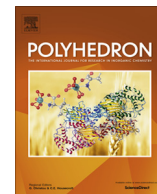Contents lists available at ScienceDirect

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Synthesis and characterisation of POC$_{sp3}$OP supported Ni(II) hydroxo, hydroxycarbonyl and carbonate complexes

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A B S T R A C T

A nickel(II) hydroxo complex (3) supported by a cyclohexyl based POC$_{sp3}$OP pincer ligand (POC$_{sp3}$OP = cis-1,3-Bis-(di-tert-butylphosphinito)cyclohexyl) is reported. Complex 3 reacts with CO to form the corresponding hydroxycarbonyl complex, (POC$_{sp3}$OP)NiCOOH (4). Complex 3 is also reactive towards CO$_2$, forming a bicarbonate species (5) that under reduced pressure loses ½ eq. of H$_2$O and CO$_2$ to give a binuclear, bridged carbonate complex (6). All compounds were characterized in the solid state by X-ray diffraction.

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1. Introduction

The chemical reactivity of late transition metal complexes containing metal–oxygen covalent bonds has attracted much interest over the last decades [1]. These bonds are generally weaker than their metal–carbon counterparts [1c], and accordingly metal hydroxo and alkoxo complexes have been suggested as reactive intermediates in many catalytic processes [2], and also to play an important part in several biological systems [3]. However, examples of mononuclear terminal hydroxo complexes of group 10 transition metals remain relatively few and typically require the steric stabilization that the tridentate pincer ligands constitute [4–6], in order to prevent formation of species with higher nuclearity such as bridged Ni(II)–(OH)–Ni(II) [7] or doubly bridged Ni(II)(OH)$_2$Ni(II) complexes [8].

Investigating the reactivity of terminal hydroxo complexes towards CO$_2$ is relevant, partly from a biological perspective, where the metalloenzyme catalysed hydration of CO$_2$ to carbonic acid takes place at a Zn–OH active site [9], but also for synthetic applications in the development of transition metal mediated functionalisations of CO$_2$, e.g. in the synthesis of organic carbonates [10]. The potential utilization of cheap and abundant CO$_2$ as a synthetic C1 source remains a major target for making the chemical industry sustainable [11].

CO$_2$ insertion into an M—X covalent bond commonly generates M—O(CO)X carboxylate species, but in enzyme chemistry Ni(II) is known to occasionally coordinate the CO$_2$ carbon. The carbon monoxide dehydrogenases (CODH's) catalyse the reversible reduction of CO$_2$ to CO at a nickel centre via the formation of a nickel–carbon bond [11b,12]. This process has been subject to biomimetic reactivity studies with Ni(II) pincer complexes, with hydroxycarbonyl species as proposed intermediates [13]. The process directly corresponds to the reverse water–gas shift reaction (RWGS), and accordingly hydroxycarbonyl species are suggested to play a crucial part as intermediates in the industrial organometallic catalysis of the forward reaction (WGS) [14].

Bicarbonate and hydroxycarbonyl complexes show a similarly low stability as the terminal hydroxo complexes, with a propensity of forming dimeric species, and it was not until recently that the first hydroxycarbonyl nickel complex was isolated and structurally characterized [13].

Whereas the reactivity of group 10 PC$_{Ar}$P hydroxide and alkoxide complexes towards CO and CO$_2$ is well documented [4e,5,6b,15], the chemistry of their PC$_{sp3}$P counterparts has not been studied. Yet coordination of an sp^3-hybridised PCP carbon expectedly gives a higher electron density at a metal centre relative an sp^2-hybridised carbon, which might be beneficial for insertion reactions into the M—OH bond. We have previously accomplished the first successful cyclometallation of a cyclohexyl-based POC$_{sp3}$OP pincer ligand, affording tridentate chelate (POC$_{sp3}$OP)NiX complexes (X = Cl, Br) followed by cyclometallation by the same ligand on iridium [16]. We here report on the synthesis of the analogous nickel hydroxo complex (POC$_{sp3}$OP)NiOH (3) via two alternative pathways. Reaction of 3 with CO or CO$_2$ gives insertion into the Ni—OH bond, affording

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the corresponding hydroxycarbonyl complex (**4**) and carbonate complex (**5**) respectively, that were both isolated and characterised by means of NMR spectroscopy and X-ray crystallography.

2. Experimental

2.1. General comments

All manipulations were performed under a nitrogen or argon atmosphere using standard Schlenk or glovebox techniques, except if noted. Solvents were purified by vacuum distillation from sodium/benzophenone ketyl radical. The complex trans-[NiCl{cis-1,3-Bis-(di-tert-butylphosphinito)cyclohexane}] (**1**) was synthesized according to known procedures [16a]. All other chemicals were purchased from commercial suppliers and used as received. ^1H, ^{13}C and ^{31}P NMR experiments were recorded on a Varian Unity INOVA 500 spectrometer, operating at 499.76 MHz (^1H). For ^1H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at $\delta = 0$ ppm. Multiplicities are abbreviated as follows: (s) singlet, (d) doublet, (t) triplet, (q) quartet, (m) multiplet, (br) broad, (v) virtual. IR spectra were obtained on a Bruker ALPHA FT-IR. Elemental analyses were performed by H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Compounds **3**–**5** failed to give a satisfactory elemental analysis and their purity was confirmed by ^1H, ^{31}P and ^{13}C NMR spectroscopy (see SI).

