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Abstract

Full Text

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BIMETALLIC DERIVATIVES OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN CAR- BONYLS

Our previous investigations in this field were devoted to developing methods for the synthesis of chromium, molybdenum, and tungsten carbonyls (¹⁻⁵) and to studying the properties of bimetallic derivatives of rhenium carbonyl (⁶). In the present work we report mixed bimetallic derivatives of the type: $C_5H_5(CO)_3Me-Me'(C_6H_5)_3$ and $[C_5H_5(CO)_3Me]_2-Me(C_6H_5)_2$ (where Me = Cr, Mo, W; Me' = Sn, Pb), which were obtained by the interaction of sodium salts of tricarbonyl- π -cyclopentadienylmolybdenum (tungsten, chromium) with triphenyltin (lead) chlorides in tetrahydrofuran solution. The compounds obtained are white or greenish-yellow crystalline substances, soluble in common organic solvents and insoluble in water. They are all quite stable in organic solvents. On treatment with hydrogen chloride, $C_5H_5(CO)_3Mo-Sn(C_6H_5)_3$ and $C_5H_5(CO)_3W-Sn(C_6H_5)_3$ in CCl_4 solution at -15° for 30 min gave, in almost quantitative yields, $C_5H_5(CO)_3Mo-Sn(C_6H_5)Cl_2$ and $C_5H_5(CO)_3W-Sn(C_6H_5)Cl_2$.

An analogous action of hydrogen chloride on $[C_5H_5(CO)_3Mo]_2-Sn(C_6H_5)_2$ and $[C_5H_5(CO)_3W]_2-Sn(C_6H_5)_2$ led to the preparation of $[C_5H_5(CO)_3Mo]_2-SnCl_2$ and $[C_5H_5(CO)_3W]_2-SnCl_2$.

The halogenated derivative compounds obtained are light-yellow crystalline substances, stable in air and soluble in common organic solvents.

Analyses, molecular weights, and IR spectra confirm the structure of the substances we synthesized. For $C_5H_5(CO)_3Mo-Sn(C_6H_5)_3$, Zavalishin, Khot'syanova, and Struchkov* carried out an X-ray structural investigation, the results of which will be published. It follows from this work that the Mo-Sn distance in the substance described is $2.85 \pm 0.02 \text{ \AA}$, which exceeds the sum of the atomic radii of the two metals according to the data of reference (⁷) by only 0.08 \AA . Similar, but considerably larger, excesses (by $0.5-0.6 \text{ \AA}$) of the metal-metal distance were also found in the bimetallic carbonyls $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ (⁸). Thus, the Mo-Sn bond, and by analogy probably the other metal-metal bonds in the compounds we describe, are covalent bonds. This is also indicated by the solubility of our bimetallic compounds in hexane and other hydrocarbons.

Experimental Part

1. $C_5H_5(CO)_3Mo-Sn(C_6H_5)_3$. Into a 250 ml round-bottom flask equipped with a stirrer, reflux condenser, dropping funnel, and nitrogen inlet, 0.25 g of dispersed Na in tetrahydrofuran was introduced, and with constant stirring 0.7 g of freshly distilled cyclopentadiene was added in small portions. To the resulting C_5H_5Na solution, 2.7 g of $Mo(CO)_6$ was added. The reaction mixture was heated at a temperature

* The X-ray structural investigation of $C_5H_5(CO)_3Mo-Sn(C_6H_5)_3$ was carried out in the structural analysis laboratory of our institute.

60–70° until the evolution of CO ceased. To the mixture, cooled to room temperature, 3.9 g of $(C_6H_5)_3SnCl$ in 15 ml of tetrahydrofuran was added with stirring. The precipitated sodium chloride was filtered off, the solvent was removed, and the remaining mass was subjected to sublimation (75°/1 mm), as a result of which 0.1 g of $Mo(CO)_6$ was isolated. The residue after removal of molybdenum carbonyl was dissolved in a mixture of petroleum ether with benzene and chromatographed on Al_2O_3 . After recrystallization from a mixture of petroleum ether and toluene, 3.5 g of tricarbonyl- π -cyclopentadienylmolybdenumtriphenyltin with m.p. 212.5–213.5° was obtained.

