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Abstract

Full Text

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MIXED BIMETALLIC ORGANIC DERIVATIVES OF RHENIUM CARBONYL

By the interaction of sodium rheniumpentacarbonyl with the chlorides of triphenyltin, diphenyltin, triphenyllead, diphenylbismuth, and cyclopentadienylirondicarbonyl, we obtained triphenyltin rheniumpentacarbonyl, triphenyllead rheniumpentacarbonyl, diphenylbismuth rheniumpentacarbonyl, cyclopentadienyldicarbonyliron rheniumpentacarbonyl, and diphenyltin di(rheniumpentacarbonyl).

All the compounds obtained are crystalline substances, soluble in polar organic solvents and insoluble in water. The iron–rhenium and bismuth–rhenium derivatives decompose in solution.

Under the action of electrophilic reagents—chlorine, bromine, and hydrogen chloride—on the rhenium–lead and rhenium–iron organic derivatives, cleavage of the metal–metal bond occurs.

Rhenium–tin organic derivatives, on reacting with the same reagents, retain the metal–metal bonds, but complete or partial replacement of phenyl radicals by halides takes place. Chlorine acts on triphenyltin rhenium pentacarbonyl, dissolved in carbon tetrachloride, with formation of trichlorostannyl rhenium pentacarbonyl. The same product was obtained by treating triphenyltin rhenium pentacarbonyl with dry hydrogen chloride in a carbon tetrachloride solution at −5 to −15°.

By the action of an excess of bromine on triphenyltin rhenium pentacarbonyl and on diphenyltin di(pentacarbonylrhenium) in a mixture of heptane with benzene, tribromostannyl rhenium pentacarbonyl and dibromostannyl di(pentacarbonylrhenium) were isolated.

When two molecules of bromine acted on triphenyltin rhenium pentacarbonyl, phenyldibromostannyl rhenium pentacarbonyl was obtained, and when one molecule of bromine acted under the same conditions on triphenyltin rhenium pentacarbonyl and diphenyltin di(pentacarbonylrhenium), diphenylbromostannyl rhenium pentacarbonyl was isolated in the first case, and phenylbromostannyl di(pentacarbonylrhenium) in the second.

By the interaction of phenyldibromostannyl rhenium pentacarbonyl with two molecules of sodium rhenium pentacarbonyl in tetrahydrofuran, monophenylstannyl tri(pentacarbonylrhenium) was obtained; this, in turn, was treated with an excess of bromine, as a result of which monobromostannyl tri(pentacarbonylrhenium) was isolated. On interaction of the latter with sodium rhenium pentacarbonyl in tetrahydrofuran, a light-yellow crystalline compound was obtained, the analytical data for which agree well with the formula $[(CO)_5Re]_3Sn—Sn—[Re(CO)_5]_3$.

Bromination of triphenyllead rhenium pentacarbonyl led to the isolation of bromorhenium pentacarbonyl and lead bromide. When bromine was applied to $C_5H_5(CO)_2Fe—Re(CO)_5$ in carbon tetrachloride solution at −10 and −15°, only bromorhenium pentacarbonyl was isolated.

Experimental Part

$(C_6H_5)_3SnRe(CO)_5$: on interaction of 2.9 g (0.0075 mole) of $(C_6H_5)_3SnCl$ with $NaRe(CO)_5$ (in 30 ml of THF), obtained from 2.45 g (0.0038 mole) of $Re_2(CO)_{10}$ and 50 ml of 0.8% sodium amalgam, at room temperature over 3.5 hours, 3.87 g (77%) of a white crystalline product with m.p. 142-143° was isolated.

Found, %: C 40.91, 40.64; H 2.27, 2.56
$C_{23}H_{15}O_5ReSn$. Calculated, %: C 40.90; H 2.22

Mol. wt. found 653, 687; calculated 676.

IR spectrum (ν—cm^{-1})*: 395 (medium), 425 (weak), 450 (medium), 523 (weak), 585 (very weak), 699 (strong), 751 (strong), 766 (strong), 1002 (weak), 1024 (weak), 1073 (medium), 1378 (weak), 1427 (medium), 1463 (medium), 1480 (weak), 1980–2030 (very weak), 2116 (strong), 2864 (strong), 2935 (strong), 3070 (medium).

