Acyl Group Migration to a Co-ordinated Double Bond: a Stable π-Oxapropenyl Complex of Manganese

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Summary One of two isomeric compounds formed in the reaction of $MeMn(CO)_5$ with *o*-styryldiphenylphosphine (sp) is believed to contain a delocalised π-1,2-dimethyloxapropenyl–metal bond.

METHYLMANGANESE PENTACARBONYL, $MeMn(CO)_5$, reacts with many ligands to give acyls of general formula $MeCOMn(CO)_4$(ligand), which are thought to be formed by migration of a methyl group from metal to co-ordinated CO. We now report the reaction of $MeMn(CO)_5$ with the potentially bidentate ligand *o*-styryldiphenylphosphine, *o*-$CH_2{:}CH{\cdot}C_6H_4{\cdot}PPh_2$ (sp; I), which forms chelate mono-olefin complexes with metal carbonyls, *e.g.* $Cr(CO)_4(sp)$,[1] $Mn(CO)_3(sp)X$ (X = Cl, Br, or I)[2] and $Fe(CO)_3(sp)$.[3] After 3 days at 35° in CH_2Cl_2, two isomeric, air-stable, yellow crystalline complexes (A) and (B) of empirical formula $C_{25}H_{20}O_4PMn$ can be isolated in yields of 44% and 24% respectively after chromatographic separation on silica gel with hexane–benzene mixtures. The appearance of three bands due to $\nu(C\equiv O)$ and a band in the $\nu(C=O)$ region, together with ^1H n.m.r. data (Table) support the formulation of (A) as an acyl, $MeCOMn(CO)_3(sp)$ (II), containing bidentate sp; the marked upfield shifts of the vinyl protons compared with the shifts of the free ligand[1] indicate that the double bond is co-ordinated. We believe the acyl group and the co-ordinated double bond are mutually *trans* (see below), but direct evidence is lacking.

Complex (B) resembles (A) in showing three $\nu(C\equiv O)$ bands (Table), and in showing a parent ion at *m/e* 470 in the mass spectrum, but the n.m.r. spectrum shows only two singlets assignable to nonequivalent methyl groups in addition to the phenyl proton resonances, and the i.r. spectrum shows no $\nu(C=O)$ band. These data are consistent with formulation (III) in which a π-oxapropenyl group is bound to the metal through a delocalised pseudo-π-allylic (three electron) bond. An alternative formulation

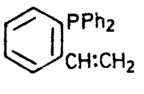
(IV), which cannot be excluded, involves a localised Mn–C σ-bond to the α-carbon atom supported by donation of the ketonic oxygen lone pair electrons to the metal.

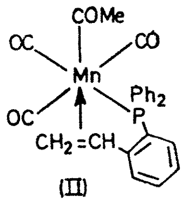
The co-ordinated acyl group of (B) is displaced by CO (70°, 100 atm., 3 days, C_6H_6) to give the Mn–C σ-bonded tetracarbonyl complex (C), (V), which shows, as expected, two methyl singlets in the n.m.r. and four $\nu(C\equiv O)$ bands and a $\nu(C=O)$ band in the i.r. (Table). The mass spectrum of (C) shows its highest peak at *m/e* 470, presumably owing to loss of CO and re-formation of (B) in the mass spectrometer. This process occurs slowly even in the solid state at 25°, and (B) can be recovered almost quantitatively by heating (C) *in vacuo* at 150°. We regard the stability of (B) with respect to (C) as evidence in favour of the delocalised structure (III) for (B).

Properties of complexes[a] *derived from* $MeMn(CO)_5$ *and* sp

Compound	M.p.[b]	$\nu(C\equiv O)$ (cm^{-1})[c]	$\nu(C=O)$ (cm^{-1})[d]	N.m.r. peaks[e]	Assignment
$MeCOMn(CO)_3(o\text{-}CH_2:CH\cdot C_6H_4\cdot PPh_2)$ (A)	134—135°	2006vs, 1924vs, 1902vs	1644m	*ca.* 7·3 (complex, 14) 3·85(1), 3·23(1), 2·78(1) (each complex) 1·39 (singlet)	Phenyl protons $CH:CH_2$ $COCH_3$
$\{[o\text{-}OC(Me)C(Me)]C_6H_4\cdot PPh_2\}Mn(CO)_3$(B)	158—162°	2021vs, 1943vs, 1934vs	—	*ca.* 7·4 (complex, 14) 2·53(3), 2·33(3), (both singlets)	Phenyl protons CH_3
$\{[o\text{-}MeCO\cdot C(Me)]C_6H_4\cdot PPh_2\}Mn(CO)_4$ (C)	125—127°	2068s, 1993vs, 1981vs, 1953vs	1622m	*ca.* 7·4 (complex, 14) 2·08(3), 1·90(3) (both singlets)	Phenyl protons CH_3

[a] All compounds gave satisfactory analyses.
[b] Köfler hot-stage; uncorrected.
[c] n-Pentane solution.
[d] KBr disc.
[e] $CDCl_3$ solution; δ in p.p.m. downfield from internal Me_4Si.


(I)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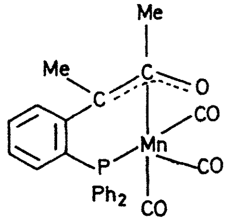
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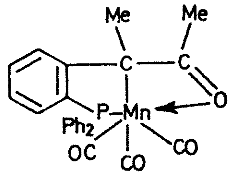
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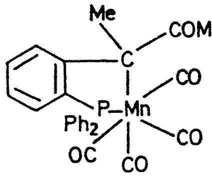
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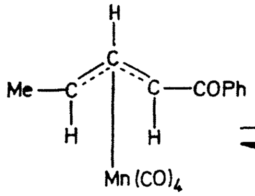
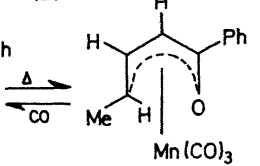

(VI)


(VII)

A π-oxapropenyl complex is a suggested intermediate in the reduction of $\alpha\beta$-unsaturated aldehydes and ketones by $HCo(CO)_4$,[4] but such a complex has not hitherto been isolated. There is an analogy between the reactions reported here and the reaction of $PhMn(CO)_5$ with butadiene to give the π-allylic complex (VI), which reversibly loses CO to give the 5π-oxapentadienyl complex (VII).[5] Moreover, *X*-ray study of the complex $(PhCH:CH\cdot CH:NPh)Fe(CO)_3$[6] establishes that there is delocalised 4π metal–azomethine bonding analogous to that present in $h^4\text{-}C_4H_6Fe(CO)_3$.

A likely precursor to (B) is an isomer of (A) in which the acetyl group is *cis* to the co-ordinated double bond. Complex (B) could then be formed by attack of the acetyl group on the double bond, followed or accompanied by a hydrogen atom shift. Since (B) is not formed directly from (A), it is likely that the latter has the vinyl and acetyl groups *trans*. An analogous attack by co-ordinated hydride on the double bond of (I) has been observed in its reaction with $HMn(CO)_5$,[7] although in this case the double bond is not initially co-ordinated.

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