$C_{26}H_{20}O_3MoSn$.	Found, %: C 52.66, 52.56; H 3.70, 3.42
	Calculated, %: C 52.43; H 3.36

Mol. wt. (cryoscopically in benzene)—found 581, 600; calculated 595.

I.R. spectrum* (ν , cm^{-1}): 446 (m); 482 (w); 512 (m); 575 (m); 590 (m); 680 (w); 725 (m); 747 (m); 822 (m); 840 (w); 996 (w); 1026 (w); 1074 (w); 1161 (w); 1192 (w); 1302 (w); 1336 (w); 1385 (m); 1408 (m); 1431 (m); 1462–1468 (w); 1481 (w); 1905–1924 (s); 1990 (s); 2860 (s); 2930 (s); 2952 (s); 3028 (m); 3070 (m); 3129 (m);

$[C_5H_5(CO)_3Mo]_2Sn(C_6H_5)_2$. To C_5H_5Na , prepared from 1.7 g of Na and 5.2 g of cyclopentadiene in tetrahydrofuran, 19.5 g of $Mo(CO)_6$ was added. After the evolution of CO ceased, 10 g of $Cl_2Sn(C_6H_5)_2$ in 30 ml of tetrahydrofuran was added to the mixture. The substance isolated, after sublimation and chromatography, in an amount of 8.5 g was recrystallized three times from a mixture of hexane with benzene; it had m.p. 190–191.5°.

$C_{28}H_{20}O_6Mo_2Sn$.	Found, %: C 43.87, 44.12; H 2.82, 2.83
	Calculated, %: C 44.03; H 2.35

Mol. wt.: found 840, 840, calculated 863.

I.R. spectrum (ν , cm^{-1}) (paste in Vaseline oil): 449 (m); 474 (m); 504 (m); 558 (s); 573 (m); 590 (m); 675 (w); 700 (w); 712 (w); 727 (m); 741 (m); 824 (s); 839 (w); 847 (w); 857 (w); 865 (w); 919 (w); 930 (w); 1010 (w); 1068 (w); 1196 (w); 1262 (w); 1310 (w); 1340 (w); 1384 (w); 1432 (m); 1470 (m); 1582 (w); 1892 (s); 1912 (s); 1923 (s); 1987 (s); 2380 (w); 2860 (s); 2930 (s); 2960 (s); 3050 (w); 3070 (w); 3113 (w).

$\text{C}_5\text{H}_5(\text{CO})_3\text{W}-\text{Sn}(\text{C}_6\text{H}_5)_3$. 17.6 g of $\text{W}(\text{CO})_6$ was added to $\text{C}_5\text{H}_5\text{Na}$, prepared from 1.15 g of Na and 3.5 g of C_5H_6 in diglyme. After evolution of CO at room temperature, 8 g of $(\text{C}_6\text{H}_5)_3\text{SnCl}$ in 30 ml of diglyme was added. After sublimation, chromatography, and twofold recrystallization from a heptane-toluene mixture, 6 g of substance with m.p. 229–230.5° was isolated.

$\text{C}_{26}\text{H}_{20}\text{O}_3\text{WSn}$.	Found, %: C 46.08, 46.07; H 3.06, 3.21
	Calculated, %: C 45.68; H 2.92

Mol. wt.: found 706, 728, calculated 705.

I.R. spectrum (ν , cm^{-1}) (crystals in Vaseline oil): 449 (m); 479 (m); 490 (m); 570 (m); 582 (m); 680 (w); 725 (s); 737 (s); 799 (w); 832 (m); 862 (w); 1000 (w); 1017 (w); 1023 (w); 1073 (w); 1162 (w); 1193 (w); 1262 (w); 1305 (w); 1338 (w); 1382 (w); 1434 (m); 1469 (m); 1486 (w); 1581 (w); 1778 (w); 1854 (w); 3025 (w); 3065 (m); 3130 (w).

