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Synthesis and characterization of Co and Ni complexes stabilized by keto- and acetamide-derived P,O-type phosphine ligands

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This supplementary material contains additional details concerning the crystal structures of the complexes reported in this paper.

Complex **1**

In the solid state structure of **1** (Figure 3)**,** determined by X-ray diffraction, the angle between the C(9)-C(14) and C(15)-C(20) phenyl rings is 67(1)°, and a π-π interaction exists between the former and the C(3)-C(8) phenyl ring, which make an angle of 21(1)°. The other distances and angles are as expected for such cobalt complexes. No hydrogen bond has been detected in this crystal structure while the main intermolecular connexions are two CH-π interactions occurring between C(7)-H(7) and C(8)-H(8), and the C(15)/C(20)* and C(9)/C(14)** phenyl rings, respectively (* and ** correspond to the following equivalent positions: -x,-1/2+y,1/2-z and -x,1/2+y,1/2-z).

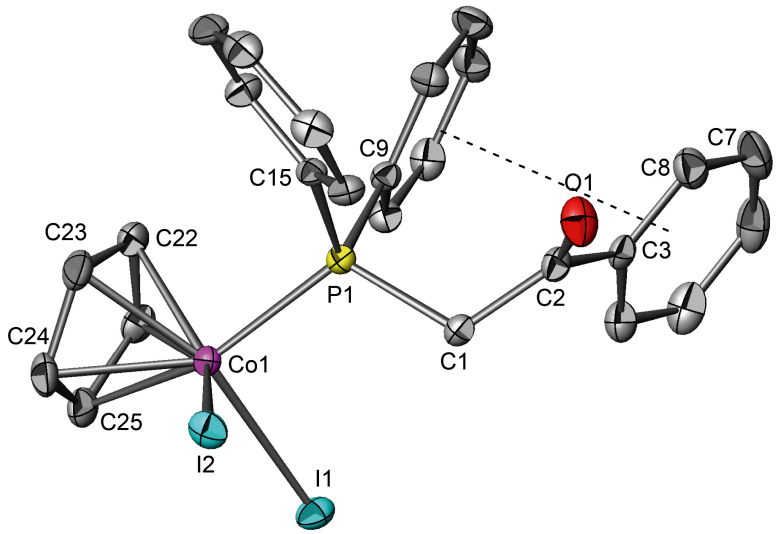

Figure 3. ORTEP view of complex **1** (the hydrogen atoms have been omitted for clarity). Displacement ellipsoids are drawn at 50% probability level. Selected distances (Å) and angles (deg.): Co1-I1, 2.593(1), Co1-I2, 2.569(1), Co1-P1, 2.231(1), P1-C1, 1.85(1), C1-C2, 1.51(1), O1-C2, 1.21(1); P1-Co1-I2, 88.9(1), C1-P1-Co1, 114.4(1), C9-P1-C15, 105.6(1).

Complex **4**

The crystal structure of **4** confirms that a five-membered heteroatomic ring has been formed which contains five different chemical elements (Figure 5).

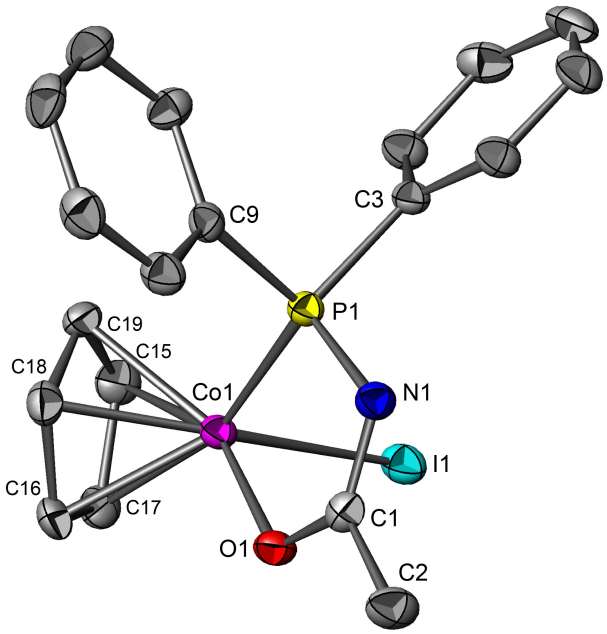

Figure 5. ORTEP view of complex **4** (hydrogen atoms omitted for clarity). Displacement ellipsoids are drawn at 50% probability level. Selected distances (Å) and angles (deg.): Co1-I1, 2.572(1), Co1-O1, 1.924(2), Co1-P1, 2.190(1), P1-N1, 1.676(2), N1-C1, 1.32(1), C1-O1, 1.29(1); O1-Co1-P1, 82.6(1), I1-Co1-P1, 94.45(2), N1-P1-Co1, 102.2(1), C9-P1-C3, 102.1(2).

