₂ as well as cobalt carbonyl compounds, Co₂(CO)₈, Co(CO)₄HgCl, and $[Co(CO)_4]_2$ Hg [1-3]. In each case, the selection of the reaction temperature and duration was made relative to the end of the liberation of metallic mercury. The schemes for almost all these reactions are obvious and the formation of unstable intermediates with Ge-Hg-M (M = Fe, Ni, Co) is beyond doubt. Only the reactions of (I) with Fe and Ni halide complexes remain unclear. Two alternative pathways may be proposed for these reactions leading to the same final products.

 $(Et_{3}Ge)_{2}Hg + \pi - CpML_{n}X - \left| \begin{array}{c} [Et_{3}GeHgX] \\ \neg Hg \\ b \ [\pi - CpML_{n}HgGeEt_{3}] (II) \\ \hline \\ (I) \\ M = Fe, \ L_{n} = (CO)_{2}; \ M = Ni, \ L_{n} = PPh_{3} \end{array} \right| \rightarrow \pi - CpML_{n}GeEt_{3} + Et_{3}GeX$ (1)

Recently, we have established that pathway (a) in reaction (1) does not obtain, while intermediate (II) participates in further transformations depending on the temperature conditions: a) symmetrization and/or b) demercuration.

(II)
$$(II) \xrightarrow{\text{(a)} 1/_2 (I) + 1/_2 [\pi - CpFe(CO)_2]_2Hg} (2)$$

$$(II) \xrightarrow{\text{(b)}} Hg + \pi - CpFe(CO)_2 - GeEt_8$$

Symmetrization reaction (2a) is typical for mercury derivatives with an M-Hg-R group, where M is a transition metal and R is an alkyl [5] or aryl group [6]. We have recently shown that π -CpFe(CO)₂-Hg-GePr-I₃ also undergoes symmetrization without any side-products [4]. These reactions apparently fit into a single scheme, while the nature of the final products is a function of the relative stability of intermediate (II).

In the present work, we attempted to clarify the factors determining this stability. The demercuration reaction proved characteristic for (I) and π -CpNi(PPh₃)Cl.

$$(1) + \pi - CpNi(PPh_3)Cl \rightarrow \pi - CpNi(PPh_3)HgGeEt_3 \rightarrow \rightarrow Hg + \pi - CpNi(PPh_3)GeEt_3 \qquad (3)$$

The mercury formation begins at a significant rate even at -70° C, while the yield of Hg over 1 h at 20°C is 95%. Changing the ratio of the initial reagents to (I)/ π -CpNi(PPh₃)Cl mole ratio = 1/2 does not suppress the demercuration reaction. Thus, the mercury yield at -50° C over 12 h is 90%. Demercuration is sharply reduced upon replacing (I) by (Et₃Si)₂Hg. The mercury yield is 20% at -40° C. The major reaction product was a new compound, [π -CpNi(PPh₃)]₂Hg (III) forms red crystals, which are moderately soluble in ordinary organic solvents. The formation of metallic mercury is virtually suppressed in the reaction of π -CpNi(PPh₃)Cl with bis-(triisopropylgermyl)mercury. The yield of (III) was 84%. The tendency noted for an increase in the yield of (III) with the concurrent suppression of the demercuration reaction is in accord with increasing strength of the EIV-Hg bond (E^{IV} = Si, Ge) in the series (Et₃Ge)₂Hg < (Et₃Si)₂Hg, (i-Pr₃Ge)₂Hg [7]. The equilibrium in type-(2a) reactions is shifted toward the left due to the irreversible demercuration of (II) by the pathway (4a) \rightarrow (II) \rightarrow (4b).

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$$[\pi\text{-Cp}_{m}M(L)_{n}]_{2}Hg + (R_{3}E^{IV})_{2}Hg \stackrel{(a)}{\longleftrightarrow} 2 [\pi\text{-Cp}_{m}M(L)_{n}Hg - E^{IV}R_{3} \\ -Hg \downarrow (b) \qquad (II) \\ \pi\text{-Cp}M(L)_{n} - E^{IV}R_{3} \\ M = Ni, L = PPh_{3}, m = n = 1, E^{IV} = Ge, R = Et, Pr-i \\ M = Fe, L = CO, m = 1, n = 2, E^{IV} = Ge, R = Et. \\ M = Co, L = CO, m = 0, n = 4, E^{IV} = Si, Ge [3], R = Et$$

