# On a novel coordination mode of phosphinine C₅H₅P†‡

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In an unprecedented coordination mode two phosphinines simultaneously bridge a Mn–Mn bond and the latter with two $Mn(CO)_3$ fragments; the distortion of the resulting central heterobicyclo[1.1.0]butane unit follows from the Mn(18VE) requirement.

The heteroarenes $C_5H_5E$ (E = N, P, As, Sb, Bi) are of principal interest owing to their ambidentate nature to act as $\eta^1(\sigma)$- and $\eta^6(\pi)$-ligands. Stability and handling of pyridine, phosphinine and, to a certain extent, arsinine allow their use as preformed ligands in complex synthesis. Contrarily, for the heteroarenes stibinine and bismuthinine generation from precursors in the coordination sphere of a metal and stabilization by complexation is called for. By far the most abundant results based on the former approach have been obtained for phosphinine $C_5H_5P$ and its derivatives.[2] With regard to the multifarious modes of coordination, phosphinines rival alkynes[3] and cyclooctatetraene (Scheme 1).[4]
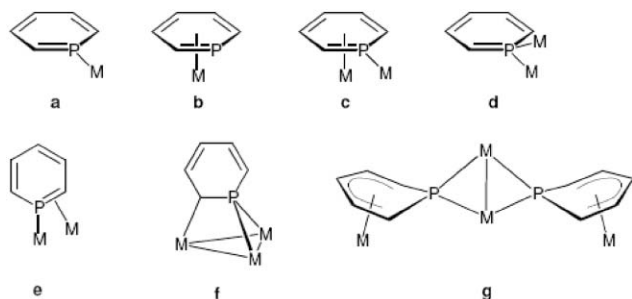
**Scheme 1** Coordination modes of the phosphinine ligand: known **a**–**f**[2b] and novel **g**.

Binary phosphinine–metal complexes with the exception of $(\eta^6\text{-}C_5H_5P)_2V$,[5] $[(1\text{-Me-}3,5\text{-Ph}_2\text{-}\eta^1\text{-}C_5H_2P)_4Rh]^+$,[6] $[\{1,5\text{-}(SiMe_3)_2\text{-}\eta^1\text{-}C_5H_3P\}_2Au]^+$ [7a] and related gold(I) complexes of silacalix[*n*]phosphinines[7b] are hitherto dominated by central metals of even atomic number. This is plausible since M–M bonded carbonyl-complex dimers like $Mn_2(CO)_{10}$ and $Co_2(CO)_8$, which are conventional starting materials in phosphinine-complex synthesis, upon attack by Lewis bases are subject to thermal or photochemical disproportionation which leads to complicated product mixtures.[8] More tractable are ternary complexes in that, *via* carbonyl substitution, the $\sigma$-complex $(\eta^5\text{-}C_5H_5)Mn(CO)_2(\eta^1\text{-}1,3,5\text{-Ph}_3\text{-}C_5H_2P)$ **1** is accessible, which can be converted photochemically into the $\pi$-complex $(\eta^5\text{-}C_5H_5)Mn(\eta^6\text{-}1,3,5\text{-Ph}_3\text{-}C_5H_2P)$ **2** [eqn (1)].[9]
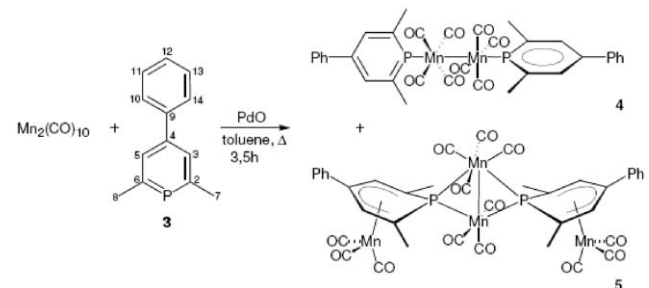
(1)
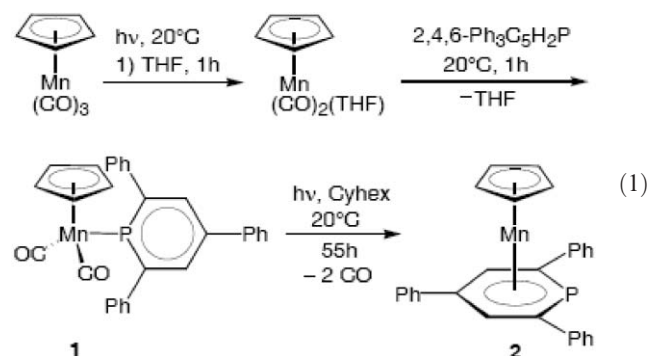
In the search for complexes which contain phosphinine as a bridging ligand, we nonetheless took recourse to $Mn_2(CO)_{10}$, whose reaction with 2,6-dimethyl-4-phenylphosphinine **3** will be reported in the following. This project also gained in interest from the surprising observation that the reaction of 4,4′,5,5′-tetramethyl-2,2′-biphosphinine with $Mn_2(CO)_{10}$ affords the diphosphamanganole complex **7** [eqn (2)].[10]

