P_2O, the Phosphorus Analogue of N_2O, as a Ligand in a Tetranuclear Cluster**

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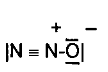
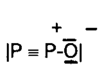
*Dedicated to Professor Gerhard Fritz
on the occasion of his 80th birthday*

After the synthesis of $[\{Cp^RNi\}_2\{W(CO)_4\}(\mu_3\text{-}PO)_2]$ (**1**, $Cp^R = C_5HiPr_4$), in which it was possible to coordinatively stabilize PO, the group homologue of NO, for the first time,[1] the next worthwhile objective was to attempt to bind further phosphorus analogues of the type N_xO_y within the coordination sphere of transition metal complex fragments. The 16-valence-electron (VE) molecule diphosphorus monoxide P_2O (**B**), which is isoelectronic with N_2O (**A**), appeared to be a particularly promising candidate.



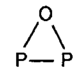
$|N\equiv\overset{+}{N}-\overset{-}{\underline{\overline{O}}}|$

A



$|P\equiv\overset{+}{P}-\overset{-}{\underline{\overline{O}}}|$

B



C

The cluster skeleton of $[\{Cp^*Fe\}\{Cp''Co\}_2(P_4)(P)]$ (**2**, $Cp^* = C_5Me_5$; $Cp'' = 1,3\text{-}tBu_2C_5H_3$), which is formed, amongst other products, by the cothermolysis of $[Cp^*FeP_5]$ and $[Cp''Co(CO)_2]$,[2] can be extended by oxidation at room temperature with atmospheric oxygen to form the tetranuclear complex **3**, which contains a PO ligand in addition to a P_2O ligand [Eq. (1)].

$$\underset{\mathbf{2}}{[\{Cp^*Fe\}\{Cp''Co\}_2(P_4)(P)]} \xrightarrow[CH_2Cl_2]{O_2,\ RT} \underset{\mathbf{3}}{[\{Cp^*Fe\}\{Cp''Co\}_3(P_2O)(PO)(P_2)]} \quad (1)$$

Cluster **3** forms brown crystals that can be handled for a short time in air. The crystals are barely soluble in nonpolar solvents but are well soluble in toluene and dichloromethane. In the ^{31}P NMR spectrum of **3** (ABMXY spin system),[3] the largest low-field shift of $\delta = 558.8$ is found for P_A (P1 in Figure 1) which is connected to three L_nM fragments. The chemical shifts and coupling constants of P_M (P2) and P_B (P3)[3] support the idea that the P_2O ligand is not "separated" into a μ_3-PO and a μ_3-P ligand.

The Co_3FeP_5 framework of **3** (Figure 1)[4] can be described as a boatlike six-membered ring (Co1,P3,P2,Co2,P5,P4) bridged by the P1O1 ligand. This results in two five-membered rings, P1,Co1,P4,P5,Co2 and P1,Co1,P3,P2,Co2: the latter is capped by the 13VE fragment Cp*Fe1, while the phosphorus atoms of the P2,P3,P4,P5 part of the six-membered ring are coordinatively bound to the 14VE fragment of Cp″Co3 (Figure 1).

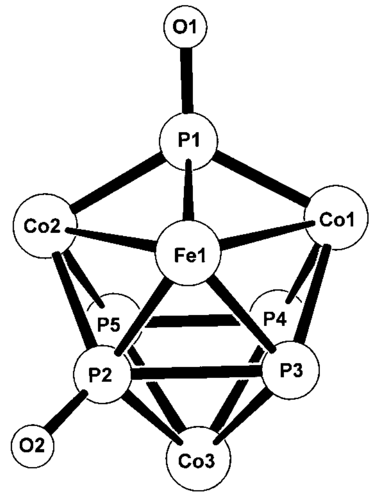


Figure 1. Structure of **3** in the crystal. The Cp* and Cp″ ligands have been omitted for clarity. Selected distances [Å] and angles [°]: P1–O1 1.496(6), P2–O2 1.509(6), P2–P3 2.456(3), P4–P5 2.151(4), P2···P5 2.574(3), P3···P4 2.560(4), Co1–P1 2.190(3), Co1–P3 2.247(3), Co1–P4 2.232(3), Co2–P1 2.206(3), Co2–P2 2.248(3), Co2–P5 2.245(3), Co3–P2 2.242(3), Co3–P3 2.302(3), Co3–P4 2.280(3), Co3–P5 2.310(3), Fe1–P1 2.161(3), Fe1–P2 2.227(3), Fe1–P3 2.271(3), Co1–Fe1 2.7164(17), Co2–Fe1 2.7215(17), Co3···Fe1 3.74, Co1···Co2 3.81, Co1···Co3 3.71, Co2···Co3 3.70; P3-P2-P5 88.34(11), P2-P3-P4 84.84(11), P3-P4-P5 95.78(13), P2-P5-P4 91.04(12), P3-P2-O2 127.2 (3).

