Addition of Organometallic Nucleophiles (Carbonylmetallates) to the Allyl Ligand of $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$. Synthesis and Structure of $(\eta^3\text{-}C_3H_5)Mn(CO)_3PEt_3$

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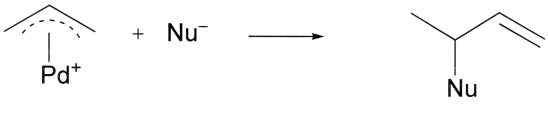
Dedicated to Professor Bernhard Lippert on the occasion of his 65th birthday

The reaction of the organometallic nucleophile $[Mn(CO)_4PEt_3]^-$ at the allyl ligand of $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ proceeds by allyl transfer from Pd(II) to Mn(–I) to give $[(\eta^3\text{-}C_3H_5)Mn(CO)_3PEt_3]$, of which the structure has been determined by X-ray diffraction.

Key words: Allyl, Carbonyl, Palladium, Manganese, X-Ray Structure Determination

Introduction

The palladium-catalyzed "allylic substitution", *i. e.* the addition of nucleophiles to the allyl ligand of *in situ* formed [1] or isolated [2] palladium(II) complexes has found wide application for the synthesis of substituted alkenes [1, 2]. The allylic alkylation by use of C nucleophiles (Tsuij-Trost reaction) is one of most important methods for the stereoselective (also asymmetric) formation of C–C bonds [1, 3] (Eq. 1).



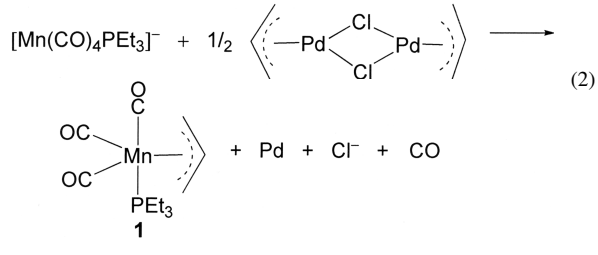
(1)

In 1968 Heck [4] reported the reaction of the organometallic nucleophile $[Co(CO)_4]^-$ with $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ which results in an allyl transfer from Pd(II) to Co(–I) to give (after addition of PPh_3) the allyl cobalt complex $[(\eta^3\text{-}C_3H_5)Co(CO)_2PPh_3]$. It was suggested that in this reaction substitution of chloride by $[Co(CO)_4]^-$ occurs to form a Pd–Co-bonded intermediate [4]. In the light of the reaction of $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ with $[(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2]$ [5, 6], which affords allyl transfer from Pd(II) to Pt(0), it seems plausible that in these reactions the attack of nucleophiles occurs at the allyl ligand, as it takes place in the reaction of $[(\eta^3\text{-}C_3H_5)Mn(CO)_4]$ or of $[Cp(CO)(NO)Mo(allyl)]^+$ with carbon nucleophiles [2]. The addition of the nucleophilic organometallic carbonyl metallates to the allyl ligand in cationic complexes has led to σ,π-bridged *bimetallic* complexes [7 – 9]. Allyl transfer from $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ to $[Fe_2(CO)_9]$ to give $[(\eta^3\text{-}C_3H_5)Fe(CO)_3Cl]$ was reported by Nesmeyanov [10]. Allyl and chloride transfer was also observed in the reactions of mercury [11] and of [(Schiff base)$Mo(CO)_4$] compounds [12] with $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ where allyl mercury chloride or [(Schiff base)(Cl)$Mo(\eta^3\text{-}C_3H_5)$] complexes, respectively, were formed.

In our group [13] the reaction of $[(\eta^3\text{-allyl})Pd(\mu\text{-}Cl)]_2$ with $[Re(CO)_5]^-$ was studied, and $[(\eta^3\text{-allyl})Re(CO)_4]$ could be obtained in high yields. In the following we report on the preparation and structure of the allyl manganese complex $[(\eta^3\text{-}C_3H_5)Mn(CO)_3PEt_3]$. Previously, η^3-allyl manganese complexes $[(\eta^3\text{-}C_3H_5)Mn(CO)_3PR_3]$ were synthesized by thermal or photolytic substitution of a CO ligand in $[(\eta^3\text{-}C_3H_5)Mn(CO)_4]$ [14 – 16] or from $[Mn(Br)(CO)_4PPh_3]$ and C_3H_5Br [17].

