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2-Phosphinophenolate Complexes: Formation and Crystal Structure of a Novel Trinuclear μ-O Nickel(II)-Tris($P^{\cap}O^{-}$ Chelate)

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A novel linear trinuclear μ-O-bridging 2-phosphinophenolate nickel(II) complex with *fac*-tris($P^{\cap}O^{-}$ chelates) in the terminal positions and the three oxygen atoms each facing the central nickel(II) cation was synthesized and structurally characterized by X-ray crystallography. To the best of our knowledge, this is the first example of an octahedral Ni(II) tris($P^{\cap}O^{-}$ chelate).

Despite the considerable scientific attention nickel(II) $P^{\cap}O^{-}$ chelates have attracted with respect to the industrial importance of the Shell Higher Olefin Process (SHOP),[1] octahedral tris($P^{\cap}O^{-}$ chelates) of nickel(II) are, to the best of our knowledge, unknown. Only a distorted octahedron formed by additional coordination of *o*-methoxy groups in a mononuclear cationic Ni(III) bis(phosphinophenolate) has been described thus far.[2] Because of the d^8 electron configuration of Ni(II) and the strength of the $P^{\cap}O^{-}$ ligand field, nickel(II) salts and 2-phosphinophenols strongly prefer the formation of diamagnetic square-planar *cis*- or *trans*-bis(2-phosphinophenolate-*P*,*O*) nickel(II) chelate complexes[3] with a 16 VE configuration, detected as decomposition products of SHOP-type catalysts.[4] The cis isomers can coordinate in a μ-O-bridging mode to other metals, as found in heterobimetallic complexes of zinc(II)[5] or cobalt(II).[6]

We now report on the formation and the molecular structure of a distorted octahedral nickel(II), the first example of a trimeric isomer of the classic bis($P^{\cap}O^{-}$ chelates). 2-Diphenylphosphino-4-methoxyphenol (**1**) was treated with TlOEt and $PhNiBr(PPh_3)_2$ at −30 °C. After removal of TlBr and concentration of the supernatant solution in a vacuum, the residue was layered with hexane, yielding single brown crystals of the trinuclear nickel(II) complex **2**,[7] which contains six equiv of THF (Scheme 1). Continued crystallization afforded small amounts of the orange *cis*-bis($P^{\cap}O^{-}$ chelate) nickel(II) complex **3**. Triphenylphosphine but no phenylnickel phosphinophenolate was detected in the mother liquor by ^{31}P NMR spectroscopy, indicating that, apart from the bromide substitution, cleavage of the Ph−Ni bond had occurred. Phenylnickel complexes $[PhNi(2\text{-}R_2P\text{-}4\text{-}R'C_6H_3O)(PR''_3)]$ (R = Ph, *c*-Hex; R′ = H, MeO; R″ = Ph, Me) are characterized by an easy dissociation of the PR''_3 ligand but are stable with respect to the Ni phenyl bond.[8] The replacement of the Ni phenyl group is therefore attributed

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(7) TlOEt (64 μL, 0.91 mmol) was added to a solution of **1** (281 mg, 0.91 mmol) in THF (10 mL), followed at −30 °C by a solution of $PhNi(PPh_3)_2Br$ (635 mg, 0.86 mmol) in THF (15 mL), which induced rapid color change to dark red-brown. The precipitate of TlBr was separated, a large part of THF was removed in a vacuum, and the concentrated solution was overlayered with *n*-hexane. Red-brown single crystals of **2** formed, in an estimated yield of 100−150 mg (30−40%). Continued crystallization provided 15−20 mg (4−6%) of orange **3** (NMR data agree within experimental acurracy with those for **3** in ref 10). Drying of the single crystals of **2** in a vacuum led to loss of THF, yielding a solvate with ca. 4 equiv THF. Anal. Calcd for $C_{130}H_{128}Ni_3O_{16}P_6$ (2308.35): C, 67.64; H, 5.59. found: C 66.82 (combustion incomplete), H 5.49.

