New Methods for Metal–Carbon Bond Formation; Reactions of $(OC)_5MnSiMe_3$ with Cyclic Ethers

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Summary When $(OC)_5MnSiMe_3$ (**1**) is treated with cyclic ethers (ring size $\leqslant$ 5), ring opening and metal–carbon bond formation occurs, under 200 lb in^{-2} of CO, high yields of products $(OC)_5Mn(COR)$ can be obtained

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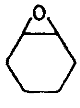
THE increasing utility of organometallic compounds in synthesis and catalysis has prompted us to seek new transition metal–carbon bond-forming reactions which utilize unconventional, yet readily available, organic precursors [1,2] We report here that $(OC)_5MnSiMe_3$ (**1**)[2,3] effects the reductive ring opening of cyclic ethers, and that high yields of manganese acyl products can be isolated when these reactions are conducted under CO

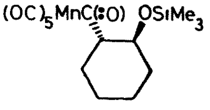
$(OC)_5MnSiMe_3$ (**1**, 2 24 mmol) was treated with 2 equiv of oxetan diluted with 9 parts (v/v) of diethyl ether under 200 lb in^{-2} of CO in a Fischer–Porter bottle After 3 h at room temperature, the solvent was removed and the residue recrystallized (pentane, -40 °C) and then sublimed at 25 °C to give $(OC)_5MnCOCH_2CH_2CH_2OSiMe_3$ (**2**) in 83% yield, m p (sealed tube) 31·5—33 °C, ^{1}H n m r (δ, $CDCl_3$) 3·50 (t, *J* 7 Hz, CH_2OSi), 3·00 (t, *J* 7 Hz, $MnCOCH_2$), 1·67 (quint *J* 7 Hz, $CH_2CH_2CH_2$), and 0 06 (s, $SiMe_3$), ^{13}C n m r [p p m , 220 K, CD_2Cl_2, $Cr(acetylacetonato)_3$] 256·8 (acyl CO), 209·3, 208·1 (5 × CO, *ca* 4 : 1), 63·5, 60·7, 26·7, and -1·4, i r (cm^{-1}, n-hexane) 2118m, 2055m, 2015s, 2007s, sh, and 1653m

TABLE Reactions of cyclic ethers with $(OC)_5MnSiMe_3$ (**1**) and CO[a].

Organic substrate	Time/ h	Product[b] $(OC)_5MnC(:O)$–X–$OSiMe_3$ X	% Isolated yield[c]
CH_2CH_2O	12	$-[CH_2]_2-$	77[d]
CH_2CHMeO	12	$-CH_2CHMe-$	85[e]
$CH_2[CH_2]_2O$	3[f]	$-[CH_2]_3-$	83[g]
$CH_2[CH_2]_3O$	12[h]	$-[CH_2]_4-$	54[i]
(A)	8	(B)	87[j]

[a] Reactions were conducted at 25 °C under 200 lb in^{-2} CO pressure utilizing 4 : 1 : 0 1 proportions of diethyl ether solvent substrate (**1**) unless stated otherwise [b] Spectral data for (**2**) are given in the text Other products were isolated as crystalline solids and were characterized by i r [absorptions within ± 5 cm^{-1} of those of (**2**)] and 200 MHz ^{1}H n m r spectroscopy [c] Yields were based upon (**1**) [d] Product was purified by column chromatography and then sublimation [e] Product was purified by column chromatography [f] Ethyl ether substrate (**1**) in the proportions 9 : 1 : 0 5 [g] Purified by recrystallization and then sublimation [h] No solvent, THF (**1**) ratio 1 : 0 01 [i] Purified by recrystallization [j] Purified by sublimation

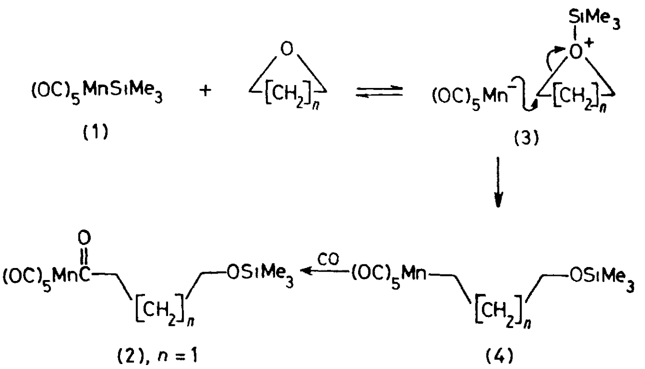

(A)



(B)

By similar procedures, other cyclic ethers (Table) were converted into $(OC)_5Mn(COR)$ products Since these substrates were either less reactive and/or more volatile than oxetan, they were employed in larger excess (Table) When (**1**) was treated with 1,1-dimethyloxiran, polymerization occurred When analogous reactions were attempted in the absence of CO, $Mn_2(CO)_{10}$ (presumably arising from labile metal alkyls) became the principal product

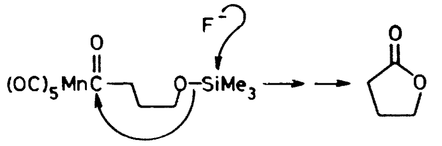
Since (**1**) has previously been shown to react with NMe_3 to yield the *isolable* ion pair $Me_3N^+SiMe_3$ $(OC)_5Mn^-$,[3] and $(OC)_5Mn^-$ is known to be a strong nucleophile,[4] we postulate that ether-ring opening occurs *via* the ion pair (**3**), as shown in the Scheme The alkyl intermediate (**4**) would subsequently undergo a well precedented[5] carbonylation to the acyl product



SCHEME Proposed pathway for the reaction of $(OC)_5MnSiMe_8$ with cyclic ethers

The ability of main-group element trimethylsilanes such as Me_3SiI to cleave ether and ester carbon–oxygen σ bonds has been widely recognized over the past few years [6] For instance, the reaction of epoxides with Me_3SiI has been recently reported to yield ring-opened silylated iodohydrins [7] The present report constitutes the first stoicheiometric demonstration that *transition metal* trimethylsilanes are capable of similar reactivity modes Acyclic organic products arising from the decomposition of $(OC)_4CoSiMe_3$ in tetrahydrofuran (THF)[8] can be readily rationalized in terms of the steps depicted in the Scheme Also, Murai has described a number of elegant transformations of organic compounds (including cyclic ethers) involving CO, Et_3SiH, and $Co_2(CO)_8$ catalyst [9] Our reactions provide precedent for a number of the steps which are postulated to occur

Finally, a number of methods exist for cleaving transition-metal–acyl carbon bonds [10] As an example, we find that the reaction of (**2**) with $[Et_2N]_3S^+$ $SiMe_3F_2^-$ (1 1 equiv , 25 °C)[11] affords butyrolactone in 90—95% (g l c) yield This transformation probably proceeds *via* an intermediate alkoxide (equation 1), since analogous intermolecular acylations have been observed to occur [12]



(2) (1)

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