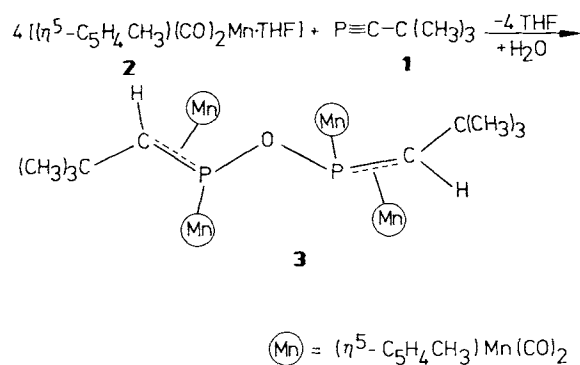


(2,2,8,8-Tetramethyl-5-oxa-4,6-diphospha-3,6-nonadiene)tetrakis[dicarbonyl-(methylcyclopentadienyl)manganese], the First Complexed Bis(phosphavinyl) Ether**

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The rich complexation chemistry of phosphalkynes, especially that of 2,2-dimethylpropylidynephosphane **1**,^[1] is supported by numerous examples.^[2] We have now observed a novel reaction type. Reaction of **1** with the manganese complex **2** surprisingly results in formation of complex **3** (see Experimental Procedure).



This compound contains the first bis(phosphavinyl) ether ligand, to which four $(\text{C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_2$ fragments are coordinated. The formation of this ligand can be formally understood as the addition of one molecule of H_2O to two molecules of **1**. Since the reaction was carried out in dried solvents under inert gas, the source of the water is not yet known. The reaction might involve the initial formation of a presumably very reactive complex with the solvent tetrahydrofuran (THF). In view of the diverse reactions of phosphalkyne complexes, such secondary reactions are certainly conceivable. Unfortunately, the introduction of D_2O into the reaction mixture did not lead to unequivocal results.

The molecular ion is readily apparent in the EI and the FD mass spectra; in addition, **3** was characterized by its elemental analysis and the usual spectroscopic data,^[3] as well as by X-ray structure analysis. As revealed in Figure 1, the bis(phosphavinyl) ether ligand functions as an eight-