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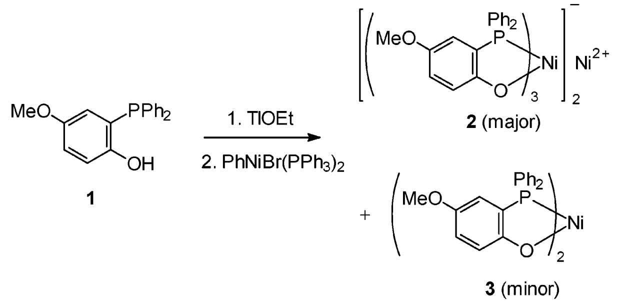
Scheme 1. Conversion of **1** to the Phosphinophenolate Nickel(II) Complexes **2** and **3**[a]



[a] THF omitted.

to a reaction with ethanol, liberated in the metalation of **1** by TlOEt. Further detailed studies will determine which phenylnickel species are attacked, i.e., the starting material PhNiBr(PPh$_3$)$_2$, an intermediate phenylnickel phosphinophenolate or both. This might help to understand the unusual formation of **2**.

The novel trinuclear μ-O-bridging P$^{\cap}$O^{-} chelate complex **2** easily loses THF. After drying of the complex at 5 Torr, elemental analysis is consistent with a residual content of ca. 4 equiv of THF. After storage for some weeks the residual amount of THF decreased from 4 to 2 mol equiv. Line broadening in the ^{1}H NMR spectrum and the apparent absence of a ^{31}P NMR phosphorus resonance of **2** is indicative of paramagnetic properties. The molecular structure of **2** was determined by single-crystal X-ray analysis (Figures 1 and 2).[9] The structure reveals a trinuclear μ-O bridged nickel chelate complex. The three nickel(II) centers display a linear arrangement of face-shared distorted octahedra. The terminal nickel ions Ni2 form facial tris(P$^{\cap}$O^{-} chelates) with the oxygen atoms directed toward and coordinating with the central nickel ion Ni1 that resides at a center of inversion. The three P$^{\cap}$O^{-} chelates are left- and right-handed three-bladed propellers with a common pseudo-C_3 axis. So far, the structure type found in **2** has been reported only for the 2-phosphinophenolate chelate complexes of typically octahedrally coordinated zinc(II), cadmium(II), and manganese(II), which are of interest as model compounds for trinuclear bioinorganic complexes.[5] For nickel(II), the structure represents the first example of octahedral coordination by phosphinophenolate ligands, which usually force a square-planar geometry around this d^{8} metal cation.

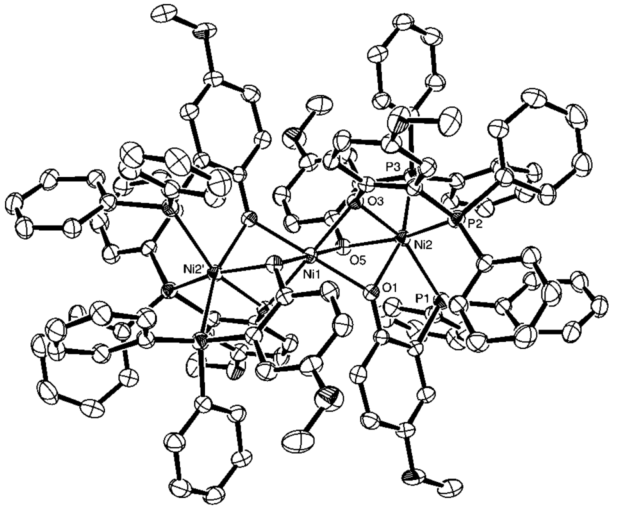


Figure 1. Molecular structure of **2**. (a) ORTEP plot with displacement ellipsoids drawn at the 25% probability level and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni1···Ni2 2.8017(7), Ni2···Ni1···Ni2′ 180.00(3), Ni−O 2.058(3)−2.072(3), Ni−P 2.4086(14)−2.4182(13); trans O−Ni1−O 180.0(2)−180(16), cis O−Ni1−O 78.65(11)−79.15(10) or 100.85(10)−100.93(10), O−Ni2−P$_{\text{chelat}}$ 82.14(8)−82.46(8), trans O−Ni2−P 160.21(8)−161.07(8), O−Ni2−O 78.73(11)−79.15(11), cis O−Ni2−P 92.37(8)−94.02(8), P−Ni2−P 102.01(5)−104.23(4).