The most remarkable structural part of **3** is the P_2O ligand. In contrast to $[\{(OC)_{13}Ru_4P\}_2O]$ (**4**),[5] in which the P_2O ligand forms a μ_6-POP bridge, here it was possible to coordinatively stabilize the N_2O-analogue P_2O for the first time. Free P_2O (**B**), which can be produced from P_2 (P_4) and ozone, has been characterized in a matrix by IR and UV/Vis spectroscopy.[6] Ab initio calculations[7a,b] showed that for P_2O the linear form **B** is somewhat more stable than the three-membered ring structure **C**.

The P2–O2 bond length of 1.509(6) Å in **3** as part of the μ_4-η^1:η^2:η^2:η^1-P_2O ligand (Figure 1) is only slightly longer than the calculated value of 1.446 Å for uncomplexed P_2O in form **B**,[7a] while the P–P bond is stretched (1.852 Å in **B**[7a]) by the twofold *side-on* and terminal coordination (σ,σ,π,π-P_2O) to 2.456(3) Å; a bond length that has been found for the intact P–P edge of the P_4 tetrahedron in the complex $[Cl(Ph_3P)_2Rh(\eta^2\text{-}P_4)]$ (**5**, 2.46 Å).[8] A P–P bond length of 2.118 Å was calculated for the energetically unfavorable bent form of P_2O.[7a] Both the μ_3-PO ligand (P1O1 in Figure 1) and the μ_3-η^1:η^2:η^1-P_2 ligand contain bond lengths within the expected range (P1–O1 1.496(6) Å[1, 9] and P4–P5 2.151(4) Å; compare with the compounds **1** and **6**).[10, 11] The P2···P5 and P3···P4 distances of 2.574(3) and 2.560(4) Å, respectively, are on the borderline,[2, 11] which may also be a result of the cluster geometry. The clear differences in the P–P bond lengths within the P2–P5 quadrangle (Figure 1) and in the chemical shifts and coupling constants,[3] as well as the comparison with **6** (3 × P_2 ligands)[11a] do not support the existence of a *cyclo*-P_4O ligand in **3**. Ab initio studies show that a planar five-membered ring is the most stable conformation for P_4O.[12] The following arguments support the idea that P_2O is not "separated" into a μ_3-PO and a μ_3-P ligand: the ^{31}P NMR chemical shifts (in this case $\delta = 558.8$ (P1) and 265.1 (P2))

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[+] Crystal structure analysis

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should then only differ slightly. For P3 as a "separated" μ_3-P ligand, a much stronger low-field shift would be expected than the observed value of $\delta = 501.6$.[2] The coupling constant of -190.7 Hz must also be considered as further support for a P2–P3 bond (2.456(3) Å in the σ,σ,π,π ligand P_2O); this value is comparable to that found in **5** (ca. 180 Hz)[8] as well as in compounds in which the *cyclo*-P_5 ligand is additionally *side-on* coordinated (d(P–P) ≈ 2.35 Å, J(P,P) ≈ −200 Hz).[2]

The Co_3FeP_5 framework can also be formally derived from the molecular structure of the complex $[\{Cp^*Co\}_3(\mu\text{-}\eta^2{:}\eta^2\text{-}P_2)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}P_2)_2]$ (**6**),[11a] by replacement of the μ-$\eta^2{:}\eta^2$-P_2 ligand by a {Cp*FeP(O)} fragment and by oxidation of one of the μ_3-$\eta^1{:}\eta^2{:}\eta^1$-P_2 ligands to P_2O. This could then form the μ_4-$\eta^1{:}\eta^2{:}\eta^2{:}\eta^1$-$P_2O$ ligand of **3** by additional *side-on* coordination of the Cp*Fe fragment.

Stable N_2O complexes are rare. A linear, terminal N_2O ligand has been proposed in complexes of the type $[Ru(NH_3)_5(N_2O)]X_2$ (X = Br, I, BF_4, PF_6), which can be stored at −5 °C.[13] No details can be given as yet about the formation of **3** from **2** by the extension of the cluster skeleton by a Cp″Co fragment.

