

CO Insertion Reactions into the M–OH Bonds of Monomeric Nickel and Palladium Hydroxides. Reversible Decarbonylation of a Hydroxycarbonyl Palladium Complex

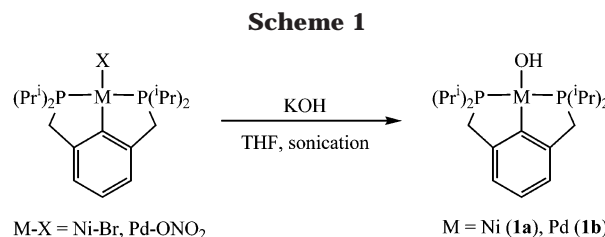
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Summary: The monomeric hydroxides $M\{C_6H_3-2,6-(CH_2P^iPr_2)_2\}(OH)$ ($M = Ni, Pd$) react with carbon monoxide, giving rise to the binuclear CO_2 complexes $[M\{C_6H_3-2,6-(CH_2P^iPr_2)_2\}]_2(\mu-CO_2-\kappa^2C, O)$ ($M = Ni, Pd$). The formation of the Pd derivative takes place via the mononuclear species $Pd\{C_6H_3-2,6-(CH_2P^iPr_2)_2\}(COOH)$, which is stable under a CO atmosphere but reversibly loses CO and H_2O on attempted isolation.

Late-transition-metal complexes containing metal–oxygen covalent bonds play an important role in many biological systems¹ and have been proposed as intermediates in numerous catalytic processes, some of them of commercial interest.² During the last two decades, much attention has been devoted to the study of the structure and chemical reactivity of group 9 and 10 hydroxo, alkoxo, and aryloxo complexes.³ Despite this, Ni and Pd complexes containing terminally bound OH ligands are still rare. A few mononuclear square-planar hydroxopalladium(II) complexes have been isolated and structurally characterized,⁴ but similar Ni complexes have not been reported, despite the higher oxophilicity of the latter. The terminal binding of OH to Ni(II) has only been authenticated in penta- or hexacoordinated coordination complexes containing low-field ligands.⁵ The scarcity of Ni and Pd monomeric hydroxides stems in part from their well-known tendency to associate forming species of higher nuclearity.⁶ Furthermore, they display a pronounced nucleophilic and basic character, and their reactivity is in some respects reminiscent of that of alkyl complexes.⁷ For instance, carbon monoxide



can formally insert into the M–OH bond,⁸ although it is not altogether certain whether this reaction takes place through a classical migratory mechanism.^{7,9} Herein we wish to report the synthesis and the crystal structure of two new square-planar organometallic hydroxides of Ni and Pd, featuring terminally bound OH ligands. To prevent dimerization of the complexes, we have used the tridentate pincer ligand 2,6-bis((diisopropylphosphino)methyl)phenyl (PCP). In addition, we will show that the $M(PCP)(OH)$ complexes react with CO, giving rise to binuclear CO_2 complexes of the composition $[M(PCP)]_2(\mu-CO_2-\kappa^2C, O)$, through $M(PCP)COOH$ intermediates. The Pd intermediate is stable in solution under a CO atmosphere but partially decarbonylates on attempted isolation to give the final product.

Sonication of a THF solution of the complex $Ni(PCP)Br$ with an excess of KOH allows the isolation of the complex $Ni(PCP)(OH)$ (**1a**) in 80% yield (Scheme 1), as yellow crystals, very soluble in common organic solvents.¹⁰ The $^{31}P\{^1H\}$ NMR spectrum of **1a** displays a singlet at δ 55.2 ppm, and the hydroxyl proton gives rise to a triplet resonance in the 1H NMR spectrum at δ –2.52 with $^3J_{HP} = 6.4$ Hz. In the IR the O–H stretch is observed at 3600 cm^{-1} .

The structural assignment of **1a** was confirmed by X-ray crystallography. In the solid state, the molecules

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(6) A search in the CCDC database (version 5.24, July 2003) afforded 54 structures of discrete Ni and Pd complexes containing μ -OH ligands.

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(10) A 2.38 g portion of $Ni(PCP)(Br)$ (5 mmol) was dissolved in 50 mL of THF. To the stirred solution was added 4.0 g (100 mmol) of grounded NaOH. The reaction mixture was sonicated over 5 h, the resulting suspension centrifuged, and the solvent evaporated under reduced pressure. The solid residue was extracted with Et_2O , affording a yellow solution, the solvent removed under vacuum, and the residue dissolved in hexane. The complex $Ni(PCP)(OH)$ (**1a**) was obtained as a yellow crystalline solid after cooling to $-30\text{ }^\circ\text{C}$. The analogous palladium complex **1b** was obtained in a similar fashion, using $Pd(PCP)(ONO_2)$ as starting material.