$[\text{C}_5\text{H}_5(\text{CO})_3\text{W}]_2\text{Sn}(\text{C}_6\text{H}_5)_2$. 15 g of $\text{W}(\text{CO})_6$ was added to a solution of $\text{C}_5\text{H}_5\text{Na}$ in 25 ml of diglyme, prepared from 1 g of Na and 2.5 g of C_5H_6 . After evolution of CO at room temperature, 13 g of $(\text{C}_6\text{H}_5)_2\text{SnCl}_2$ was added. The reaction mass was treated by the method described above. A yellow crystalline product with m.p. 207–209° was obtained.

$\text{C}_{28}\text{H}_{20}\text{O}_6\text{W}_2\text{Sn}$.	Found, %: C 35.50, 35.46; H 2.03, 2.10
	Calculated, %: C 35.78; H 2.13

* The I.R. spectra were measured by Yu. N. Sheinker and G. G. Dvoryantseva, for which we express our gratitude to them.

Mol. wt.: found 850, 867; calculated 939.

$\text{C}_5\text{H}_5(\text{CO})_3\text{W}-\text{Pb}(\text{C}_6\text{H}_5)_3$. To $\text{C}_5\text{H}_5\text{Na}$, obtained from 1.15 g of Na and 3.5 g of cyclopentadiene in 30 ml of diglyme, 17.6 g of $\text{W}(\text{CO})_6$, dissolved in 40 ml of diglyme, was added. The reaction mixture was heated at 120–130° until the evolution of CO ceased. Then, at room temperature, 10.5 g of $(\text{C}_6\text{H}_5)_3\text{PbCl}$ in 30 ml of diglyme was added. After sublimation, chromatography, and repeated recrystallization (heptane–benzene), 4 g of a yellow compound with m.p. 210–211.5° was isolated.

$\text{C}_{26}\text{H}_{20}\text{O}_3\text{WPb}$.	Found %: C 41.04, 40.97; H 2.88, 2.81
	Calculated %: C 40.5; H 2.6

Mol. wt.: found 860, 773; calculated 771.

IR spectrum (ν , cm^{-1}): 442 (m); 478 (m); 487 (m); 558 (m); 578 (m); 730 (m); 750 (s); 833 (m); 1000 (m); 1019 (m); 1060 (w); 1172 (w); 1190 (w); 1300–1331 (w); 1383 (w); 1410 (m); 1434 (m); 1465–1480 (m); 1573 (w); 1880 (s); 1892 (s); 1908 (s); 1978 (s); 2860 (s); 2930 (s); 2965 (s); 3025 (m); 3070 (m); 3130 (m).

$C_5H_5(CO)_3Mo—Pb(C_6H_5)_3$. To C_5H_5Na , prepared from 0.1 g of Na and 0.3 g of C_5H_6 in tetrahydrofuran, 1.32 g of $Mo(CO)_6$ was added. After evolution of CO, 1.8 g of $(C_6H_5)_3PbCl$ in 20 ml of tetrahydrofuran was added. A yellow crystalline product was isolated in an amount of 0.6 g, m.p. 205°.

$C_{26}H_{20}O_3MoPb$. Found %: C 46.14, 46.00; H 3.04, 3.12
Calculated %: C 45.68; H 2.93

Mol. wt.: found 704, 660, 681; calculated 683.

IR spectrum (ν , cm^{-1}) (paste in Vaseline oil): 445 (s); 468 (w); 482 (m); 500 (s); 568 (s); 586 (s); 730 (s); 747 (s); 823 (s); 1000 (m); 1020 (m); 1060 (w); 1160 (w); 1190 (w); 1263 (w); 1300 (w); 1330 (w); 1384 (m); 1435 (s); 1470 (m); 1573 (w); 1900–1930 (s); 1988 (s); 2866 (s); 2940 (s); 3020 (m); 3040 (m); 3060 (m); 3100 (w); 3125 (w).

$C_5H_5(CO)_3Cr—Sn(C_6H_5)_3$. To C_5H_5Na , obtained from 0.3 g of Na and 0.85 g of C_5H_6 in diglyme (25 ml), 3 g of $Cr(CO)_6$ was added. The reaction mixture was heated until the evolution of CO ceased. At room temperature, 2.5 g of $(C_6H_5)_3SnCl$ in 25 ml of diglyme was added. A white crystalline product with m.p. 220–222° was obtained.