(2)
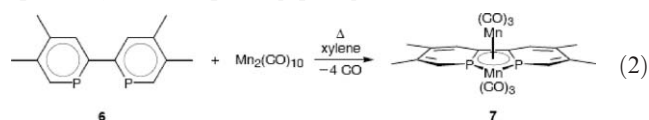
How would a mononuclear phosphinine behave under comparable conditions?

Thermal reaction of **3** with $Mn_2(CO)_{10}$ yields (phosphinine)$_2$-$Mn_2(CO)_8$ (**4**) and (phosphinine)$_2Mn_4(CO)_{13}$ (**5**), that is a mixture of products of conventional (**4**) and unconventional (**5**) composition (Scheme 2); the structure of both products was determined by X-ray diffraction (Fig. 1 and 2).§

Accordingly, the disubstitution product **4** features axial coordination of two phosphinine ligands to a $(CO)_4MnMn(CO)_4$ backbone as expected from steric considerations. The more

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**Scheme 2** PdO-activated reaction of 2,6-dimethyl-4-phenylphosphinine **3** with dimanganesedecacarbonyl.

**Fig. 1** Structure of compound **4** in the crystal (vibrational ellipsoids represent 50% probability). Selected bond lengths [pm] and angles [°]: Mn1–Mn1a 290.32(12), Mn1–P1 222.96(12), Mn1–C15 180.4(6), P1–Mn1–Mn1a 178.71(6), C15–Mn1–Mn1a 84.06(18), C15–Mn1–Mn1a–C17a 45.8, C15–Mn1–P1–C6 40.2(3). Additional "a" letters in the atom labels indicate the symmetry operation $(-x, 1 - y, z)$.
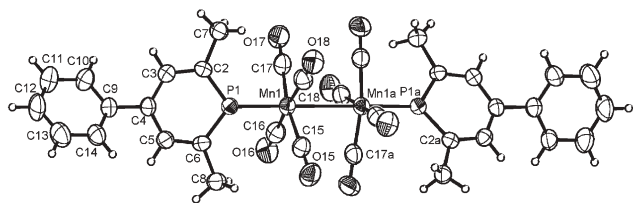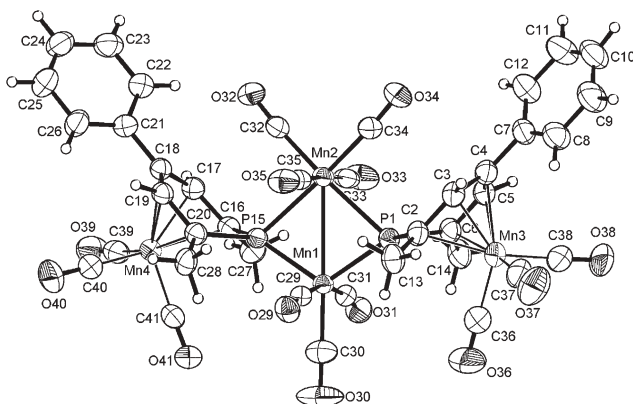