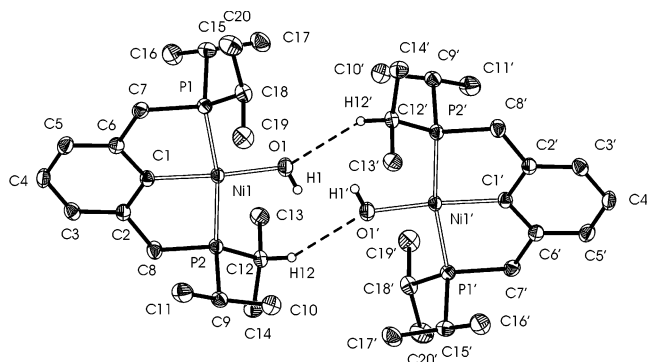


Figure 1. ORTEP diagram of Ni(PCP)(OH) (**1a**). Two molecules, oriented to form a pair, are shown. Selected bond distances (Å) and angles (deg): Ni1–O1 = 1.865(2), Ni1–C1 = 1.917(2), Ni1–P1 = 2.1516(6), Ni1–P2 = 2.1569(7), O1–O1' = 3.159(3), H1–O1' = 2.65(3), C12–O1' = 3.224(3), H12–O1' = 2.41(2); O1–H1–O1' = 131(3), C12–H12–O1' = 145.4(2).

of **1a** are arranged forming pairs. Figure 1 shows an ORTEP perspective of one such pair.¹¹ The Ni–O bond length, 1.865(17) Å, is comparable to that found in other nickel square-planar complexes.¹² The Ni–OH units are opposite to one another in those pairs, and the vectors defined by the O–H bonds are oriented in an antiparallel fashion. This particular disposition may help to stabilize the molecular pair through an attractive dipole–dipole interaction. However, the distance between the oxygen atoms, 3.159(3) Å, rules out the presence of O–H···O hydrogen bonds, which are characterized by O···O distances within the range 2.7–2.8 Å.¹³ Nevertheless, the proximity of the two Ni(PCP)–OH units gives rise to other noteworthy contacts. Thus, the isopropyl hydrogen atom H12 is close to the oxygen O1' of the neighboring molecule (2.41(2) Å). The C12–O1' distance, 3.224(3) Å, is in good agreement with the value expected for a nonclassical C–H···O hydrogen bond.¹⁴ Although interactions of this kind are weaker than classical O–H···O bonds, their capability to stabilize supramolecular structures, especially in the solid state, is well established.¹⁵ These interactions are not maintained in solution, since cryoscopic measurements in benzene solution (concentration range 0.017–0.031 M) afforded a constant value of the molecular weight of 420(8), consistent with that of the monomer (413.1).

The analogous palladium hydroxide Pd(PCP)(OH) (**1b**) can be prepared similarly from Pd(PCP)Cl and KOH, but the yield is noticeably increased (ca. 80%) if the chloride is previously converted in the nitrate complex Pd(PCP)ONO₂ by reaction with AgNO₃ (Scheme 1).¹⁰ Its spectroscopic features are similar to those of **1a**: the hydroxyl group gives rise to a triplet

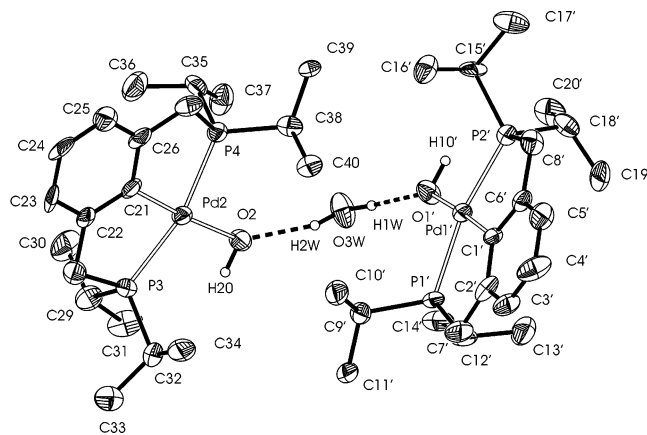


Figure 2. ORTEP diagram of the complex [Pd(PCP)(OH)]₂·H₂O (**1b**). Selected bond distances (Å) and angles (deg): Pd2–O2 = 2.050(7), Pd2–C21 = 1.981(10), Pd2–P3 = 2.273(3), Pd2–P4 = 2.286(3), O3W–O2 = 2.770(11), H2W–O2 = 1.86(5); O3W–H2W–O2 = 177(11), O3W–H1W–O1 = 148(10).

in the proton NMR spectrum at δ –1.26 ppm ($^3J_{\text{HP}}$ = 3.2 Hz), and the IR absorption due to the OH stretch appears at 3620 cm^{–1}.