This ring is almost planar with a maximum deviation out of the ring of 0.03 Å for Co(1) and P(1). This ring makes a dihedral angle of 41(1)°, 59(1)° and 76°(1) with the cyclopentadienyl ring, the C(3)-C(8) phenyl ring and the C(9)-C(14) phenyl ring, respectively. The angle between the two phenyl rings was 89(1)°, against 67° and 62° in complexes **1** and **3**, respectively. No specific π–π interaction or classical H-bond was observed. From the crystal packing point of view, the main intermolecular connexions are three short CH-π interactions [C(5)-H(5) → cyclopentadienyl ring, C(7)-H(7) → C(3)/C(8) phenyl ring and C(13)-H(13) → C(9)/C(14) phenyl ring, with distances from the hydrogen atoms to the centroids of 2.90(1) Å, 2.72(1) Å and 3.00(1), respectively).

Complex *trans*-**5**

In the crystal structure of *trans*-**5** (Figure 6), the dihedral angle between the least-squares planes through the five-membered heteroatomic ring Ni(1)-P(1)-C(3)-C(2)-O(1) and the phenyl ring is 30(1)°.

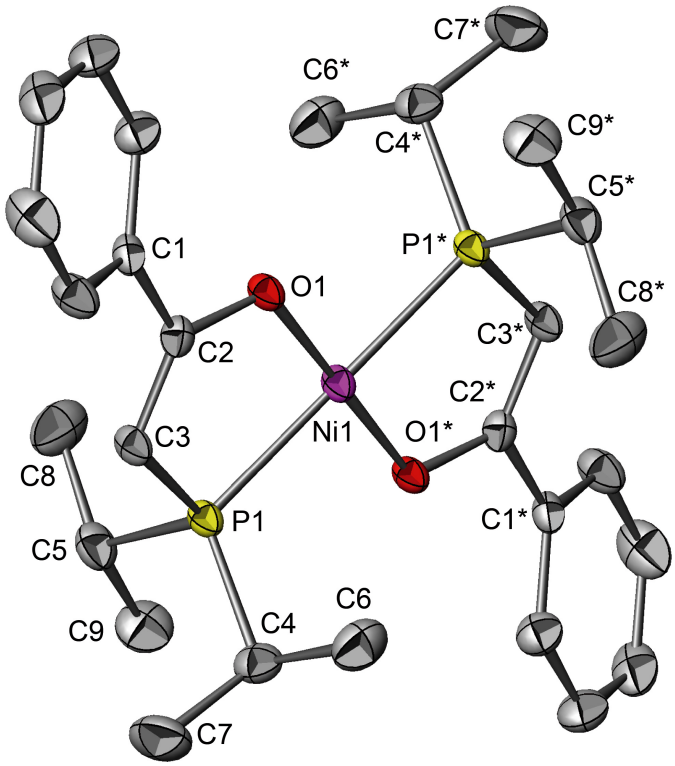

Figure 6. ORTEP view of complex *trans*-**5** (the hydrogen atoms have been omitted for clarity). Displacement ellipsoids are drawn at 50% probability level. Symmetry code for equivalent positions *: -x, 2-y, -z. Selected distances (Å) and angles (deg.): Ni1-O1, 1.850(1), Ni1-P1, 2.199(1), P1-C3, 1.769(2), C2-C3, 1.354(3), C2-O1, 1.32(1), C2-C1, 1.49(1), P1-C4, 1.836(2), P1-C5, 1.841(2); O1-Ni1-P1, 87.0(1); O1-Ni1-O1*, 180.0(1), C3-P1-Ni1, 97.9(1), C2-O1-Ni1, 119.4(2), O1-C2-C3, 123.0(2).