Results and Discussion

The title complex **1** was obtained in our group by addition of $Na[Mn(CO)_4PEt_3]$ (synthesized by reduction of the dimer (not the monomer) $[Mn_2(CO)_8(PEt_3)_2]$ [18 – 20] with sodium amalgam) to $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ (Eq. 2). The tetracarbonyl phosphine manganates



(2)

1

Table 1. Bond lengths (Å) and bond angles (deg) of **1** and of $(\eta^3\text{-}C_3H_5)Mn(CO)_2\,[P(OMe_3)]_2$.

	1	$(\eta^3\text{-}C_3H_5)Mn(CO)_2\,[P(OMe_3)]_2$
Mn–C1	1.772(4)	1.75(2), 1.83(2)
Mn–C2	1.803(6)	–
Mn–C3	2.197(4)	2.22, 2.23
Mn–C4	2.120(6)	2.114(15)
Mn–P	2.322(2)	2.175, 2.219(5)
C1–O1	1.153(4)	1.13, 1.17(2)
C2–O2	1.160(5)	–
C3–C4	1.384(6)	1.38(2), 1.40(2)
C1–Mn–C1a	97.6(3)	97.7(7)
C3a–Mn–C3	67.8(3)	67.0(6)
C1–Mn–C3	97.1(2)	96.1(7)
C1–Mn–C3a	164.4	166.1(6)
C1–Mn–P	87.4(1)	87.2
C2–Mn–P	174.2(2)	–
O1–C1–Mn	176.5(4)	178.3(15)
O2–C2–Mn	176.8(5)	179.1(15)
C3–C4–C3a	124.7(7)	124.5(15)

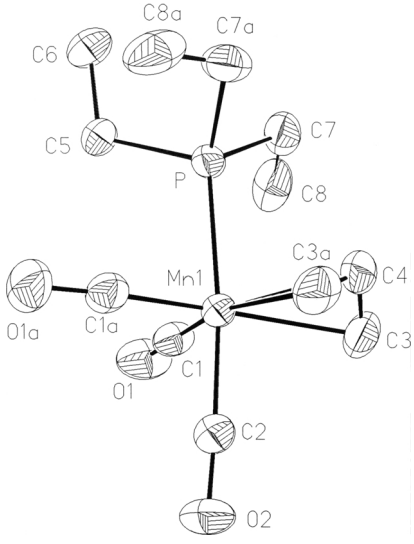


Fig. 1. Molecular structure of **1**.

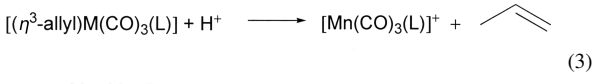
$[Mn(CO)_4PR_3]^-$ have been often used in organometallic synthesis [21, 22]. The yellow complex **1** shows in the IR spectrum three CO absorptions of similar intensity.

The structure of **1** (Fig. 1) could be determined by X-ray diffraction. Suitable crystals of **1** were obtained from a solution in *n*-pentane at −35 °C. The complex has crystallographic mirror symmetry as required by space group $P2_1/m$, $Z = 2$, and a composition which excludes a center of inversion. The molecular structure of **1** can be considered as a distorted octahedron with the phosphine and allyl ligands in *cis*-positions. The bond lengths and bond angles can be compared with those of the allyl complex $\{(\eta^3\text{-}C_3H_5)Mn(CO)_2\text{-}[P(OMe)_3]_2\}$ [15] where the corresponding values are remarkably similar (Table 1).

As in other allyl complexes, the allyl group is symmetrically bonded to the metal atom, the shortest Mn–C distance being to the central allyl carbon atom [15].