It was established that in this reaction of mercury salts of Fe, Ni, and Co with organosilicon and organogermanium mercury derivatives (4), the formation of mercury in the reaction of (III) with (I) begins immediately upon thawing of the reaction mixture, while prolonged maintenance at 20°C or elevated reaction temperatures up to 90-100°C is required for the other reactions. These reactions again demonstrated the greatest lability of intermediate π -CpNi-(PPh₃)-Hg-GeEt₃ and provide an explanation for the absence of the mercurating effect of (I) on π -CpNi(PPh₃)Cl.

Equimolar mixtures of $Co_2(CO)_8$ or $Co(CO)_4$ HgCl with (I) rather rapidly form mercury [3]. We have shown that the demercuration of the intermediates may be suppressed under comparable conditions by doubling the initial concentrations of $Co_2(CO)_8$ or $Co(CO)_4$ HgCl.

$$2\operatorname{Co}_{2}(\operatorname{CO})_{8} + (\operatorname{R}_{3}\operatorname{E}^{\mathrm{IV}})_{2}\operatorname{Hg} \rightarrow [\operatorname{Co}(\operatorname{CO})_{4}]_{2}\operatorname{Hg} + 2\operatorname{R}_{3}\operatorname{E}^{\mathrm{IV}} - \operatorname{Co}(\operatorname{CO})_{4}$$
(5)

$$\operatorname{E}^{\mathrm{IV}} = \operatorname{Si}, \ \operatorname{R} = \operatorname{Et}; \ \operatorname{E}^{\mathrm{IV}} = \operatorname{Ge}, \ \operatorname{R} = \operatorname{Et}, \ \operatorname{Pr-}i$$

$$2\operatorname{Cl}\operatorname{Hg}\operatorname{Co}(\operatorname{CO})_{4} + (\operatorname{Et}_{3}\operatorname{Ge})_{2}\operatorname{Hg} \rightarrow 2\operatorname{Hg} + 2\operatorname{Et}_{3}\operatorname{Ge}\operatorname{Cl} + [\operatorname{Co}(\operatorname{CO})_{4}]_{2}\operatorname{Hg}$$
(6)

(4)

The yields of $[Co(CO)_4]_2$ Hg are rather high (54-80%). The proposed scheme for the formation of the mercury salts of transition metals, $[\pi-Cp_mM(L)_n]_2$ H by the symmetrization of intermediates $\pi-Cp_mM(L)_n$ -Hg-EIVR₃ is quite likely not the only pathway. It is reasonable to assume the participation of these intermediates in the exhaustive substitution of the second fragment F₃EIV, for example,

$$Et_{3}SiHgCo(CO)_{4} + Co_{2}(CO)_{8} \rightarrow [Co(CO)_{4}]_{2}Hg + Co(CO)_{4}SiEt_{3}$$
(7)

EXPERIMENTAL

The preparation of the starting solutions and the reactions were carried out in evacuated ampuls.

Reaction of π -CpNi(PPh₃)Cl with bis(triethylsily1)mercury. A solution of 1.47 g (3.30 mmoles) bis(triethylsily1)mercury (IV) in 10 ml toluene was added slowly to a solution of 2.79 g (6.60 mmoles) π -CpNi(PPh₃)Cl in 40 ml toluene cooled to -40°C and left overnight. The mixture turned orange and 0.66 mg-atom (20%) mercury precipitated. Toluene was replaced in the mother liquor by hexane. The temperature of the mixture was brought to -10°C to give 1.98 g (61.7%) [π -CpNi(PPh₃)]₂Hg (III), mp 179-181°C (dec.). Found: C 55.39; H 4.49%. Calculated for C₄₆H₄₀Ni₂P₂Hg: C 56.80; H 4.11%. Fractionation of the mother liquor gave 2.46 mmoles (37%) Et₃SiCl identified by gas-liquid chromatography.

Analogously, 10.69 mmoles π -CpNi(PPh₃)Cl in 50 ml toluene and 5.34 mmoles bis(triisopropylgermyl)mercury in 15 ml toluene at 20°C over 2 h gave 4.37 g (84%) (III) and 8.00 mmoles (75%) triisopropylgermanium chloride.