$C_{26}H_{20}O_3CrSn$. Found %: C 56.57, 56.44; H 3.66, 3.67
Calculated %: C 56.62; H 3.63

Mol. wt.: found 530, 510; calculated 551.

$C_5H_5(CO)_3Mo—Sn(C_6H_5)Cl_2$. 3 g of $C_5H_5(CO)_3Mo—Sn(C_6H_5)_3$ in 20 ml of CCl_4 at -15° for 15 min was treated with dry HCl. The small precipitate that formed was filtered off, and the filtrate was removed in vacuo. 2.1 g (95%) of a slightly yellowish-greenish compound with m.p. 109–110° was isolated (recrystallization from an *n*-heptane–benzene mixture, 4:1).

$C_{14}H_{10}O_3MoO_3SnCl_2$ (512). Found %: C 32.79, 32.88; H 2.06, 2.05; Cl 14.36, 14.45
Calculated %: C 32.80; H 1.95; Cl 13.86

$C_5H_5(CO)_3W—Sn(C_6H_5)Cl_2$. By the action of dry HCl on a solution of 1.5 g of $C_5H_5(CO)_3W—Sn(C_6H_5)_3$ in 30 ml of CCl_4 at -15° for 15 min, 0.65 g (52%) of a yellow crystalline substance with m.p. 112–114° (from heptane) was isolated.

$C_{14}H_{10}O_3WSnCl_2$. Found %: C 28.20, 28.27; H 1.84, 1.87; Cl 11.58, 11.83
Calculated %: C 28.00; H 1.67; Cl 11.83

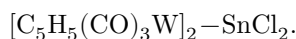
Mol. wt.: found 600; calculated 600.

$[C_5H_5(CO)_3Mo]_2-SnCl_2$. A solution of 1 g of $[(C_5H_5(CO)_3Mo)]_2-Sn(C_6H_5)_2$ in 25 ml of CCl_4 at -15° for 2 h was treated with dry HCl. After removal

the solvent, the residue was recrystallized from benzene. This gave 0.7 g (71.4%) of yellow crystals with m.p. $200-201^\circ$.

$C_{16}H_{16}O_6Mo_2SnCl_2$.	Found, %:	C 28.34, 28.35; H 1.51, 1.53; Cl 11.18, 11.47
	Calculated, %:	C 28.23; H 1.47; Cl 10.44

Molecular weight: found 663, 685; calculated 680.



Dry HCl was passed for 30 min at -15° through a solution of 0.8 g of $[C_5H_5(CO)_3W]_2-Sn(C_6H_5)_2$ in CCl_4 . The solvent was removed; the residue gave a dry crystalline product, which was recrystallized from a heptane-benzene mixture. This gave 83.3% of a yellow crystalline substance with m.p. $225-226^\circ$.

$C_{16}H_{10}O_6W_2SnCl_2$.	Found, %:	C 22.42, 22.29; H 1.05, 1.02; Cl 8.29, 8.45
	Calculated, %:	C 22.43; H 1.17; Cl 8.29

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REFERENCES CITED

1. K. N. Anisimov, A. N. Nesmeyanov, DAN, **26**, No. 1, 57 (1940).
2. A. N. Nesmeyanov, K. N. Anisimov et al., ZhKhN, **4**, 249 (1959).
3. A. N. Nesmeyanov, E. P. Mikheev et al., ZhKhN, **4**, 503 (1959).
4. A. N. Nesmeyanov, K. N. Anisimov et al., ZhKhN, **4**, 1827 (1959).
5. A. N. Nesmeyanov, E. P. Mikheev et al., ZhKhN, **4**, 1958 (1959).
6. A. N. Nesmeyanov, K. N. Anisimov et al., DAN, **156**, No. 2, (1964).

7. *International Tables for X-ray Crystallography*, Birmingham, 1962.

8. L. F. Dahl, E. Ishishi, R. E. Rundle, *J. Chem. Phys.*, **26**, 6, 1750 (1957).

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