Complexes **1a** and **1b** are extremely hygroscopic. The attainment of anhydrous samples is especially difficult in the case of the Pd derivative. The attempts to obtain a suitable crystal for X-ray diffraction resulted in the isolation of crystals of the hemihydrate [Pd(PCP)(OH)]₂·H₂O, whose crystal structure is shown in Figure 2.¹⁶ The water molecule bridges two crystallographically independent Pd(PCP)OH units and acts as a hydrogen bond donor to the two hydroxylic O atoms. The average Pd–OH bond length, 2.052 Å, is somewhat larger than that reported for other hydroxide complexes of Pd(II) (1.966–2.022 Å)⁴ or Pd(IV) (2.010 Å).¹⁷ The O1'···O3 and O2···O3 distances are 2.77(1) Å, identical within experimental error, indicative of a strong hydrogen bond interaction.¹³

Treatment of a solution of the nickel hydroxide **1a** in benzene or THF with an excess of CO results in the formation of a complex mixture of products that could not be identified. However, if a hexane solution of the mentioned complex is treated with 0.5 equiv of CO, a yellow microcrystalline solid precipitates, identified as the binuclear complex {[Ni(PCP)]₂(μ -CO₂- κ^2 -C,O)} (**2a**) (Scheme 2).¹⁸ In contrast with this behavior, the reaction of the Pd hydroxide **1b** with an excess of CO allows the isolation of the analogous μ -CO₂ derivative, **2b**, in moderate yield.¹⁹ Compounds **2a** and **2b** display spectroscopic features that are consistent with their formulation as binuclear complexes asymmetrically bridged

(11) Crystal data for **1a** at 173(2) K: C₂₀H₃₆NiOP₂, fw 413.14, monoclinic, space group *P2₁/c*, *a* = 8.9176(10) Å, *b* = 25.106(3) Å, *c* = 10.5817(12) Å, α = 90°, β = 111.011(2)°, γ = 90°, *V* = 2211.6(4) Å³, *Z* = 4. The final *R* factor was 0.0372 for 5107 independent reflections with *I* > 2 σ (*I*) (wR2 = 0.0752). GOF = 0.950.

(12) (a) Campora, J.; Lopez, J. A.; Maya, C. M.; Palma, P.; Carmona, E.; Valerga, P. *J. Organomet. Chem.* **2002**, *643*, 331 and references therein. (b) Campora, J.; Maya, C. M.; Palma, P.; Carmona, E.; Graiff, C.; Tiripicchio, A. *Chem. Commun.* **2003**, 1742.

(13) Huheey, J. E.; Keiter, E. A.; Keiter, R. C. *Inorganic Chemistry, Principles of Structure and Reactivity*, 4th ed.; Harper Collins College: New York, 1993.

(14) Alkorta, I.; Rozas, I.; Elguero, J. *Chem. Soc. Rev.* **1998**, *27*, 163.

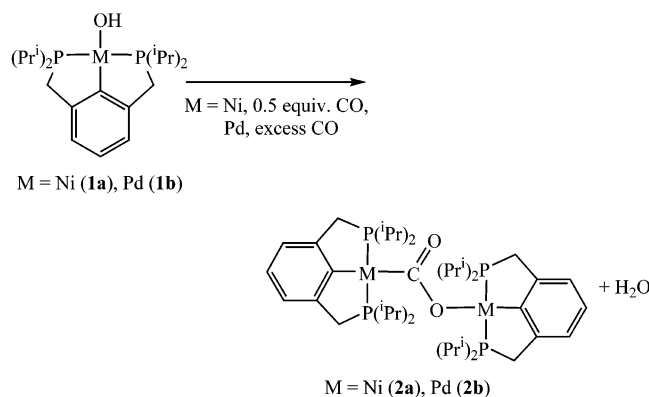
(15) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441.

(16) Crystal data for [Pd(PCP)(OH)]₂·H₂O (**1b**) at 173(2) K: C₄₀H₇₄O₃P₄Pd₂, fw 939.67, monoclinic, space group *P2₁/n*, *a* = 16.706(6) Å, *b* = 13.192(5) Å, *c* = 20.320(8) Å, α = 90°, β = 98.004(7)°, γ = 90°, *V* = 4435(3) Å³, *Z* = 4. The final *R* factor was 0.0648 for 5802 independent reflections with *I* > 2 σ (*I*) (wR2 = 0.1320). GOF = 0.946.