Experimental Section

3: $[\{Cp^*Fe\}\{Cp''Co\}_2(P_4)(P)]$ (**2**)[2] (180 mg, 0.22 mmol) was dissolved in dichloromethane (40 mL) and stirred for 1 min at room temperature in air (open reaction vessel) (longer exposure to air results in complete decomposition) and then stirred in a closed reaction vessel for 18 h (monitored by ^{31}P NMR spectroscopy). After removal of the solvent, the brown residue was dissolved in dichloromethane (ca. 5 mL), treated with silylated silica gel (ca. 2 g) and dried under an oil pump vacuum until a pouring consistency was obtained. Column chromatography (column: 8 × 1.0 cm, silylated silica gel, petroleum ether, water cooled; petroleum ether/diethyl ether (2/1)) yielded **3** (52 mg; 22% relative to **2**) as a dark brown fraction. The large amount of brown residue retained on the column material could not be eluted by any common solvent.

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[3] Spectroscopic data of **3**: ^1H NMR (200.14 MHz, C_6D_5H of the solvent C_6D_6 as internal standard), ^{31}P NMR (81.02 MHz, 85% H_3PO_4 extern.). ^1H NMR: $\delta = 5.79$ (s, 1H), 5.66 (s, 1H), 5.51 (s, 1H), 5.32 (s, 1H), 5.02 (s, 1H), 4.88 (s, 1H), 4.78 (s, 1H), 4.71 (s, 1H), 4.15 (s, 1H), 1.86 (s, 15H), 1.75 (s, 9H), 1.74 (s, 9H), 1.70 (s, 9H), 1.53 (s, 9H), 1.33 (s, 9H), 1.22 (s, 9H); ^{31}P NMR: ABMXY spin system ($P_A = P1$, $P_B = P3$, $P_M = P2$, $P_X = P5$, $P_Y = P4$), $\delta = 558.8$ (s, P_A), 501.6 (dd, P_B), 265.1 (dd, P_M), 120.9 (dd, P_X), 99.7 (dd, P_Y), $^1J(P_BP_M) = -190.7$, $^1J(P_XP_Y) = -289.9$, $^nJ(P_BP_Y) = 91.6$, $^nJ(P_MP_X) = 137.3$ Hz (n is probably 2); IR (pentane): $\tilde{\nu}$(PO) [cm^{-1}] = 1182 (m, br), 1163 (m, br).

[4] Crystal structure data for **3**: $C_{49}H_{78}Co_3FeO_2P_5$, $M_r = 1086.60$, monoclinic, space group $P2_1/n$, $a = 10.5809(16)$, $b = 21.0882(17)$, $c = 24.391(4)$ Å, $\beta = 101.825(18)°$, $V = 5326.8(12)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.355$ Mg m^{-3}, $T = 293(2)$ K, Θ range: 1.96–23.95°, measured reflections: 51646, independent reflections: 8096 ($R_{int} = 0.1456$), R values: final R value ($I > 2\sigma(I)$): $R1 = 0.0639$, $wR2 = 0.1289$, all data: $R1 = 0.1549$, $wR2 = 0.1481$. Diffractometer: Stoe IPDS, structure solution: direct methods, program: SHELXS-97, refinement: full-matrix least-squares against F^2. Program for refinement: SHELXL-97, data/parameters: 8096/688. One of the Cp″ ligands is rotationally disordered. Crystallographic data (excluding structure factors) for the structure reported in this publication have been deposited as supplementary publication no. CCDC-120672 with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge from: CCDC, 12 Union Road, Cambridge CB21EZ (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Rhodium-Induced Selective B(3)/B(6)-Disubstitution of *ortho*-Carborane-1,2-dithiolate**

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Dedicated to Professor Hubert Schmidbaur
on the occasion of his 65th birthday

Ever since the discovery of 1,2-dicarba-*closo*-dodecaborane(12), the chemistry of this exceptionally stable carborane and its 1,7- and 1,12-isomers has aroused considerable interest. Although C-functionalization had readily been accomplished from the beginning,[1] and more recently the complete substitution at all boron positions has been achieved,[2] the selective synthesis of B-substituted derivatives proved to be rather difficult.[3] We have recently reported on the synthesis of the 16e rhodium complex $[Cp^*Rh\{S_2C_2(B_{10}H_{10})\}]$ (**1**),[4] and suggested that this species may be promising for further transformations owing to its electron deficiency at the rhodium center, the reactivity of the rhodium–sulfur bonds, and the potential activation of B–H

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