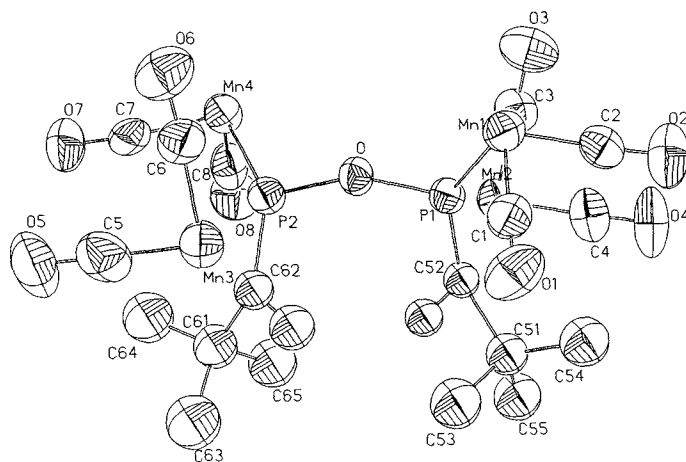


Fig. 1. Molecular crystal structure of **3**; for clarity, the methylcyclopentadienyl moieties are omitted. Selected bond lengths [pm] and angles [°]: Mn1-P1 223.6(4), Mn2-P1 240.2(3), P1-C52 171(1), Mn2-C52 215.7(9), Mn4-P2 222.6(3), Mn3-P2 243.8(3), Mn3-C62 215.6(10), P2-C62 170(1), P1-O 166.5(7), O-P1-C52 107.7(7), O-P2-C62 107.2(7), P1-O-P2 154.8(7). Space group $P2_1/c$, $a = 1218.6(3)$, $b = 1808.2(6)$, $c = 2031.4(7)$ pm, $\beta = 96.66(2)^\circ$, $Z = 4$, $R_{\text{int}} = 0.072$, $R_w = 0.053$, $\rho_{\text{calc}} = 1.42$ g cm^{-3} , $F_{000} = 1960$, AED2 Siemens-Stoe, graphite monochromator, $\lambda = 0.7107 \text{ \AA}$ ($\text{MoK}\alpha$), measuring range $3^\circ \leq 2\theta \leq 60^\circ$; $h(0/17)$, $k(0/25)$, $l(-29/29)$, 3150 measured, 3070 independent reflections with $I > 2.0\sigma(I)$, $R_{\text{merge}} = 0.056$. Structure solution: Patterson and differential Fourier methods, all non-hydrogen atoms refined anisotropically, H atoms calculated at ideal positions. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-52488, the names of the authors, and the journal citation.

electron donor. Of the four manganese complex fragments, two are bonded to the phosphorus atoms, which thus act as phosphanes, and the other two are bonded η^2 -like to the C=P double bond of the ligand.

The noticeable broadening of the NMR signals prompted us to carry out magnetic measurements. They revealed a field-dependent paramagnetism for **3** between 50 K and room temperature. The magnetic moment increases monotonically between 77.6 K ($\mu_{\text{eff}} = 4.57 \mu_B$ per Mn) and 293.8 K (5.44). The μ_{eff} values correspond to two unpaired electrons per Mn atom. Between 20 and 1.3 K, the paramagnetism is strongly field-dependent; between 50 K and room temperature, the susceptibility obeys the Curie-Weiss law ($\theta = -53.5$ K). Since the 18-electron rule is formally valid for all manganese atoms in **3**, this finding is particularly surprising. Tetragonally or trigonally distorted coordinated Mn^I (d^6) provides a possible explanation, especially since the Mn-Mn distances (Mn1-Mn2 410.6 and Mn3-Mn4 416.0 pm) rule out the possibility of magnetic interactions.

Experimental Procedure

A solution of $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_2]$ (1 g, 1.38 mmol) in 400 mL of THF was irradiated under inert gas in a water-cooled photolysis vessel. The evolution of CO ceased after 90 min (≈ 150 mL at 25°C). The solution of the solvent complex **2** thereby obtained was concentrated to 150 mL, cooled in a sodium chloride-ice bath, and then treated with **1** (1 g, 1.10 mmol). The mixture was stirred under constant pressure for 6 h at room temperature and the solvent was then removed in an oil-pump vacuum. The residue was dissolved in 20 mL of *n*-hexane and transferred to a column (silica gel 0.05-0.2, 40×2 cm, *n*-hexane). Unreacted **2** was first eluted with *n*-hexane, followed by a second, unstable, uncharacterized brown fraction with hexane/toluene (1:1) and, finally, deep orange **3** with toluene/ether (1:1). The solvent was removed and the residue was recrystallized from toluene/ CH_2Cl_2 (1:1). Deep orange crystals: yield 480 mg (25%, based on the total amount of **2**), m.p. = $142\text{--}145^\circ\text{C}$.

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1, 78129-68-7; 2, 51922-84-0; 3, 109907-06-4; $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_3]$, 12108-13-3.

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- [3] Spectroscopic data of **3**: $^1\text{H-NMR}$ (60 MHz, CCl_3D , TMS, 25°C): $\delta = 5.31$ (s, C_5H_4 (8H)), 4.80 (s, C_5H_4 (8H)), 4.26 (s, CH (2H)), 2.11 (s, CH_3 (6H)), 1.96 (s, CH_3 (6H)), 1.36 (s, $\text{C}(\text{CH}_3)_3$ (18H)); $^{31}\text{P-NMR}$ (90 MHz, H_3PO_4 ext., 25°C): $\delta = +414.89$ (s); IR (ν_{CO} [cm^{-1}], KBr): 1964 vs, 1935 vs, 1929 vs, 1903 s, 1866 vs; FD-MS (160°C, toluene, ether): m/z 978 (M^{\oplus}).