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Chemistry

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Abstract

Full Text

Chemistry

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ACYLATION OF CYCLOPENTADIENYL- RHENIUM TRICARBONYL

We have previously described a new method for the synthesis of cyclopentadienylrhenium tricarbonyl ⁽¹⁾.

In the present work we describe the Friedel–Crafts acylation of this compound. With acetyl chloride it forms acetylcyclopentadienylrhenium tricarbonyl in a yield of 67%, and with benzoyl chloride–benzoylcyclopentadienylrhenium tricarbonyl–61%. Acetyl- and benzoylcyclopentadienylrhenium tricarbonyl are crystalline substances, readily soluble in ordinary organic solvents and insoluble in water; with 2,4-dinitrophenylhydrazine they form the corresponding 2,4-dinitrophenylhydrazones.

For the acetyl- and benzoylcyclopentadienylrhenium tricarbonyl obtained, IR spectra* were recorded (see the experimental part), in which characteristic vibration frequencies are present: CH–3120 cm⁻¹, 3130 and 3110 cm⁻¹; (CO)₃Re–2034, 1930 cm⁻¹, 2043, 1950, 1915 cm⁻¹; C=O–1691 cm⁻¹, 1649 cm⁻¹.

Experimental Part

All operations were carried out in an atmosphere of nitrogen.

Acetylcyclopentadienylrhenium tricarbonyl.

To 1 g (0.003 mole) of C₅H₅Re(CO)₃, dissolved in 70 ml of methylene chloride, were added 0.8 g (0.006 mole) of AlCl₃ and 0.28 g (0.003 mole) of CH₃COCl. The reaction mixture was heated (30–35°) until the evolution of HCl ceased and, after cooling, was decomposed with acidified water. After separation of the organic layer, the latter was washed 3 times with water and dried over Na₂SO₄.

The solvent was removed. The residue was recrystallized from petroleum ether (40–60°). 0.76 g (67%) of a white crystalline substance with m.p. 79–80° was isolated.

C₁₀H₇O₄Re. Found, %: C 31.74, 31.96; H 1.84, 1.80; Re 49.00, 49.47
Calculated, %: C 31.83; H 1.85; Re 49.33

IR spectrum (paste in Vaseline oil) (ν , cm^{-1}): 515 (s), 598 (s), 675 (w), 710 (w), 835 (m), 865 (m), 890 (m), 917 (w), 962 (m), 1020 (m), 1045 (m), 1060 (m), 1115 (m), 1273 (s), 1335 (m), 1365 (s), 1411 (m), 1455 (s), 1691 (s), 1930 (s), 2034 (s), 2860 (s), 2930 (s), 3120 (s).

Acetylcyclopentadienylrhenium tricarbonyl with 2,4-dinitrophenylhydrazine forms a dark-red 2,4-dinitrophenylhydrazone with m.p. 231° .

$\text{C}_{16}\text{H}_{11}\text{O}_7\text{N}_4\text{Re}$. Found, %: N 10.57, 10.41
Calculated, %: N 10.05

Benzoylcyclopentadienylrhenium tricarbonyl.

1 g (0.003 mole) of $\text{C}_5\text{H}_5\text{Re}(\text{CO})_3$ was dissolved in 60 ml of carbon disulfide free from hydrogen sulfide. With stirring, 0.8 g (0.006 mole) of AlCl_3 was introduced, and 0.5 g (0.003 mole) of $\text{C}_6\text{H}_5\text{COCl}$ was added gradually.

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

The reaction mixture was heated to the boiling point of the solution for 4.5 h. After decomposition of the reaction mixture, the carbon disulfide solution was dried over Na_2SO_4 , then the solvent was removed, and the solid residue was sublimed in vacuo. Starting material, 0.4 g, was isolated. The remaining resinous solid mass was treated with hexane with activated carbon. On cooling, a white crystalline substance was isolated in an amount of 0.8 g (61%). After repeated recrystallization (petroleum ether $40\text{--}60^\circ$), the melting point of the product was $99.5\text{--}100^\circ$.

Found, %: C 41.14, 41.26; H 2.04, 2.13; Re 42.08, 42.48
 $\text{C}_{15}\text{H}_9\text{O}_4\text{Re}$. Calculated, %: C 41.00; H 2.05; Re 42.36

IR spectrum (paste in Vaseline oil) (ν , cm^{-1}): 510 (s.), 565 (m.), 598 (m.), 705 (m.), 728 (m.), 745 (m.), 764 (s.), 805 (m.), 840 (m.), 857 (m.), 868 (sh.), 920 (sh.), 940 (sh.), 959 (sh.), 1130 (m.), 1038 (m.), 1069 (m.), 1080 (sh.), 1112 (sh.), 1174 (m.), 1220 (sh.), 1297 (s.), 1317 (m.), 1340 (m.), 1370 (s.), 1419 (sh.), 1460 (s.), 1586 (m.), 1604 (m.), 1649 (s.), 1915 (s.), 1950 (s.), 2043 (s.), 2860 (s.), 2930 (s.), 3110 (m.), 3130 (m.).

Benzoylcyclopentadienylrhenium tricarbonyl with 2,4-dinitrophenylhydrazine forms the red 2,4-dinitrophenylhydrazone, m.p. 246° .

Found, %: N 9.36, 9.21
 $\text{C}_{21}\text{H}_{13}\text{N}_4\text{O}_7\text{Re}$. Calculated, %: N 9.03

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