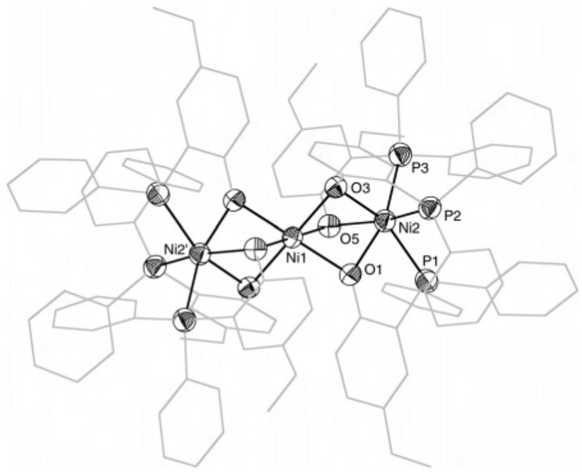


Figure 2. Schematic representation of **2**.

The Ni−O and Ni−P bonds in **2** are longer than those observed in known square-planar nickel-2-phosphinophenolate chelate complexes (Ni−O 1.856−1.984 Å, Ni−P 2.126−2.232 Å)[2,3d−3h] because of μ-O coordination, increased electron density on Ni, and steric effects by three as compared to two phosphinophenolate ligands. This also causes smaller O−Ni2−P angles within the chelate rings than in nickel mono- or bis(chelates) (84.45−89.45°). The trans O−Ni1−O arrangement is linear, but the cis O−Ni1−O angles are smaller or larger by about 11° than in the ideal octahedron because of the above-mentioned distortions.

The nature of the orange side product **3**, which was, in fact, the expected nickel(II) *cis*-bis(phosphinophenolate) solvated by THF, was established by multinuclear NMR spectroscopy and comparison with an independently synthesized sample (see below). Complexes **2** and **3** contain, on average, two P$^{\cap}$O^{-} ligands per nickel and thus are structural isomers with different degrees of association. To investigate whether the preference of the uncommon structure of **2** compared to the favored bis(P$^{\cap}$O^{-} chelate) is due to the formation path or to energetic factors (i.e., the mesomeric

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(9) Crystallographic data for **2**: $C_{138}H_{144}Ni_3O_{18}P_6$, $M = 2452.48$; monoclinic, $P21/n$ (No. 14); $a = 15.344(3)$ Å, $b = 21.235(4)$ Å, $c = 19.134(4)$ Å; $\beta = 101.82(3)°$; $V = 6102(2)$ Å^3; $Z = 2$; $D_c = 1.335$ g·cm^{-3}; absorb coeff $\mu = 0.604$ mm^{-1}; $T = 200$ K; crystal size $0.31 \times 0.15 \times 0.14$ mm; $F(000)$ 2580; θ range 3.18−27.49 °; index range $-19 \leq h \leq 19$, $-27 \leq k \leq 27$, $-24 \leq l \leq 24$; 60037 reflections collected, 13907 independent, 7728 reflections $>2\sigma$, $R(\text{int}) = 0.0719$; 13907 data/10 constraints/732 parameters were used for the refinement $S = 1.040$; R1/wR2 $[I > 4\sigma(I)] = 0.0705/0.1800$, R1/wR2 (all data) $= 0.1391/0.2145$. Nonius Kappa CCD, $\lambda(\text{Mo K}_{\alpha}) = 0.71073$ Å, numerical absorption correction, $T_{\min} = 0.8988$, $T_{\max} = 0.9328$, all non-H atoms were anisotropically refined except C and O of the disordered THF molecules.

