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Abstract

Full Text

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BINUCLEAR DERIVATIVES OF CARBONYLS OF MOLYBDENUM, TUNGSTEN, MANGANESE, AND RHENIUM

In previous studies ([1,2]) we described mixed bimetallic derivatives of the carbonyls of chromium, molybdenum, tungsten, rhenium, and iron. In the present work we report newly obtained bimetallic derivatives:

$C_5H_5(CO)_3Mo—Mn(CO)_5$; (I) $C_5H_5(CO)_3Mo—Re(CO)_5$ (II)

$C_5H_5(CO)_3W—Mn(CO)_5$; (III) $C_5H_5(CO)_3W—Re(CO)_5$ (IV)

They were synthesized by the interaction of sodium salts of tricarbonyl-π-cyclopentadienylmolybdenum (tungsten) with chlorides of pentacarbonyls of manganese and rhenium. As by-products of the reaction, $[C_5H_5(CO)_3Mo]_2$ and $[C_5H_5(CO)_3W]_2$ were isolated.

The compounds obtained are stable in air and can readily be recrystallized from petroleum ether (40-60°) or *n*-hexane. They dissolve well in polar organic solvents; in nonpolar solvents they dissolve only on heating; they are insoluble in water. All compounds are colored. Products I and III have a brick-red color; products II and IV are yellow-orange.

On heating to their melting points they are stable and decompose far above their melting temperatures.

In the IR spectra there are vibrational frequencies characteristic of the principal groups of atoms constituting the molecules of cyclopentadienylmetal carbonyls and their derivatives ([3]):

CH—3130—3120 cm^{-1};
Me(CO)—2110—2008 cm^{-1}; 1992—1900 cm^{-1};
C_5H_5Me—1435—1425 cm^{-1}; 1382—1360 cm^{-1}, 1135—1115 cm^{-1};
1070—1015 cm^{-1}; 965—824 cm^{-1}.

The spectra contain vibrational frequencies at 1870 and 1865 cm^{-1}, which some investigators assign to characteristic vibrational frequencies of bridging carbonyl

groups ([4]). At present, without additional investigations, which are now being carried out, we cannot state definitely the structure of the compounds obtained.

Experimental Part

$C_5H_5(CO)_3Mo—Mn(CO)_5$. To $C_5H_5Mo(CO)_3Na$, prepared from 7.3 g (0.028 mole) of $Mo(CO)_6$ and 0.7 g of C_5H_5Na in a solution of tetrahydrofuran, 6.35 g (0.028 mole) of $ClMn(CO)_5$ (in 50 cm^3 of THF) was added at room temperature. After stirring for two hours, the solvent was removed, and the solid mixture was subjected to sublimation in high vacuum. $Mo(CO)_6$, 3.2 g, was isolated. After removal of $Mo(CO)_6$, the residue was treated several times with hot *n*-hexane. Obtained: 2.6 g of red crystals with m.p. 80.5-81.5°. Molecular weight (cryoscopic, in benzene) found: 420, 450. Calculated: 440.

Found, %: C 35.63; 35.53; H 1.28; 1.21
$C_{13}H_5O_8MoMn$. Calculated, %: C 35.44; H 1.14

IR spectrum (ν, cm^{-1})*: 400 (m), 411 (w), 444 (m), 446 (s), 492 (s), 565 (s), 588 (m), 610 (w), 643 (s), 668 (s), 710 (s), 763 (w), 790 (w), 829 (s), 839 (m), 860 (m), 888 (w),

* (s)—strong, (m)—medium, (w)—weak intensity.

931 (w), 1018 (m), 1070 (m), 1360 (m), 1380 (m), 1428 (m), 1470 (m), 1878 (s), 1900 (s), 1960 (s), 1992 (s), 2029 (s), 2088 (s), 2460 (m), 2690 (m), 2740 (m), 2860 (s), 2940 (s), 2970 (s), 3120 (m).

After additional treatment with heated tetrahydrofuran followed by cooling to −70°, a crystalline crimson substance—$C_5H_5Mo(CO)_3]_2$—was isolated in an amount of 1.8 g, m.p. 215-218°. Lit.: m.p. 215-217° ([5]).