$(C_6H_5)_2Sn[Re(CO)_5]_2$: on addition of 2.8 g (0.008 mole) of $(C_6H_5)_2SnCl_2$ to $NaRe(CO)_5$ (40 ml of THF), obtained from 5.6 g (0.008 mole) of $Re_2(CO)_{10}$ and 100 ml of 0.8% sodium amalgam over 2.5 hours at 20-25°, 3.8 g (51%) of a colorless (with a yellowish tint) crystalline product with m.p. 139° was isolated.

Found, %: C 28.59, 28.58; H 1.17, 1.29
$C_{22}H_{10}O_{10}Re_2Sn$. Calculated, %: C 28.55; H 1.09

Mol. wt. (in benzene) found 902, 901; calculated 925.

IR spectra (ν—cm^{-1}): 403 (medium), 426 (weak), 447 (medium), 525 (weak), 586 (strong), 699 (weak), 746 (medium), 761 (medium), 1432 (weak), 1469 (very weak), 1970–2000 (very weak), 2025 (strong), 2100 (strong), 2119 (medium), 2864 (medium), 2933 (strong).

$Cl_3SnRe(CO)_5$: a) upon the action of an excess of Cl_2 on a solution of 0.5 g (0.00075 mole) of $(C_6H_5)_3SnRe(CO)_5$ in CCl_4 (20 cm^3) at a temperature of −5° for 15 min, 0.28 g (70%) of a colorless product was isolated, decomposing at 220° without melting.

Found, %: C 10.56, 10.62; Cl 19.19, 20.00
$C_5O_5ReSnCl_3$. Calculated, %: C 10.88; Cl 19.33

b) Over 0.5 hour at −5 and −10° an excess of anhydrous HCl was passed through a solution of 0.3 g (0.00045 mole) of $(C_6H_5)_3SnRe(CO)_5$ in CCl_4 (20 cm^3). Obtained was 0.18 g (75%) of a white product, which at 220° decomposes without melting.

Found, %: C 10.41, 10.58; Cl 19.74, 20.10
$C_5O_5ReSnCl_3$. Calculated, %: C 10.88; Cl 19.33

$Br_3SnRe(CO)_5$: 0.4 g (0.0025 mole) of Br_2 reacts with 0.6 g (0.0009 mole) of $(C_6H_5)_3SnRe(CO)_5$ in 20 ml of solution (heptane—benzene, 1 : 1) at 0°–(−5°) over 1 hour. The colorless product, isolated in an amount of 0.6 g (98%), at a temperature of 220° decomposes without melting.

Found, %: C 8.62
$C_5O_5ReSnBr_3$. Calculated, %: C 8.76

$Br_2Sn[Re(CO)_5]_2$: 0.22 g (0.00024 mole) of $(C_6H_5)_2Sn[Re(CO)_5]_2$ in 25 ml of solution (heptane—benzene, 1 : 1) reacts with an excess of Br_2 at a temperature of −10° over 0.5-1 hour. A white crystalline product was isolated in an amount of 0.22 g (98%). It does not melt up to 300°. Mol. wt. found 957, 961; calculated 931.

Found, %: C 12.54; 12.62
$C_{10}O_{10}Re_2SnBr_2$. Calculated, %: C 12.89

$C_6H_5Br_2SnRe(CO)_5$: upon interaction of 0.5 g (0.00075 mole) of $(C_6H_5)_3SnRe(CO)_5$ in 30 ml of solution (heptane—benzene, 1 : 1) with 0.24 g (0.0015 mole) of Br_2 under cool— cooling to −10° for 0.5 hour, 0.32 g (64%) of a product was obtained, which melts at 129—130°.

