Anionic Tungsten Carbonyl Complexes Containing Dithiocarboxylate, Dithiocarbamate, and Xanthate Ligands

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The reaction of $Et_4N[W(CO)_5Cl]$ with sodium dithiobenzoate, ethylxanthate, or various dithiocarbamates gave the corresponding salts $Et_4N[W(CO)_4(SSCX)]$ (X = Ph, NEt_2, N(H)*t*-Bu, NPh_2, OEt) which contain the dithio ligand in a chelating bonding mode. Two of them (X = N(H)*t*-Bu, NPh_2) were characterized by X-ray crystallography. The tungsten atom resides in the center of a slightly distorted octahedron surrounded by a symmetrically bidentate planar dithio ligand and four CO groups. Reaction with PPh_3 or PMe_3 at elevated temperature gave the tricarbonyl complexes $Et_4N[W(CO)_3(PR_3)(SSCX)]$ and in one case a ring-opened addition product, $Et_4N[W(CO)_4(PMe_3)(SC(S)OEt)]$. For two of them X-ray structure determinations were carried out. A comparison of the four structures shows that while the W–C bond length decreases progressively with increasing electron density at the tungsten atom, the W–S and W–P bond lengths remain essentially constant.

Key words: Tungsten, Dithiocarboxylate Complexes, Dithiocarbamate Complexes, Xanthate Complexes, Carbonyl Complexes