**Fig. 2** Structure of compound **5** in the crystal (vibrational ellipsoids represent 50% probability). Selected bond lengths [pm] and angles [°]: Mn1–Mn2 280.45(6), Mn1–P1 218.78(8), Mn2–P1 244.46(9), Mn1–P1–Mn2 74.28(3), Mn1–C29 182.8(3), Mn1–C30 177.1(3), Mn1–C31 183.0(3), Mn2–C32 182.5(3), Mn2–C33 184.2(3), Mn2–C34 182.0(3), Mn2–C35 184.3(3), P1–C2 180.6(3), P1–C6 181.9(3), C2–C3 141.3(4), C3–C4 142.8(4), C4–C5 142.2(4), C5–C6 139.9(4), Mn3–C2 220.8(3), Mn3–C3 213.5(3), Mn3–C4 215.8(3), folding C2–6/C2–P1–C6 38.24(17), C16–20/C16–P15–C20 40.12(16).

complicated structure of **5** can be described as a $(CO)_4MnMn(CO)_3$ backbone which is unsymmetrically bridged by two phosphinine ligands, the latter utilizing their heteroatoms; additionally, each phosphinine, by means of its π-electron system, coordinates to a $Mn(CO)_3$ fragment. This unsymmetrical bridging may be rationalized by the fact that $\eta^5$-coordination of a $(CO)_3Mn(d^7)$ fragment to a phosphinine generates an open cymantrene[11] structure in which the P atom disposes of three free valence electrons. The two bridging P atoms each form a 2e-2c bond to the $Mn(CO)_3$ unit of the $Mn_2(CO)_7$ backbone and contribute one electron to a PMnP 2e-3c bond involving the $Mn(CO)_4$ unit. In this fashion, all three types of Mn atoms reach an 18 valence-electron configuration. This interpretation of the bonding conditions concords with phosphinine ring folding and the disparate bond lengths Mn1–P1, Mn1–P15 short (218.8 pm) and Mn2–P1, Mn2–P15 long (244.5 pm). The atoms Mn1, Mn2, P1, and P15 generate a planar heterobicyclo[1.1.0]butane frame; the central Mn–Mn bond (280.4 pm) in **5** is considerably shorter than that in **4** (290.3 pm). The coordination sphere $Mn1P_2C_3$ in **5** may be described as distorted trigonal bipyramidal, the environment in $Mn2P_2C_4$ approximates to octahedral. Just as in variant **c**

(Scheme 1), phosphinine in **5** acts as an 8e ligand; however, in **5** it uses its full bridging potential in that, by means of its σ electrons at the P atoms, it bridges the central $Mn_2(CO)_7$ backbone and, by its carbon centered π electrons, two peripheral $Mn(CO)_3$ units.

With regard to the mode of formation, based on the Mn:CO ratio it may be assumed that **4** is the primary and **5** the consecutive product. Accordingly, **4** is thought to be attacked by excess $Mn_2(CO)_{10}$ and the loss in phosphinine aromaticity in **5** is compensated by the bond energy of the cymantrene unit formed. The driving force of this adduct formation benefits from the fact that, compared with "closed" cyclopentadienyl $C_5H_5^-$, "open" pentadienyl $C_5H_7^-$ possesses better π-donor *and* better δ-acceptor properties.[11c] The redox character of this reaction—$Mn^0$ [in $Mn_2(CO)_{10}$] is converted into $Mn^I$ [in open cymantrene]—can be accounted for by assigning the formal oxidation number $C^{-1/5}$ in the $C_5H_5$ section of the $\eta^5$-phosphinine ligand. The unusual Mn–P–Mn bridging structure follows from the requirement that, in order to maintain Mn(18VE) configurations, the entry of two 3e ligands $(CO)_3Mn-\eta^5-C_5H_5P$: must be compensated by the exit of three 2e ligands :C=O from $Mn_2(CO)_{10}$, thus accounting for the $Mn_2(CO)_7$ backbone.