Found, %: C 19.13, 18.86; H 1.05, 0.85.
$C_{11}H_5O_5ReSnBr_2$. Calculated, %: C 19.36; H 0.74

$C_6H_5SnRe(CO)_5$: 2.0 g (0.0029 mole) of $C_6H_5Br_2SnRe(CO)_5$ and $NaRe(CO)_5$, prepared from 2.1 g (0.0029 mole) of $Re_2(CO)_{10}$ and 30 ml of THF, with 40 ml of 0.8% sodium amalgam, react at 20—25° for 1—1.5 hours. The isolated 1.4 g (40.1%) of a light-yellow crystalline product melts at 189°:

Found, %: C 21.73, 21.63; H 0.54, 0.81
$C_{21}H_5O_{15}Re_3Sn$. Calculated, %: C 21.46; H 0.43

* The IR spectra were measured by Yu. N. Sheinker and G. G. Dvoryantseva, to whom the authors express their gratitude.

$BrSn[Re(CO)_5]_3$: a) 2 g (0.0021 mole) of $Br_2Sn[Re(CO)_5]_2$ was added to $NaRe(CO)_5$, prepared from 0.7 g (0.00105 mole) of $Re_2(CO)_{10}$ and 14 ml of 0.8% sodium amalgam in 50 ml of THF for 1 hour at −20—25°. A white product was isolated. It does not melt up to 300°.

Found, %: C 14.95, 15.04;
$C_{15}O_{15}Re_3SnBr$. Calculated, %: C 15.29

b) Bromination with an excess of Br_2 of 0.3 g (0.00025 mole) of $C_6H_5Sn[Re(CO)_5]_3$ at −5—10° for 0.5 hour leads to the formation of a white product, not melting up to 300°.

Found, %: C 14.97; 14.90
$C_{15}O_{15}Re_3SnBr$. Calculated, %: C 15.29

$[Re(CO)_5]_3Sn—Sn[Re(CO)_5]_3$: 1.1 g (0.0015 mole) of $Br_3SnRe(CO)_5$ was added to $NaRe(CO)_5$, prepared from 2 g (0.003 mole) of $Re_2(CO)_{10}$ and 40 ml of sodium amalgam in 30 ml of THF, at 20—25° for 1.5 hours. The obtained yellow product does not melt up to 300°.

Found, %: C 16.29; 16.42
$C_{30}O_{30}Re_6Sn_2$. Calculated, %: C 16.41

$(C_6H_5)_3PbRe(CO)_5$: 1.45 g (0.003 mole) of $(C_6H_5)_3PbCl$ was added to $NaRe(CO)_5$, prepared from 1 g (0.0015 mole) of $Re_2(CO)_{10}$ and 20 ml of 0.8% sodium amalgam in 50 ml of THF, at 50° for 1.5 hours. 1.7 g (78%) of a white crystalline product with m.p. 131—133° was isolated.

Found, %: C 36.19, 36.17; H 2.08, 1.98; Pb 26.97, 26.95
$C_{23}H_{15}O_5RePb$. Calculated, %: C 36.13; H 1.97; P

$C_5H_5Fe(CO)_2Re(CO)_5$: 0.65 g (0.003 mole) of $C_5H_5Fe(CO)_2Cl$ reacts with $NaRe(CO)_5$, prepared from 1 g (0.0015 mole) of $Re_2(CO)_{10}$ and 20 ml of 0.8% sodium amalgam, for 2.5 hours at room temperature (20—25°). 0.74 g (48%) of a brown crystalline product with m.p. 72—74° was obtained.

Found, %: C 28.99, 28.90; H 1.06, 1.05; Fe* 10.84, 10.93
$C_{12}H_5O_7ReFe$. Calculated, %: C 28.70; H 0.99; F

Molecular weight found 504, 503 (cryoscopically, in benzene), calculated 503.

$(C_6H_5)_2BiRe(CO)_5$: $NaRe(CO)_5$, prepared from 2 g (0.003 mole) of $Re_2(CO)_{10}$ and 40 ml of 0.8% sodium amalgam, reacts with 2.44 g (0.006 mole) of $(C_6H_5)_2BiCl$ for 0.5 hour at 20—25°. Sublimation ($t = 40^\circ/1 \cdot 10^{-2}$ mm) gives 2.8 g (66%) of a light-brown crystalline product with m.p. 60°.

Found, %: C 29.06, 29.31; H 1.31, 1.11
$C_{17}H_{20}O_{10}ReBi$. Calculated, %: C 29.47; H 1.46

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* Pb and Fe were determined by the polarographic method by E. A. Terent' eva.

Note: Figure translations are in progress. See original paper for figures.