(17) (a) Canty, A. J.; Jin, H.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1995**, *503*, C16. (b) Canty, A. J.; Jin, H.; Roberts, A. S.; Skelton, B. W.; White, A. H. *Organometallics* **1996**, *15*, 5713.

(18) A suspension of 207 mg (0.5 mmol) of Ni(PCP)(OH) (**1a**) in 3 mL of hexane cooled to –80 °C was treated with 5.6 mL of dry CO (0.25 mmol). The cooling bath was removed and the reaction mixture treated at room temperature for 30 min and then cooled again to –80 °C and filtered. The remaining yellow solid, [Ni(PCP)]₂(μ -CO₂- κ^2 -C,O) (**2a**), was washed with cooled hexane (2 × 1 mL) and dried under vacuum. Yield: 60%.

Scheme 2



by a CO₂ unit.²⁰ Thus, their ³¹P{¹H} spectra consist of two singlets (**2a**, δ 55.7 and 60.8 ppm; **2b**, 58.0 and 60.0 ppm), evincing the chemical inequivalence of the two M(PCP) moieties. Their IR spectra show characteristic absorptions due to the ν_s (**2a**, 1479 cm⁻¹; **2b**, 1461 cm⁻¹) and ν_{as} (**2a**, 1159 cm⁻¹; **2b**, 1217 cm⁻¹) stretching modes of the bridging CO₂ fragment, and the carboxylic carbon atom resonates at low field in the ¹³C spectra: that of **2a** gives rise to a triplet of triplets at δ 206.3 ppm (³J_{CP} = 21.4 and 6.0 Hz), while that of **2b** shows as a slightly broad singlet at δ 197.8 ppm.

Complex **2b** has been further characterized by X-ray crystallography (Figure 3).²¹ In the solid state, the molecules of **2b** are disordered. The Pd–C(=O)O–Pd fragment is found in two equally probable orientations. As a consequence, the crystallographically imposed symmetry averages the bond distances and angles within the Pd(PCP) moieties, although those within the CO₂ unit can be considered reliable. The C21–O1 bond (1.210(7) Å) is somewhat shorter than the C21–O2A bond (1.277(6) Å), and the O1–C21–O2A angle is 122.9(5)°. These parameters are similar to those found in other binuclear complexes containing μ-CO₂-κ²O,C ligands, which usually display one short “C=O” and one long “C–O” bonds and an O–C–O angle close to 120°.²²

The reaction of complex **1b** with CO in C₆D₆ was monitored by ³¹P{¹H} NMR. If approximately stoichiometric amounts of CO (ca. 1 equiv) are used, the signals of **2b** appear, together with a low-intensity singlet (ca. 10% relative intensity) at δ 62.0 ppm, indicative of the formation of a new complex, **3b**. The introduction of increasingly larger amounts of CO causes the intensity of the latter signal to grow at the expense of those of **2b** (Scheme 3). A nearly complete (ca. 90%) conversion of **2b** into **3b** can be achieved under 3.5 bar of CO, in a

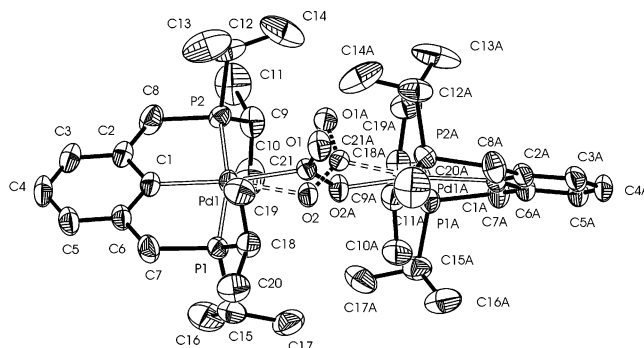
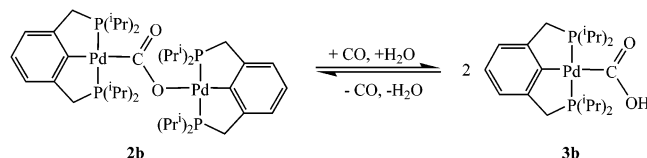


Figure 3. ORTEP diagram of [Pd(PCP)]₂(μ-CO₂-κ²C,O) (**2b**). Selected bond distances (Å) and angles (deg): Pd1–C21 = 2.110(6), Pd1–C1 = 2.046(3), O1–C21 = 1.210(7), O2A–C21 = 1.277(6), Pd1–O2 = 2.112(4); Pd1–C21–O1 = 119.9(4), Pd1–C21–O2A = 122.9(5), C21–O2A–Pd1A = 120.2(3), C1–Pd1–C21 = 170.11(17).