Reaction of $[\pi-CpNi(PPh_3)]_2Hg$ with bis(triethylgermyl)mercury (I). A solution of 1.28 g (2.47 mmoles) (I) in 10 ml toluene was added to a solution of 2.40 g (2.47 mmoles) $[\pi-CpNi-(PPh_3)]_2Hg$ in 20 ml toluene. The color of the mixture turned from orange-red to brown after 2-3 min. A precipitate of 0.94 g (95%) mercury formed. A significant portion of the toluene was removed and replaced by hexane. Low-temperature crystallization gave 2.02 g (75%) triethyl(triphenylphosphine- π -cyclopentadienylnickel)germanium, mp 119-120°C (dec.) [2].

Reaction of $[\pi-CpFe(CO)_2]_2Hg$ with bis(triethylgermyl)mercury. A solution of 0.72 g (1.30 mmoles) $[\pi-CpFe(CO_2]_2Hg$ and 0.68 g (1.30 mmoles) (I) in 20 ml toluene was heated at 100°C for 6 h. A precipitate of 0.52 g (~100%) mercury formed. Toluene was removed in vacuum. The residue gave 2.34 mmoles (90%) triethyl(dicarbonyl- π -cyclopentadienyliron)germanium.

<u>Reaction of $[Co(CO)_4]_2$ Hg with bis(triethylsilyl)mercury.</u> A mixture of 2.18 g (4.02 mmoles) $[Co(CO)_4]_2$ Hg and 1.79 g (4.15 mmoles) (IV) was shaken at about 20°C for 24 h. The precipitate of 0.98 g (77%) mercury was removed and the residue was distilled in vacuum to give 1.29 g (56%) triethylsilylcobalt tetracarbonyl, bp 69-70°C (1 mm), n_D^{22} 1.5200. Found: C 42.03; H 4.92%. Calculated for C₁₀H₁₅COSiO₄: C 41.95; H 5.24%.

Reaction of $Co(CO)_4HgCI$ with bis(triethylgermyl)mercury. A solution of 1.99 g (3.84 mmoles) (I) in 10 ml toluene was added to a solution of 3.12 g (7.67 mmoles) $Co(CO)_4HgCI$ in 20 ml toluene. The mixture turned from yellow to light orange over 10 min. A precipitate of 6.25 mg-atom (82%) mercury formed. The solvent and volatile products containing 5.7 mmoles (74%) Et₃GeCl were removed in vacuum. Low-temperature crystallization of the residue from hexane gave 1.37 g (66%) $[Co(CO)_4]_2$ Hg.

CONCLUSIONS

1. Organosilicon and organogermanium mercury derivatives may act as mercurating agents of carbonyl and half-sandwich complexes of transition metals.

2. The nature of the substituents at the mercury atom in the intermediates of these reactions as well as the reaction conditions determine the pathways for the further transformation of these species.

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NEW PARAMETRIZATION FOR MINDO/3 CALCULATIONS OF THE STRUCTURE OF COMPOUNDS

WITH N-N BONDS

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The semiempirical MINDO/3 quantum chemical method [1] parametrized to reproduce the enthalpies of formation and equilibrium geometrical indices of organic molecules is commonly employed to solve problems in quantum chemistry. One of the inadequacies which narrows the range of application of this method is the incorrect description of atoms having unshared electron pairs. As a consequence, errors arise in the determination of the optimal conformations, underestimation of O-O and N-N bonds, the prediction of O-O and F-F bridging bonds which do not actually exist, and the significant underestimation of the enthalpies of formation of compounds. In our view, these disadvantages are related to the nonoptimal selection of the reference compounds used for the parametrization. Although Dewar et al. [1] do not directly list these compounds, it is clear from their work that H_2 , N_2 , O_2 , F_2 , CO, NO, and other diatomic molecules were used in the parametrization procedure.

We considered it logical, in light of the special nature of the chemical bonds in these compounds (with very short bond lengths, as a rule, in comparison with other molecules) to exclude these molecules from the list of reference molecules in the selection of the parameters. We also used a scheme proven helpful for organophosphorus compounds: the set of one-atom parameters of the method was not altered, while only the values of the two-atom parameters, α_{XY} and B_{XY} in the formulas for the approximation of the resonance integrals and node-node inter-actions [1] were varied. Such a selection was carried out for molecules with N-N bonds, for

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