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The Reaction of Tris(triphenylphosphine)platinum with an Ironcarbonyl Mercurial. Further Synthesis of New Oligometallic Chains

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We have recently described the reaction between zerovalent complexes of platinum or palladium and various organomercurials, the initial step being the carbenoid insertion of L_2M moiety into the mercury–element σ-bond [1, 2]. Thus far the element has been mostly the carbon or halogen atom. Yet we have used mercuric as well as cadmium or zinc derivatives of triorganogermane and -stannane in this reaction in order to construct the four-atom chains made of different metal atoms [3, 4]. In this Letter, we report that this reaction can be extended to the ironcarbonyl mercurial to afford σ-platinumiron derivatives and novel four-atom heterometallic chains.

Iron pentacarbonyl is known to form readily the dimercurial $Fe(CO)_4(HgX)_2$ which is not soluble, however. Much more soluble are diammino derivatives, for instance bis(pyridine)di(chloromercuri)irondicarbonyl [5] which has been chosen as a starting compound. Tetrahydrofurane as an electron donating solvent promotes the decomposition of platinum-mercury compounds. Therefore the insertion product I can be isolated only on chilling.

$$\mathrm{XHg{-}Fe(py)_2(CO)_2{-}HgX} \xrightarrow{\mathrm{L_3Pt}}$$

$$\underset{\mathrm{I}}{\mathrm{XHg{-}Fe(py)_2(CO)_2{-}Hg{-}PtL_2{-}X}} \xrightarrow[\mathrm{-Hg}]{}$$

$$\underset{\mathrm{II}}{\mathrm{XHg{-}Fe(py)_2(CO)_2{-}PtL_2X}}$$

At room temperature a rather rapid demercuration gives II in high yield. The presence of Pt–Hg σ-bond in I has been detected by the mercury elimination upon treatment with CF_3COOH that is characteristic of this kind of intermetallic compounds. At the moment we are not able to exclude the alternative structure for I resulting from the insertion of L_2Pt between mercury and iron atoms. Further reaction of II with L_3Pt yields the diplatinum derivative IV. The tetrametallic intermediate III appears to be unstable and decomposes even at –30 °C, which is presumably connected with the stronger electro-donating effect of Pt–Fe bond compared to Pt–Hg. The neighbour electron-withdrawing groups are well known to increase the stability of intermetallic chains [3].

$$\mathrm{XHg{-}Fe(py)_2(CO)_2{-}PtL_2X} \xrightarrow{\mathrm{L_3Pt}}$$

$$\underset{\mathrm{III}}{\mathrm{X{-}PtL_2{-}Hg{-}Fe(py)_2(CO)_2PtL_2X}} \xrightarrow[\mathrm{-Hg}]{}$$

$$\underset{\mathrm{IV}}{\mathrm{XPtL_2{-}Fe(py)_2(CO)_2{-}PtL_2X}}$$

Thus metal carbonyl mercurials appear to be capable of reacting with zerovalent complexes of platinum metals just like real organomercurials. Now the work on mercuric derivatives of manganese and rhenium carbonyls is in progress.

Experimental

Chloromercuri-bis(pyridine)dicarbonylironmercur-bis-(triphenylphosphine)platinumchloride (I)

The solution of 0.37 g (0.05 mmol) of bis(pyridine)di(chloromercuri)irondicarbonyl [5] in 50 ml THF was chilled to –30 °C and, under argon, 0.5 g of $(Ph_3P)_3Pt$ in 25 ml of toluene were added. The dark-red colour appeared immediately. The reaction mixture was maintained during 24 h at 0 °C. The light yellow product was crystallized. Crystals were washed with toluene, then pentane to afford 0.64 g (87%) of I, m.p. 286–288 °C. *Anal.* Found: C 38.54, H 2.76, Hg 26.81, Cl 5.21. $C_{48}H_{40}N_2O_2Cl_2FeHg_2P_2Pt$ (calc.): C 39.42, H 2.74, Hg 27.44, Cl 4.86 %.

Chloromercuri-bis(pyridine)dicarbonyliron-bis(triphenylphosphine)platinumchloride (II)

To 0.37 g of the same ironmercurial in 30 ml THF were added, under argon, at room temperature 0.5 g of $(Ph_3P)_3Pt$ in 25 ml of benzene. After 5 h the separating mercury was removed, the filtrate was evaporated to dryness and the residue thoroughly washed with a hexane–benzene mixture (5:1). 0.47 g (74%) of II was obtained, m.p. 268–270 °C. *Anal.* Found: C 45.22, H 3.12, Hg 14.94, Cl 5.38. $C_{48}H_{40}N_2O_2Cl_2FeHgP_2Pt$ (calc.): C 45.68, H 3.18, Hg 15.86, Cl 5.63 %.

Di-[bis(triphenylphosphine)platinumchloride]-bis(pyridine)irondicarbonyl (IV)

To a solution of II (0.63 g, 0.5 mmol) in 50 ml THF were added under argon at room temperature 0.5 g of $(Ph_3P)_3Pt$. Mercury was removed after 24 h, the filtrate was evaporated to one-half volume and the product was precipitated with hexane (20 ml). After washing with hexane–benzene, 0.8 g (81%) of IV was obtained, m.p. 242–246 °C. *Anal.* Found: C 56.66, H 3.88, Cl 4.04. $C_{84}H_{70}N_2O_2Cl_2FeP_4Pt_2$ (calc.): C 56.97, H 3.96, Cl 4.00 %.

The carbonyl stretching frequencies are reported in the Table. IR spectra were obtained in KBr disks by use of a Beckmann UR-10 spectrophotometer.

TABLE I. Carbonyl IR Bands (cm^{-1}) in Mercury and Platinum Derivatives of Bis(pyridine)irondicarbonyl.

Compound	ν_{CO}	
$Fe(py)_2(CO)_2(HgCl)_2$	2008	2070
I	1980	2050
II	1945	1985
IV	1930	1965

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