

η^4 -Phosphole tricarbonylmanganates: a new type of chelating ligands for transition metals

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Abstract

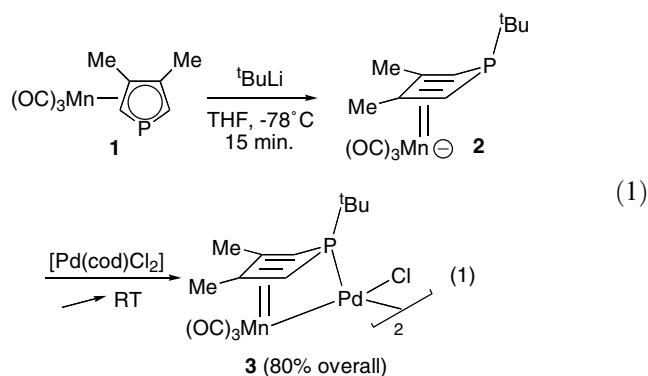
3,4-Dimethylphosphacymantrene (**1**) reacts with *tert*-butyllithium to give the corresponding (η^4 -3,4-dimethyl-1-*tert*-butylphosphole)tricarbonylmanganate (**2**) which can act as a chelating ligand (L) toward a Pd₂Cl₂ dimeric core. The X-ray crystal structure of L₂Pd₂Cl₂ (**3**) shows a bite angle of 60.5°.

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1. Introduction

The most representative η^5 -phospholyl complexes such as phosphacymantrenes (M = Mn(CO)₃) and phosphaferrrocenes are characterized by low-lying LUMOs with a significant localization at phosphorus [1,2]. As a result, alkyl- and aryl-lithiums (RLi) attack the ring of these species at P from the *exo*-side [3,4]. The resulting η^4 -phosphole-metallates can be viewed as potential chelating ligands for transition metals due to the favorable stereochemical disposition of their two coordinating sites RP: and M⁻. We have tested this possibility in the case of 3,4-dimethylphosphacymantrene **1** [5]. The nucleophilic attack was carried out with *tert*-butyllithium (Eq. (1))



The resulting manganese **2** was only identified by its ³¹P resonance at 17 ppm (δ ³¹P(**1**) = -45 ppm). The conversion appears to be quantitative. The manganese was then reacted in situ with {PdCl₂(cod)} to give the bimetallic complex **3** [6]. As expected, the α -CH's of the ring appear at high fields: δ ¹H 2.54 vs 4.38 for **1** [5]; δ ¹³C 51.06 vs 96.8 for **1** [5]. The complex was fully characterized by X-ray crystal structure analysis (Fig. 1). This is a classical Pd₂Cl₂ dimer. The

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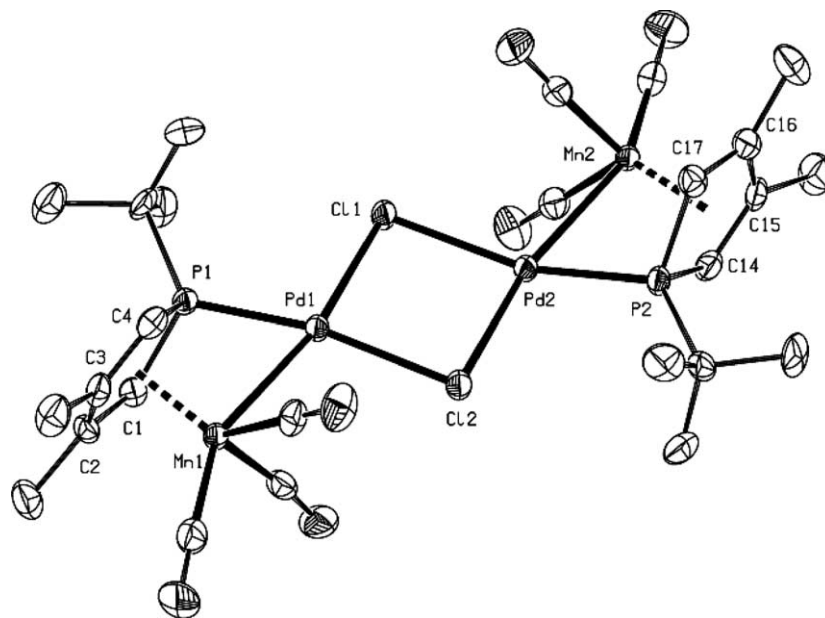