$C_5H_5(CO)_3Mo—Re(CO)_5$. To C_5H_5Na, prepared from 0.3 g Na and 1.2 cm^3 cyclopentadiene in 100 ml tetrahydrofuran, 3.91 g (0.014 mole) $Mo(CO)_6$ was added. The reaction was conducted at 70° for two hours until carbon monoxide evolution had completely ceased. To the cooled reaction mixture (to room temperature) 5.2 g (0.014 mole) $ClRe(CO)_5$ was introduced. After completion of the reaction, the solvent was removed in vacuo. Unreacted $Mo(CO)_6$ was isolated by sublimation in high vacuum. The residue was recrystallized from *n*-heptane. 2.3 g of yellow-orange crystals, m.p. 100-100.5°, was obtained.

Found, %: C 27.45; 27.58; H 0.91; 0.83
$C_{13}H_5O_8MoRe$. Calculated, %: C 27.32; H 0.87

IR spectrum (ν, cm^{-1}): 396 (m), 425 (m), 450 (m), 468 (s), 487 (m), 503 (s), 573 (s), 585 (s), 606 (s), 711 (w), 763 (w), 824 (s), 850 (w), 897 (w), 922 (w), 942 (w), 967 (m), 1015 (m), 1062 (m), 1115 (m), 1143 (m), 1183 (w), 1266 (w), 1363 (m), 1382 (m), 1428 (m), 1435 (m), 1470 (m), 1549 (m), 1870 (s), 1900 (s),

1950 (s), 1975 (s), 2008 (s), 2038 (s), 2109 (s), 2200 (w), 2285 (w), 2450 (m), 2500 (m), 2570 (w), 2600 (w), 2735 (m), 2865 (s), 2930 (s), 2965 (s), 3125 (m).

As a by-product, 0.7 g of $[C_5H_5Mo(CO)_3]_2$, m.p. 215-217°, was isolated.

$C_5H_5(CO)_3W—Mn(CO)_5$. 4 g (0.015 mole) of $BrMn(CO)_5$ in 30 ml tetrahydrofuran (as a suspension) was added to $C_5H_5W(CO)_3Na$, prepared from 5.28 g (0.015 mole) $W(CO)_6$ and 1 g C_5H_5Na in 100 ml diglyme. The reaction mixture was vigorously stirred for 2 h. After the reaction was complete, the solvent was distilled off. Unreacted $W(CO)_6$ was removed by sublimation in high vacuum. The residue was extracted with *n*-hexane. From hexane 1.8 g of dark-red crystals, m.p. 90-91°, was isolated.

Found, %: C 29.64; 29.81; H 1.09; 1.10
$C_{13}H_5O_8WMn$. Calculated, %: C 29.55; H 0.95

In addition to the product with m.p. 90-91°, 1 g of red-violet $[C_5H_5W(CO)_3]_2$, m.p. 240-243°, was isolated. Lit.: m.p. 240-242° ([5]).

$C_5H_5(CO)_3W—Re(CO)_5$. 5.21 g of $ClRe(CO)_5$ in 50 cm^3 tetrahydrofuran (at room temperature) was added to $C_5H_5W(CO)_3Na$, prepared in 100 cm^3 diglyme from 0.3 g Na, 1.5 cm^3 C_5H_6, and 5.1 g $W(CO)_6$. After stirring for two hours at 25°, the solvent was removed. Unreacted $W(CO)_6$ was isolated by sublimation in vacuum. The residue was recrystallized from *n*-hexane. 1.3 g of a yellow crystalline substance, m.p. 110-111.5°, was obtained.

Found, %: C 23.89; 23.98; H 0.96; 0.91
$C_{13}H_5O_8WRe$. Calculated, %: C 23.67; H 0.76

IR spectrum (ν, cm^{-1}): 400 (m), 425 (w), 440 (m), 462 (m), 473 (s), 490 (s), 520 (w), 568 (s), 585 (s), 605 (s), 708 (w), 740 (w), 762 (w), 797 (w), 837 (s), 856 (m), 925 (w), 965 (w), 1015 (w), 1032 (w), 1065 (m), 1115 (w), 1135 (w), 1160 (w), 1265 (w), 1362 (m), 1381 (m), 1425 (m), 1469 (m), 1865 (s), 1895 (s), 1948 (s), 1955 (s), 1978 (s), 1986 (s), 2009 (s), 2038 (s), 2110 (s), 2275 (w), 2435 (w), 2476 (m), 2600 (w), 2870 (s), 2930 (s), 3130 (m).

$[C_5H_5W(CO)_3]_2$ was isolated in an amount of 1.2 g, m.p. 244-246°. The IR spectra were measured by Yu. N. Sheinker and G. G. Dvoryantseva, to whom the authors express their gratitude.

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