Preparation and Molecular Structure of (3-Acetyl-4,5-dihydrofuran-2-yl)tetracarbonylmanganese(I)

By Charles P. Casey,* Roger A. Boggs, David F. Marten, and Joseph C. Calabrese
(*Department of Chemistry, University of Wisconsin, Madison, Wisconsin* 53706)

Summary Treatment of *cis*-(2-oxacyclopentylidene)nonacarbonyldimanganese with butyl-lithium followed by acetyl chloride gives (3-acetyl-4,5-dihydrofuran-2-yl)-tetracarbonylmanganese whose molecular structure was determined by *X*-ray crystallography.

We recently reported the stoicheiometric generation of anions α to the carbene carbon atom of transition-metal carbene complexes and the deuteriation, alkylation, and condensation reactions of these anions.[1] Here we report an unusual rearrangement product which was obtained when the anion of the cyclic metal carbene complex (**1**) was treated with acetyl chloride.

Treatment of (**1**)[2] with BuLi (1 equiv.) in THF at −78° followed by the addition of AcCl (1 equiv.) at −20° gave (3-acetyl-4,5-dihydrofuran-2-yl)tetracarbonylmanganese(I) (**2**) (m.p. 61·5—62·5°, 25%), separated by thick layer chromatography.

The structural assignment of (**2**) is based upon elemental analysis, $M^+ = 277{\cdot}9609$, $\delta(CS_2,Me_4Si)$ 2·87 (s, 3H, $COCH_3$), 3·18 (t, 2H, *J* 5, CH_2CH_2O), 4·31 (t, 2H, *J* 5, CH_2CH_2O), and $_{max}$ 2085m, 2040w, 1998s, 1982s, and 1945s cm^{-1}.

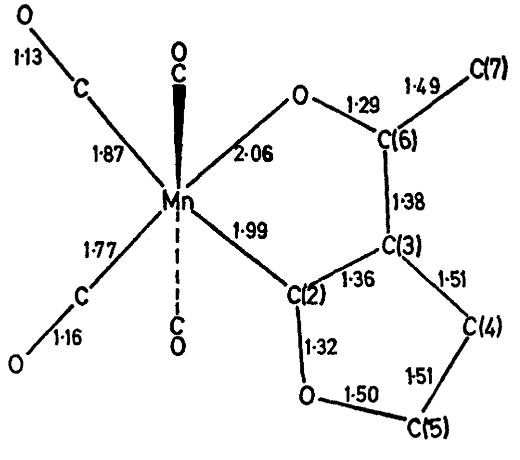
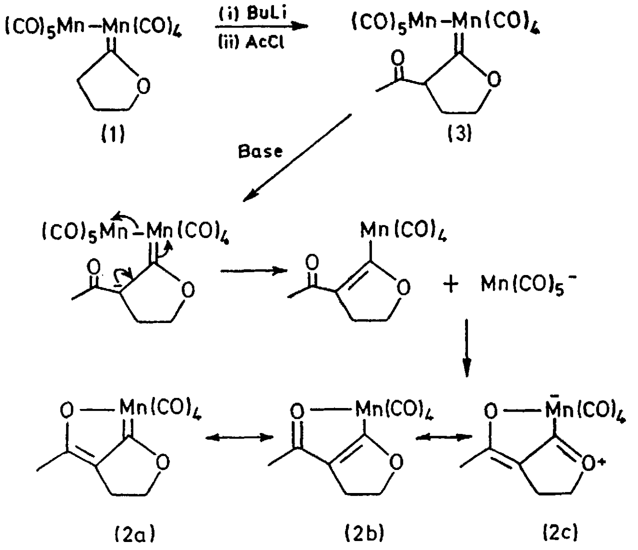


Figure. *The molecular structure of* (3-*acetyl*-4,5-*dihydrofuran*-2-*yl*)*tetracarbonylmanganese*(I). *With the exception of the two axial* CO's *and the hydrogen atoms, all of the atoms lie within* 0·04 Å *of the mean plane defined by the manganese atom and the* 3-*acetyl*-4,5-*dihydrofuran*-2-*yl ligand. The axial* CO's *have* Mn–C *bond lengths of* 1·89 *and* 1·84 Å *and* C–O *bond lengths of* 1·12 *and* 1·14 Å *respectively.*

To confirm the structure of (**2**) and to determine whether the complex could best be described as a metal–carbene complex (**2a**) or as a vinyl organometallic (**2b**), an *X*-ray crystallographic study of (**2**) was undertaken. Compound (**2**) crystallizes as volatile yellow needles with two molecules in a triclinic cell (space group $P\bar{1}$) with $a = 8{\cdot}310(3)$, $b = 10{\cdot}576(3)$, $c = 7{\cdot}026(2)$ Å, $\alpha = 90{\cdot}09°$ (3), $\beta = 105{\cdot}58°$ (3), $\gamma = 79{\cdot}26°$ (3). 1080 independent observations (Cu-K_α) were measured with a Syntex $P\bar{1}$ autodiffractometer and corrected for atomic absorption. Conventional heavy-atom techniques were used to determine the structure (Figure). The least-squares refinement which in the last stages include co-ordinates for all hydrogen atoms gave $R_1 = 0{\cdot}052$ and $R_2 = 0{\cdot}064$. The structure shows a distorted octahedral arrangement of ligands about the central Mn atom with the planar 3-acetyl-4,5-dihydrofuran-2-yl group acting as a bidentate ligand. The near equality of the C(2)–C(3) [1·359(9) Å] and the C(3)–C(6) [1·377(9) Å] bond lengths can best be understood in terms of the delocalized structure described by resonance forms (**2a**—**c**). The short C(2)–O [1·322(7) Å] bond length and the near planarity of the C(5), O, C(2), C(3), and Mn atoms [maximum deviation from planarity less than 0·04 Å] are readily explained in terms of resonance form (**2c**). The CO ***trans*** to the acetyl oxygen shows a substantial *trans* influence with a long C–O distance [1·159(9) Å] and a short Mn–C distance [1·765(9) Å] illustrating the inability of oxygen to compete with CO as an acceptor ligand. Similar tetracarbonylmanganese(I) compounds having the oxygen atom of an acetyl group bonded to manganese have been prepared.[3]

We propose that the dinuclear acylated carbene (**3**) is formed initially in this reaction (Scheme) and then undergoes base-induced deprotonation. The dinuclear anion could then undergo loss of $Mn(CO)_5^-$ to give a co-ordinately unsaturated complex which is subsequently attacked internally by the acyl oxygen atom to give the co-ordinately saturated product (**2**). We have previously observed expulsion of $Mn(CO)_5^-$ from the dinuclear anion acetylnonacarbonyldimanganese.[4]



Scheme

We thank the National Science Foundation and the Eli Lilly Company for support of this research.

(*Received*, 15*th January* 1973; *Com.* 046.)

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