Fig. 1. ORTEP drawing of one molecule of **3**. Main bond lengths (Å) and angles (°). Only one monomeric unit is described: Pd(1)–Cl(1) 2.448(1), Pd(1)–Cl(2) 2.486(1), Pd(1)–P(1) 2.187(1), Pd(1)–Mn(1) 2.6590(8), Mn(1)–P(1) 2.474(1), Mn(1)–C(1) 2.199(4), Mn(1)–C(2) 2.180(4), Mn(1)–C(3) 2.163(4), Mn(1)–C(4) 2.192(4), P(1)–C(1) 1.771(4), P(1)–C(4) 1.764(4), P(1)–C(5) 1.864(4), C(1)–C(2) 1.389(5), C(2)–C(3) 1.445(5), C(3)–C(4) 1.397(6); Cl(1)–Pd(1)–Cl(2) 85.41(4), P(1)–Pd(1)–Cl(1) 107.81(5), P(1)–Pd(1)–Cl(2) 166.67(4), P(1)–Pd(1)–Mn(1) 60.46(3), Cl(1)–Pd(1)–Mn(1) 168.03(3), Cl(2)–Pd(1)–Mn(1) 106.41(3), C(4)–P(1)–C(1) 88.8(2), C(1)–P(1)–C(5) 114.3(2), C(4)–P(1)–C(5) 114.7(2).

P–Pd–Mn bite angles lie around 60.5° . The Mn–Pd bonds are rather short at ca. 2.66 Å (compare with the three different Pd–Mn bonds of a cluster between 2.58 and 2.82 Å [7]). The phosphole ring loses its aromaticity: equal C–C bonds in **1** ca. 1.420(8) Å vs C_α – C_β ca. 1.39 and C_β – $C_{\beta'}$ 1.445(5) Å in **3**. The bending of the phosphole ring around C_α – $C_{\alpha'}$ and away from manganese increases slightly from ca. 2.1 in **1** [5] to 6.1–6.8° in **3**. Surprisingly, the P–C ring bonds remain short at 1.76–1.77 Å and are equal to those of **1** [5]. The P–Mn separation only slightly increases from 2.387 in **1** [5] to 2.474 Å in **3**, and so does the Mn–C₄ plane distance at 1.757(1) in **1** [5] vs 1790(2) Å in **3**. Finally, since the Mn(CO)₃ ligating unit is a far more powerful π -acceptor than the phosphole, it increases the Cl → Pd π -backbonding and strengthens the *trans*-Cl–Pd bond.

It is clear that the pathway leading to **3** can be easily generalized: P–R and M[−] can be varied almost at will. We plan to investigate the coordination chemistry and the catalytic applications of this new family of chelating ligands.

2. X-ray crystal structure of compound **3**

Single crystals of **3** were grown by slow diffusion of hexanes into a dichloromethane solution of the complex into an NMR tube at room temperature. Data were col-

lected at 150 K on a Nonius Kappa CCD diffractometer using an Mo K α ($\lambda = 0.71073$ Å) X-ray source and a graphite monochromator.

Formula: C₂₆H₃₄Cl₂Mn₂O₆P₂Pd₂·2(CH₂Cl₂); $M = 1067.90$ g/mol; orthorhombic; space group $Pna2_1$; $a = 18.7720(10)$ Å, $b = 12.6180(10)$ Å, $c = 16.8400(10)$ Å, $V = 3988.8(4)$ Å³; $Z = 4$; $D = 1.778$ g/cm³; $\mu = 2.025$ cm^{−1}; $F(000) = 2112$. Crystal dimensions 0.18 × 0.18 × 0.18 mm. Total reflections collected 20,051 and 8835 with $I > 2\sigma(I)$. Goodness-of-fit on F^2 1.001; $R(I > 2\sigma(i)) = 0.0380$, $wR_2 = 0.0703$ (all data), 426 parameters; maximum/minimum residual density 0.588(0.064)/−0.440(0.064) e/Å³. The crystal structure was solved in SIR 97[8] and refined in SHELXL-97 [9] by full-matrix least-squares using anisotropic thermal displacement parameters for all non-hydrogen atoms.

Appendix A. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. 237205. Copies of the data can be obtained free of charge, on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-0-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2004.06.044.

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