The crystal packing reveals many intermolecular CH-π interactions and especially a short one involving the phenyl ring and the C(8)-H(8) group (2.73(1) Å) (Table S-1). These atoms and the ring centroid form an angle of 146(1)°.

Table S-1. Analysis of X-H···Cg(π-Ring) interactions in complex *trans*-**5**

X-H(I)	Res(I)	Cg(J)	[ARU(J)]	H···Cg	X-H···Cg	X···Cg
C(6)-H(6A)	[1] ->	Cg(1)	[1555.01]	3.0379	99.63	3.345(3)
C(8)-H(8B)	[1] ->	Cg(1)	[1555.01]	2.9745	93.91	3.195(3)
C(8) -H(8C)	[1] ->	Cg(3)	[1455.01]	2.7335	146.15	3.589(3)

[1555] = X,Y,Z
[2575] = -X,2-Y,-Z
[1455] = -1+X,Y,Z

Cg(1) = Ni1,P1,O1,C2,C3
Cg(3) = C1,C10,C11,C12,C13,C14

Complex **6**

In the structure of *cis*-[Ni($\mathbf{L}^3$)$_2$] (**6**), no specific π–π stacking or classical hydrogen bond has been detected but numerous CH-π interactions exist in the crystal packing.

Complex **7**

In the structure of complex **7** (Figure 8), the dihedral angle between the phenyl rings at P(1) is 75(1)° and the dihedral angles between the least-squares planes through the heteroatomic ring and the phenyl rings are almost the same i.e. 70(1)° and 73(1)° for C(3)-C(8) and C(9)-C(14), respectively. No specific π–π stacking or classical hydrogen bond was detected is this crystal structure.

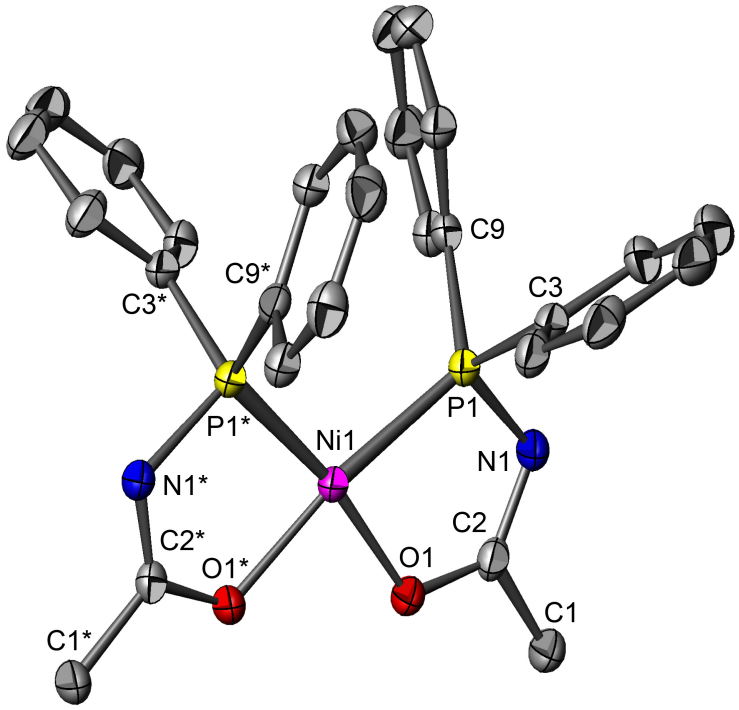

Figure 8. ORTEP view of complex **7** (the hydrogen atoms have been omitted for clarity). Displacement ellipsoids are drawn at 50% probability level. Symmetry code for equivalent positions *: 1-x, y, 1/2-z. Selected distances and angles: Ni1-O1, 1.891(1) Å; Ni1-P1, 2.153(1) Å, P1-C3, 1.816(2) Å; P1-C9, 1.805(2) Å; P1-N1 1.686(2) Å; C2-O1, 1.299(2) Å; C1-C2, 1.497(3) Å; C2-N1, 1.313(3) Å; P1-Ni1-P1* 105.2(1)°; O1-Ni1-O1*, 87.8(1)°; P1-Ni1-O1, 171.3(1)°; C2-O1-Ni1, 118.0(1)°; O1-C2-C1, 125.0(2)°.