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Reaction of Tetracarbonyl(π-allyl)manganese with Carbon Nucleophiles[1]

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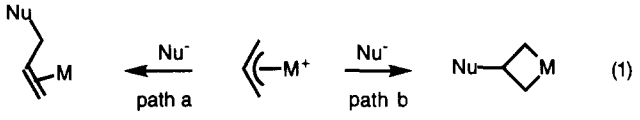
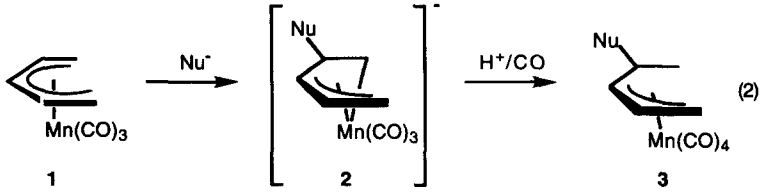
Abstract: ***Nucleophilic attack on tetracarbonyl(π-allyl)manganese takes place at the terminus of the π-system, generating allylated products in 44-95% yield after oxidation. Stabilized nucleophiles (pK_a 12-20) give mainly bis allylation whereas nonstabilized nucleophiles (pKa 25-35) give mono allylation.***

The reaction of π-allyl transition metal complexes with nucleophiles has been examined in detail and utilized for the synthesis of a variety of natural products.[2] In most cases, reaction occurs at the terminus of the π-system, generating allylated products after removal of the transition metal template (Eq. 1, path a). The



(1)

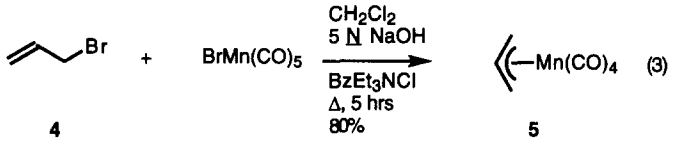
literature does contain, however, several reports of nucleophilic attack at the central carbon of the π-allyl group, leading to metallocyclobutanes (Eq. 1, path b).[3] Although π-allyl manganese complexes have been known for at least thirty years,[4] the literature does not contain reports of the reaction of these complexes with carbon nucleophiles.[5] Our interest in π-allyl manganese complexes originated from the investigation in these labs of the reactions of nucleophiles with η^5-pentadienyl manganese complexes. It has been demonstrated that nucleophilic attack at the C2/C4 position of tricarbonyl(η^5-pentadienyl)manganese, followed by reaction of the resulting (σ,η^3-pentenediyl)manganese anion with acid under a blanket of carbon monoxide provides π-allyl manganese complex **3** (Eq. 2).[6] In order to extend the utility of this process in organic synthesis, an examination of the reactivity of tetracarbonyl(π-allyl)manganese complexes was undertaken. This paper reports the initial results of this study.



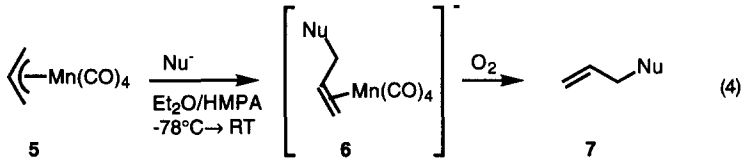
(2)

1 **2** **3**

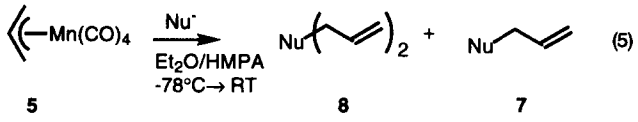
Tetracarbonyl(π-allyl)manganese (**5**) was prepared according to the procedure of Gibson et al.[7] Reaction of allyl bromide with bromopentacarbonylmanganese[8] in a mixture of dichloromethane and 1 N sodium hydroxide, containing benzyltriethylammonium chloride as the phase transfer catalyst, generated complex **5** in approximately 80% yield (Eq. 3). This π-allyl manganese complex is a slightly air sensitive solid which is stable for weeks if stored at 0 °C.