This study reveals that the palette of coordination modes **a–f** (Scheme 1) must be extended by variant **g**, in which two phosphinines bridge four metal atoms and each phosphinine serves as a $\mu_3(\eta^5$-pentadienyl-$\mu_2$-phospha) ligand. A distinct feature in **5** is phosphinine folding with concomitant dearomatization, which is commonly observed only upon addition of a nucleophile generating a phosphacyclohexadienyl entity $C_5H_5PR^-$.[2c]

## Notes and references

§ Octacarbonyl-1$\kappa^4C$,2$\kappa^4C$-bis(2,6-dimethyl-4-phenylphosphinine-1$\kappa P$,2$\kappa P$)dimanganese(*Mn–Mn*) (**4**) and heptacarbonyl-1$\kappa^3C$,2$\kappa^4C$-bis[μ-(tricarbonyl(2,6-dimethyl-4-phenyl-$\eta^5$-phosphinine)manganese-1:2$\kappa^2P$)]dimanganese(*Mn–Mn*) (**5**).

All manipulations were carried out under exclusion of air and protection from light. The ligand **3** was prepared as described[12] *via* the pyrylium route.

A solution of $Mn_2(CO)_{10}$ (573 mg, 1.47 mmol) in toluene (15 mL) was supplied with a small amount of PdO and heated under reflux during 1 h. After the addition of 2,6-dimethyl-4-phenylphosphinine **3** (588 mg, 2.94 mmol), dissolved in 5 mL of toluene, heating was continued for 2.5 h. After filtration over silica gel the orange-red filtrate was reduced to a volume of 2 mL and chromatographed using silica gel 60 (2.5 × 30 cm). Elution with petroleum ether (40/60) yielded excess ligand and unreacted $Mn_2(CO)_{10}$ (yellow solution). Elution with toluene gave **5** and subsequent elution with THF supplied **4**. The orange-red THF eluate was reduced to 10 mL, layered with 5 mL of petroleum ether (40/60) and stored for 15 d at −20 °C to furnish 345 mg (0.47 mmol, 32%) of **4** as orange-red needles, which included 2 mol equiv. of THF. Solubility: good in THF, fair in toluene, poor in THF.
$^1$H-NMR (500 MHz, THF-$d_8$, RT, [Δδ] = coordination shift $\delta_{compl} - \delta_{Lig}$): δ = 7.99 [0.24], $J_{HP}$ = 20.0 Hz, H$_{3,5}$; 2.85 [0.11], $J_{HP}$ = 19.2 Hz, H$_{7,8}$; 7.62 [0.02], H$_{10,14}$; 7.44 [−0.03], H$_{11,13}$; 7.35 [−0.04], H$_{12}$. $^{31}$P-NMR (202 MHz, THF-$d_8$, RT): δ = 219.4 [25.3]. $^{13}$C-NMR (100 MHz, THF-$d_8$, RT): δ = 163.9 [−4.6], $J_{CP}$ = 17.7 Hz, C$_{2,6}$; 137.0 [4.9], $J_{CP}$ = 22.6 Hz, C$_{3,5}$; 140.3 [−3.0], $J_{CP}$ = 25.1 Hz, C$_4$; 24.1 [−0.5], $J_{CP}$ = 17.3 Hz, C$_{7,8}$; 142.6 [0.4], C$_9$; 128.2 [−0.6], C$_{10,14}$; 129.9 [2.3], C$_{11,13}$; 128.6 [1.0], C$_{12}$; 225.1, CO.
C/H analysis, calc. for $C_{34}H_{26}Mn_2O_8P_2 \cdot 2C_4H_8O$ (878.61 g mol$^{-1}$): C 57.42, H 4.82; found C 57.81, H 5.83%.