Similarly, the parent complex $[(\eta^3\text{-}C_3H_5)Mn(CO)_4]$ which previously was prepared from $(\eta^1\text{-}C_3H_5)\text{-}Mn(CO)_5$ [23] could be obtained from $Na[Mn(CO)_5]$ and $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ [24]. Thus, the addition of organometallic nucleophiles to $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$, which was introduced by Heck [4], provides a general method for the synthesis of allyl metal complexes.

The reactions of the allyl complexes $[(\eta^3\text{-}C_3H_5)\text{-}M(CO)_3L]$ (M = Mn, Re; L = CO, PR_3) with $HBF_4 \cdot Et_2O$ or trifluoromethane sulfonic acid afford the highly unsaturated 14-electron cations $[M(CO)_3L]^+$ (Eq. 3) which are valuable starting compounds for reactions with various donor ligands [13, 24, 25].



(3)

M = Mn, Re
L = CO, PR_3

Experimental Section

$[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ [26] and $[Mn_2(CO)_8[(PEt_3)_2]$ [18] have been obtained as described previously.

*$[(\eta^3\text{-}C_3H_5)Mn(CO)_3PEt_3]$ (**1**)*

The solution of $Na[Mn(CO)_4PEt_3]$ [from 285 mg (0.5 mmol) of $[Mn_2(CO)_8(PEt_3)_2]$ and 4 mL of 0.8 % sodium amalgam in 15 mL of THF] is added to a solution of 183 mg (0.5 mmol) of $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ in 10 mL of THF. Immediately the mixture turns black. After reaction for 1 h at r.t. the solvent is removed *in vacuo* at −20 °C. The residue is extracted with 10 mL of *n*-pentane (three times), and the solvent is again removed *in vacuo* to give a yellow powder. Yield 200 mg (67 %). – $C_{12}H_{20}MnO_3P$ (298.1): calcd. C 48.35, H 6.76; found C 48.86, H 6.68. – IR (Nujol, cm^{-1}): ν = 2003s, 1930s, 1904 (CO). – ^1H NMR (270 MHz, CD_2Cl_2): δ = 1.78 m (2H), 2.42 m (2H), 3.95 m (1H) (allyl), 1.51 m (6 H, CH_2), 1.05 m (9 H, CH_3). – ^{13}C NMR (CD_2Cl_2): δ = 42.09 (CH_2), 95.39 (CH) (allyl), 7.97, 17.74 (Et).

*X-Ray structure determination of **1***

$C_{12}H_{20}MnO_3P$ (298.19), Synthex R3, crystal size: 0.5 × 0.4 × 0.4 mm^3, pale-yellow cube, monoclinic, space group

$P2_1/m$, a = 7.688(2), b = 10.099(3), c = 10.081(3) Å, β = 103.13(2)°, V = 762.2(4) Å^3, Z = 2, density (calcd.) 1.30 Mg m^{-3}, absorption coefficient 1.0 mm^{-1}, $F(000)$ = 312 e, MoK_α radiation, λ = 0.71073 Å, temperature 293(2) K, ω scans, scan speed variable, 2.8 – 30° min^{-1} in ω, scan width (ω) 1.1°, scan range 2θ = 4.14 – 45.08°; $-8 \leq h \leq 8$, $0 \leq k \leq 10$, $-10 \leq l \leq 10$, 2135 collected reflections, 1070 independent reflections, R_{int} = 0.0499, 926 observed reflections with $F \geq 4\sigma(F)$, semi-empirical absorption correction, transmission max. and min. 0.036 and 0.022; structure solution by Patterson Methods with SHELXTLPLUS 4.11, full-matrix least-squares refinement on F^2; hydrogen atoms: riding model, fixed isotropic U; data / restraints / parameters 1068 / 0 / 90, data to parameter ration 11.9 : 1, GoF = 1.061, residuals [$F \geq 4\sigma(F)$]: $R1$ = 0.0366, $wR2$ = 0.0928, residuals (all data) $R1$ = 0.0435, $wR2$ = 0.0979, largest diff. peak and hole 0.195 and −0.186 e Å^{-3} refinement program SHELX-93 [27].

CCDC 820098 ontains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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