Initial attempts to react π-allyl manganese complex **5** with nucleophiles using the conditions developed for reactions of (η^5-pentadienyl)manganese complex **3** failed to generate products resulting from nucleophilic attack on the π-allyl moiety. However, replacement of tetrahydrofuran with diethyl ether as the solvent allowed for the isolation of products resulting from nucleophilic addition. Thus, reaction of a variety of nucleophiles with π-allyl manganese complex **5** in a mixture of diethyl ether and HMPA at -78°C, followed by warming to room temperature for 1.5 hours and oxidation of the reaction mixture generated allylated products **7** in 44-70% yield (Eq. 4, Table 1, entries a-f). Nucleophilic attack at the terminus of the π-allyl group provided η^2-olefin manganese anion **6** which decomposed readily in the presence of oxygen to provide allylated products **7**. No evidence of products resulting from attack at the central carbon of the π-allyl complex was found.



When diethyl lithiomalonate, ethyl lithioacetoacetate, or α-lithioacetophenone was reacted with π-allyl manganese complex **5**, products resulting from diallylation predominated (Eq. 5, Table 1, entries g,h,i). Attempts to curtail this double allylation by lowering the reaction temperature failed, and no reaction took place without warming the reaction mixture to room temperature. Reaction of diethyl lithiomalonate with two or more equivalents of complex **5**, in an attempt to form only the diallyation product, still gave a mixture of mono- and diallylation products. It should be noted that reaction of diethyl lithiomethylmalonate with complex **5** followed by oxidation produced the monoallylated product **7** in 54% yield (Table 1, entry j).



Nu⁻ = $(CO_2Et)_2CHLi$, $(CO_2Et)CHLiCOCH_3$, $PhCOCH_2Li$

Table 1. Nucleophilic Attack on Tetracarbonyl(π-allyl)manganese (5).

Entry	Nucleophile	Product	Yield	Ref.[a]
a	2-lithio-1,3-dithiane	**7**	61%[b]	9
b	2-methyl-2-lithio-1,3-dithiane	**7**	44%[b]	10
c	$(CH_3)_2CLiCO_2Et$	**7**	69%	11
d	Ph_2CHLi	**7**	56%	12
e	Ph_3CLi	**7**	52%	13
f	$(CH_3)_2CLiCN$	**7**	64%	14
g	$(CO_2Et)_2CHLi$	**7/8**	13/76%[c]	15/16
h	$CH_3CO(CO_2Et)CHLi$	**7/8**	20/74%[c]	17/18
i	$PhCOCH_2Li$	**7/8**	8/87%[c]	19/20
j	$(CO_2Et)CMeLi$	**7**	54%	21

[a] Spectroscopic data for all compounds matched data reported in the literature. [b] Product inseparable from unreacted nucleophile. Yield determined from proton NMR spectrum and gas chromatography by integration. [c] Inseparable mixture of products. Ratio determined by proton NMR spectrum and gas chromatography by integration.

Nucleophilic attack on tetracarbonyl(π-allyl)manganese complexes therefore offers potential for utilization in organic synthesis. Examination of the reactivity of nucleophiles with substituted π-allyl manganese complexes, including those produced by reaction of η^5-pentadienyl manganese complexes with nucleophiles, is currently underway.

Experimental

General procedure for reaction of (π-allyl)manganese complexes with nucleophiles: Lithiated nucleophiles (1.33 eq.) were prepared by reaction with LDA in freshly distilled diethyl ether for twenty min at -78 °C (entries c, f-j) or by reaction with *n*-BuLi (2.5 M solution in hexanes) in freshly distilled diethyl ether at -78 °C followed by stirring for 1.5 h at rt (entries a, b, d, e). In each case 2 mL of HMPA was added to the solution of the lithiated nucleophile prior to addition of complex **5**. One equivalent of tetracarbonyl(π-allyl)manganese (**5**), dissolved in 2.5 mL freshly distilled diethyl ether, was added by cannula to the solution at -78° C. The solution was allowed to stir at room temperature for 1.5 hours, after which time O_2 was bubbled through the solution at 0 °C. The solution was allowed to stir in the air at room temperature overnight. The reaction mixture was then filtered through Celite, and the resulting solution was washed with 50 mL of saturated aqueous ammonium chloride solution, 50 mL of saturated aqueous sodium chloride solution, and 50 mL of 1N HCl. The solution was then dried over anhydrous $MgSO_4$, filtered and the solvent evaporated under reduced pressure. Silica gel chromatography of the residue provided purified material. All compounds were identified by comparison of ^1H and ^{13}C NMR spectroscopy, infrared spectroscopy, and mass spectrometry data to information reported in the literature.

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References and Notes

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