From the also orange-red toluene eluate after reducing to 7 mL and layering with 15 mL of petroleum ether (40/60) after 5 d at 0 °C 210 mg (0.21 mmol, 29%) of **5** were obtained as red, cube shaped crystals, which included 0.5 mol equiv. of toluene. Solubility: good in THF, benzene, toluene, fair in petroleum ether.
$^1$H-NMR (500 MHz, THF-$d_8$, RT, [Δδ] = coordination shift): δ = 6.28 [−1.47], $J_{HP}$ = 9.3 Hz, H$_{3,5}$; 2.06 [−0.68], $J_{HP}$ = 15.3 Hz, H$_{7,8}$; 7.36–7.56,

$H_{10-14}$. ^{31}P-NMR (202 MHz, THF-$d_8$, RT): $\delta$ = 214, 217, 200 [20, 23, 26]. ^{13}C-NMR (100 MHz, THF-$d_8$, RT): $\delta$ = 69.3 [−99.2], $J_{CP}$ = 20.0 Hz, $C_{2,6}$; 106.4 [−25.7], $C_{3,5}$; 102.6 [−39.7], $C_4$; 27.0 [2.4], $J_{CP}$ = 14.4 Hz, $C_{7,8}$; 27.6 [3.0], $J_{PC}$ = 13.7 Hz, $C_{8,7}$; 136.6 [−5.6], $C_9$; 129.8 [1.0], $C_{10,14}$; 128.9 [1.3], $C_{11,13}$; 128.2 [0.6], $C_{12}$; 228.4, 228.2, 226.0, 222.0, 221.8, CO.

C/H analysis, calc. for $C_{39}H_{26}Mn_4O_{13}P_2 \cdot 0.5C_7H_8$ (1030.39 g mol$^{-1}$): C 49.54, H 2.93; found C 53.59, H 3.70%. Repeated analyses failed to decrease this deviation. EI-MS of **4** and **5** only yielded peaks for the ligand **3** and its fragments.

**4**·2THF: $C_{42}H_{42}Mn_2O_{10}P_2$, $M_r$ = 878.58, orthorhombic, $Aba2$, $a$ = 19.7993(14), $b$ = 27.5435(18), $c$ = 7.6297(8) Å, $V$ = 4160.8(6) Å$^3$, $T$ = 193 K, $Z$ = 4 (crystallographic twofold symmetry), $\rho_{calc}$ = 1.403 Mg m$^{-3}$, $\mu$(MoK$\alpha$) = 0.740 mm$^{-1}$, $F(000)$ = 1816, STOE IPDS diffractometer, MoK$\alpha$ radiation ($\theta_{max}$ = 26°), 13989 collected reflections, 4014 unique ($R_{int}$ = 0.086), 2328 observed, GOF = 0.846, Flack parameter (absolute structure) = 0.02(3), $R$ = 0.0447, w$R_2$ = 0.0913, hydrogen atoms have been refined on calculated positions using the riding model.¶

**5**·0.5toluene: $C_{42.5}H_{30}Mn_4O_{13}P_2$, $M_r$ = 1030.36, triclinic, $P\bar{1}$, $a$ = 8.9492(8), $b$ = 14.8524(13), $c$ = 16.7326(15) Å, $\alpha$ = 105.427(7), $\beta$ = 95.207(7), $\gamma$ = 92.097(7)°, $V$ = 2130.8(3) Å$^3$, $T$ = 193 K, $Z$ = 2, $\rho_{calc}$ = 1.606 Mg m$^{-3}$, $\mu$(MoK$\alpha$) = 1.298 mm$^{-1}$, $F(000)$ = 1038, STOE IPDS2 diffractometer, MoK$\alpha$ radiation, 24204 collected reflections ($\theta_{max}$ = 25°), 7422 unique ($R_{int}$ = 0.079), 5516 observed, $GOF$ = 0.914, $R$ = 0.0322, w$R_2$ = 0.0760. Hydrogen atoms have been located and refined isotropically (toluene hydrogen atoms on calculated positions), the solvent molecule was disordered due to an inversion center.¶

All calculations have been performed using the programs SHELXS-97 and SHELXL-97.[13]

¶ CCDC 602395 (**4**) and 602394 (**5**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606739e

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