Synthesis and *X*-ray Structure of Tetramethylammonium *cis*-Acetylbenzoyltetracarbonylmanganate(I)

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Summary Reaction of methyl-lithium with benzoylpentacarbonylmanganese(I) gives *cis*-acetylbenzoyltetracarbonylmanganate(I) anion which was isolated as the tetramethylammonium salt and characterized by *X*-ray crystallography.

The reaction of lithium reagents with transition-metal carbonyl compounds is known to occur at the electropositive carbonyl carbon to give anions which have been isolated in several cases.[1] In contrast, metal carbene complexes, such as $(CO)_5W(OMe)Ph$, undergo attack by lithium reagents only at the carbene carbon atom and not at co-ordinated CO.[2] We were interested in determining the site of attack of lithium reagents on acylpentacarbonylmanganese(I) compounds,[3] which are closely related to metal-carbene complexes

$$(CO)_5MnCOPh + MeLi \rightarrow [cis(CO)_4Mn(COMe)(COPh)]^-M^+$$

(1)

a; M = Li

b; M = Me_4N

Reaction of a slight excess of methyl-lithium with benzoylpentacarbonylmanganese(I) in tetrahydrofuran (THF) at −78° gives a yellow solution of lithium *cis*-acetylbenzoyltetracarbonylmanganate(I), (**1a**), ν 2044(w), 1962(s), 1946(s), and 1929(s) cm^{-1}. The reaction of *p*-tolyllithium with acetylpentacarbonylmanganese(I) under similar conditions gave the same i.r. spectrum in the CO stretching region. Removal of solvent from (**1a**) under reduced pressure at 0°, followed by addition of aqueous tetramethylammonium chloride solution, gave the yellow tetramethylammonium salt, (**1b**), which was recrystallized from CH_2Cl_2–ether at −25° (30%, m.p. 87–89°, n.m.r. $[^2H_8]$-THF) δ 7·2 (5H, br s), 3·24 (12H, br s), 2·36 (3H, s).

The yellow crystals of (**1b**) (Figure) are monoclinic, space group $P2_1/c$, $a = 10{\cdot}35$, $b = 15{\cdot}58$, $c = 12{\cdot}09$ Å, $\beta = 100{\cdot}99°$, $D_m = 1{\cdot}36$, $D_c = 1{\cdot}35$ g cm^{-3} for $Z = 4$. Solution and refinement was based on 1249 unique reflections recorded on a four-circle Syntex P$\bar{1}$ autodiffractometer using graphite-crystal monochromated Mo-K_α radiation. Standard Patterson and Fourier techniques were used to solve the structure while full matrix least squares refinement using absorption corrected data ($\mu = 7{\cdot}53$ cm^{-1}) has given an R_1 value of 6·85.

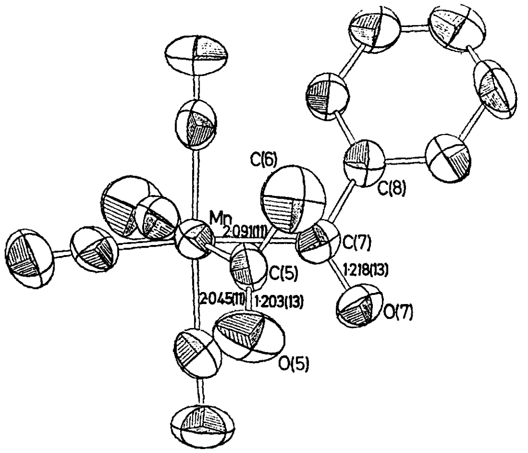

Figure. ORTEP diagram of the molecular structure of (**1b**). 50% probability envelopes for the vibrational ellipsoids of non-hydrogen atoms are shown. The cation has been omitted for clarity. Important bond angles (°) are Mn–C(5)–C(6), 120·9(9); C(6)–C(5)–O(5), 114·4(10); Mn–C(7)–C(8), 123·6(8); C(8)–C(7)–O(7), 114·9(9); C(5)–Mn–C(7), 81·2(4).

Thermal decomposition of (**1b**) in THF at 70° for 15 min gives acetophenone in good yield, while treatment of a THF solution of (**1b**) at 0° with bromine gives 1-phenylpropane-1,2-dione as the major product.

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[1] G. R. Dobson and J. R. Paxson, *J. Amer. Chem. Soc.*, 1973, **95**, 5925 and refs. therein.

[2] C. P. Casey and T. J. Burkhardt, *J. Amer. Chem. Soc.*, 1973, **95**, 5833.

[3] Johnson and Pearson have reported that a variety of nucleophiles attack acetylpentacarbonylmanganese at the acyl carbon; R. W. Johnson and R. G. Pearson, *Inorg. Chem.*, 1971, **10**, 2091.