effect of the 4-methoxy group, enhancing the basicity and donor ability of the phenolate oxygen), an independent synthesis was carried out by reacting **1** with nickelocene (molar ratio 2:1). This organometallic Ni species does not require an auxiliary base and thus does not produce salt side products, is unable to coordinate bis- or tris-(P$^\cap$O$^-$ chelates) via μ-O-coordination, and undergoes thermodynamically controlled phenolysis (acid−base reaction) under reflux conditions. Heating of ligand **1** with nickelocene in THF (15 h) led to orange crystals of the monomer *cis*-**3** THF.[10] This compound is highly soluble in THF and $CDCl_3$ and only partly soluble in hexane. Alternatively, heating of ligand **1** with nickelocene in toluene (15 h at 80 °C) produced brown solid **4** that was found to be completely insoluble in all of the aforementioned solvents.[11] The elemental composition of **4** is consistent with the unsolvated nickel(II) bis(P$^\cap$O$^-$ chelate), but the unusually low solubility indicates rather stable aggregation, possibly by Ni−O bridging interactions, that is stable even under prolonged heating in boiling THF. The formation of **3** in THF provides evidence that **3** is thermodynamically more stable than **2**. The low solubility of **4**, not observed for unsolvated nickel(II) bis(P$^\cap$O$^-$ chelates) obtained from 2-phosphinocresols and nickelocene in refluxing benzene,[3e] is also evidence that an increase of the basicity of the O$^-$-donor site might influence the formation and structure of nickel(II) P$^\cap$O$^-$ chelate complexes, favoring association via μ-O bridging bonds. The unusual formation of the trinuclear species **2** is thus the product of a kinetically controlled reaction path. The reaction probably takes place because of a suitable interplay of rapid (bromide by phenolate) and slower (phenyl by ethoxy) substitution reactions at −30 °C, with possible stabilization of intermediate Ni species by triphenylphosphine ligands and/or THF and final coordination of Ni(II) bis- or tris-(P$^\cap$O$^-$ chelates) to nonchelate Ni(II) species. Further investigations will be required to determine whether the reaction is just limited to **2** and closely related nickel(II) complexes with increased O$^-$-donor strength or whether it has more generally applicability. In any case, this example shows that square-planar complexes are not the only structure types available from this 3d^8 metal ion and P$^\cap$O$^-$ chelate ligands; with suitable reagents and reaction conditions, the formation of novel clusters with octahedral nickel P$^\cap$O$^-$ chelates is also possible. This widens our knowledge on paramagnetic multinuclear nickel(II) clusters that are of interest for biology as well as physics and material sciences.[12]

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Supporting Information Available: Experimental details for the syntheses of **2**−**4**, NMR data, color diagram of **2**, X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) A solution of **1** (212 mg, 0.69 mmol) and nickelocene (65 mg, 0.34 mmol) in THF (5 mL) was refluxed for 15 h. Partial removal of the solvent afforded 200 mg (78%) of **3**. Anal. Calcd for $C_{38}H_{32}O_4P_2Ni\cdot C_4H_8O$ (745.41): C, 67.68; H, 5.41. Found: C, 67.49; H, 5.77. ^{13}C NMR: δ 56.1 (OMe), 113.1, 117.5 (τ, $N = 58.4$ Hz, C-2), 118.7 (τ, $N = 16.5$ Hz), 121.8, 127.9 (τ, $N = 50.9$ Hz, C-*i*), 128.6 (τ, $N = 10.7$ Hz, C-*m*), 130.8 (C−p), 132.8 (τ, $N = 10.6$ Hz, C-*o*), 151.4 (br, τ, $N = 8.1$ Hz, C-4), 169.9 (τ, $N = 17.4$ Hz, C-1 in cis configuration). ^{31}P NMR ($CDCl_3$): δ 34.2.

(11) Solutions of **1** (184 mg, 0.597 mmol) and nickelocene (56.4 mg, 0.298 mmol) in toluene (each 5 mL) were combined and heated to 80 °C for about 15 h. The solvent was removed in a vacuum, and the residue was washed with hexane and ether to give 140 mg (70%) of a pale-brown solid **4**, insoluble in $CDCl_3$, C_6D_6, acetone-d_6, or THF-d_8. Anal. Calcd for $(C_{38}H_{32}NiO_4P_2)_x$ $(673.32)_x$: C, 67.79; H, 4.79. Found: C, 67.24; H 4.88.

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