Supplementary data

Experimental procedure and analytical data for the new compounds

$[Mn(CO)_4\{(PPh_2)_2C(H)SO_3\}]$ (3). To a solution of 0.10 g (0.15 mmol) of $[Mn(CO)_4\{(PPh_2)_2C=S\}]ClO_4$ (mmol), 40 μL of an aqueous solution of hydrogen peroxide (30% H_2O_2, 0.78 mmol) were added. The resulting mixture was stirred for 1 h at room temperature. Then, the solution was washed with water (3 x 5 mL) and the dichloromethane solution filtered off through diatomaceous earth. Evaporation of the solvent under vacuum afforded a white solid corresponding to **3**. This was recrystallized by slow diffusion of hexane into a dichloromethane solution of the compound. Yield: 0.07 g, 75%. Elemental analysis (%) calcd for $C_{29}H_{21}MnO_7P_2S$: C 55.25, H 3.36; found: C 55.08, H 3.48.

$K[Mn(CO)_4\{(PPh_2)_2CSO_3\}]$ (K-7). To a solution of complex $[Mn(CO)_4\{(PPh_2)_2C(H)SO_3\}]$ (3) (0.09 g, 0.14 mmol) in 15 mL of dichloromethane, an excess of KOH (0.5 g, 8.9 mmol) was added. The resulting mixture was vigorously stirred for 2 h at room temperature. Then the solution was filtered off and the solvent evaporated to dryness under vacuum to yield a white solid, which was washed twice with hexane (20 mL). Yield: 78 mg, 84%. Elemental analysis (%) calcd for $C_{29}H_{20}KMnO_7P_2S$: C 52.10, H 3.02; found: C 52.11, H 3.21.

$[Mn(CO)_4\{(PPh_2)_2C(Cl)SO_3\}]$ (8). To a solution of $[Mn(CO)_4\{(PPh_2)_2C(H)SO_3\}]$ (3) (0.09 g, 0.14 mmol) in 15 mL of dichloromethane, concentrated HCl (35%, d = 1.18 g/mL, 0.42 mL, 1.6 mmol) and hydrogen peroxide (30%, 0.24 mL, 2.34 mmol) were added. The mixture was stirred for 12 h at room temperature. Then, the solution was washed with water (3 x 15 mL) in order to extract the excess of HCl and H_2O_2. The dichloromethane phase was then filtered off through diatomaceous earth. The solvent was evaporated to dryness under vacuum to afford a white solid, which was washed twice with diethyl ether. The compound can be crystallized from dichloromethane/Hexane. Yield: 50 mg, 53%. Elemental analysis (%) calcd for $C_{29}H_{20}ClMnO_7P_2S$: C 52.39, H 3.03; found: C 52.38, H 3.17.