Scheme 3



pressurized NMR tube.²³ The latter complex has been identified as a hydroxycarbonyl complex, on the basis of its ¹H and ¹³C{¹H} NMR spectra. A proton resonance at δ 11.0 ppm and a triplet in the low-field region of the carbon spectrum (δ 214.4 ppm, ²J_{CP} = 12.1 Hz) are attributable to the Pd-bound COOH functionality. The process depicted by Scheme 3 is reversible, and when the excess of CO was removed, **2b** was cleanly regenerated from **3b**. This observation indicates that the latter is unstable with respect to decarbonylation.

Transition-metal hydroxycarbonyl complexes have received much attention, due to their role in the catalytic water-gas shift reaction^{24,25} and the reduction of carbon dioxide.²⁶ These complexes usually tend to decompose by elimination of CO₂ (decarboxylation) or OH⁻,²⁶ and therefore the reversible CO release (decarbonylation) from a M–COOH unit is a unusual process.²⁴ Very few examples of reversible CO insertion into a M–OH bond have been reported before,²⁷ although it has been recently suggested that this process might also take place during the reaction of a Ir hydroxo complex with CO.²⁸

In summary, we have prepared and characterized two mononuclear square-planar hydroxides of composition

(19) A 230 mg (0.5 mmol) portion of Pd(PCP)(OH) (**1b**) was dissolved in 25 mL of THF, and CO was bubbled in over 1 min. The solvent was evaporated under vacuum and the solid residue extracted with Et₂O. The compound [Pd(PCP)]₂(μ-CO₂-κ²C,O) (**2b**) was obtained, after addition of some hexane and cooling to –30 °C, as a white microcrystalline solid. Yield: 50%.

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(21) Crystal data for **2b** at 150(2) K: C₄₁H₇₀O₂P₄Pd₂, fw 931.65, monoclinic, space group C2/c, a = 21.6438(3) Å, b = 10.85640(10) Å, c = 20.8083(2) Å, α = 90°, β = 111.3890(10)°, γ = 90°, V = 4552.65(7) Å³, Z = 4. The final R factor was 0.0277 for 4093 independent reflections with I > 2σ(I) (wR2 = 0.0745), GOF = 1.032.

(22) See for instance: (a) Szalda, D. J.; Chou, M. H.; Fujita, E.; Creutz, C. *Inorg. Chem.* **1992**, *31*, 4712. (b) Gibson, D. H.; Sleadd, B. A.; Mashuta, M. S.; Richardson, J. F. *Organometallics* **1997**, *16*, 4421. (c) Gibson, D. H.; Ding, Y.; Andino, J. G.; Mashuta, M. S.; Richardson, J. F. *Organometallics* **1998**, *17*, 1998.

(23) A solution of 35 mg (0.076 mmol) of Pd{C₆H₃-2,6-(CH₂PⁱPr₂)₂-(OH)} (**1b**) in 0.6 mL of C₆D₆ was placed under 3.5 atm of CO at 25 °C, affording a mixture of two complexes: (i) [Pd{C₆H₃-2,6-(CH₂PⁱPr₂)₂}]₂(μ-CO₂-κ²C,O) (**2b**; 10% yield) and (ii) Pd{C₆H₃-2,6-(CH₂PⁱPr₂)₂}(COOH) (**3b**; 90% yield).

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(27) A single precedent is known for this type of process: Bennett, M. A.; Jing, H.; Willis, A. C. *J. Organomet. Chem.* **1993**, *451*, 249.

(28) Lee, D. W.; Jense, C. M.; Morales-Morales, D. *Organometallics* **2003**, *22*, 4744.

M(PCP)(OH) (M = Ni (**1a**), Pd (**1b**)). Compound **1a** reacts with 0.5 equiv of CO, affording the binuclear CO₂ complex **2a**, whereas the reaction of **1b** with an excess of CO leads to the mononuclear hydroxycarbonyl derivative Pd(PCP)COOH (**3b**), which has been characterized under a CO atmosphere. In the absence of CO complex **3b** reversibly decarbonylates, giving **2b**, the palladium analogue of **2a**. Further studies on the insertion chemistry of mononuclear hydroxides of Ni and Pd are currently under way.

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Supporting Information Available: Text giving experimental procedures and characterization data for all new complexes and tables giving X-ray crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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