2.2. Crystallography

XRD-quality crystals of compounds **2**–**6** were obtained through recrystallization from benzene or hexane. Intensity data were collected with an Oxford Diffraction Excalibur 3 system, using ω-scans and Mo Kα ($\lambda = 0.71073$ Å) radiation [17]. The data were extracted and integrated using Crysalis RED [18]. The structure was solved by direct methods and refined by full-matrix least-squares calculations on F^2 using SHELXTL5.1 [19]. Molecular graphics were generated using CrystalMaker® 8.3.5 [20].

2.3. Preparation of trans-[NiONO₂{cis-1,3-Bis-(di-tert-butylphosphinito)cyclohexane}] (**2**)

Complex **1** (40.0 mg, 0.080 mmol) and AgNO₃ (24.2 mg, 0.142 mmol) were dissolved in THF (5 mL) and the mixture was stirred over night at RT, whereafter the solvent was removed in vacuo. Extraction with Et₂O and evaporation of the solvent afforded **2** as a brick red, microcrystalline solid. Yield: 32.3 mg (77%). ^1H NMR (C_6D_6): δ 3.42 (dt, $J = 3.5$ Hz, $J = 10.5$ Hz, CH₂CHO, 2H), 1.85 (t, $J = 11.0$ Hz, HC-Ni, 1H), 1.77–1.72 (m, CH₂CH₂CHO, 2H), 1.36 (vt, $J = 13.5$ Hz, ^tBu, 36H), 1.37–1.35 (m, CH₂CH₂CH₂, 1H), 0.92–0.79 (m, CH₂CH₂CHO, 2H and CH₂CH₂CH₂, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 87.6 (vt, $J_{PC} = 14.3$ Hz, CH₂CHO, 2C), 54.1 (t, $J_{PC} = 14$ Hz, HC-Ni, 1C), 39.4 (vt, $J_{PC} = 11.3$ Hz, C(CH₃)₃, 2C), 37.8 (vt, $J_{PC} = 17.3$ Hz, C(CH₃)₃, 2C), 33.4 (vt, $J_{PC} = 11.6$ Hz, CH₂CH₂CHO, 2C), 27.8 (vt, $J_{PC} = 6.7$ Hz, C(CH₃)₃, 6C), 27.5 (vt, $J_{PC} = 6.3$ Hz, C(CH₃)₃, 6C), 21.3 (s, CH₂CH₂CH₂, 1C). $^{31}P\{^1H\}$ NMR (C_6D_6): (180.3 δ (s). IR (ATR): $\nu_{as}(NO_2) = 1465$ cm^{-1}, $\nu_s(NO_2) = 1287$ cm^{-1}, $\nu(NO) = 1021$ cm^{-1}. Anal. Calc. for $C_{22}H_{45}NNiO_5P_2$ (524.24): C, 50.40; H, 8.65; N, 2.67. Found: C, 50.60; H, 8.66; N, 2.64%.

2.4. Preparation of trans-[NiOH{cis-1,3-Bis-(di-tert-butylphosphinito)cyclohexane}] (**3**)

Method I. **1** (75.0 mg, 0.15 mmol) and NaOH (60.0 mg, 1.50 mmol) were dissolved in THF (5 mL) and the mixture was heated to 70 °C for a period of 14 days. The reaction was concentrated in vacuo, redissolved in pentane and filtered through celite. Storage at −30 °C afforded **3** as yellow crystals. Yield: 20.1 mg (28%).

Method II. **2** (78.6 mg, 0.15 mmol) and NaOH (60.0 mg, 1.50 mmol) were dissolved in THF (5 mL) and the reaction was stirred at RT for 24 h. The solvent was removed in vacuo and the solid residues dissolved in pentane and filtered through celite. Removal of the solvent afforded **3** as a yellow powder. Yield: 39.5 mg (55%). ^1H NMR (C_6D_6): δ 3.52–3.46 (m, CH₂CHO, 2H), 1.96–1.93 (m, CH₂CH₂CHO, 2H), 1.56 (t, $J_{PH} = 11.5$, HC-Ni, 1H), 1.52 (vt, $J = 13.0$ Hz, ^tBu, 18H), 1.48 (vt, $J = 13.5$ Hz, ^tBu, 18H), 1.50–1.47 (m, CH₂CH₂CH₂, 1H), 1.03–0.93 (m, CH₂CH₂CHO, 2H and CH₂CH₂CH₂, 1H), −2.71 (t, $J_{PH} = 6.0$, Ni-OH, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 87.8 (vt, $J_{PC} = 17$ Hz, CH₂CHO, 2C), 54.6 (t, $J_{PC} = 16$ Hz, HC-Ni, 1C), 39.3 (vt, $J_{PC} = 10$ Hz, C(CH₃)₃, 2C), 37.3 (vt, $J_{PC} = 16$ Hz, C(CH₃)₃, 2C), 33.7 (vt, $J_{PC} = 12$ Hz, CH₂CH₂CHO, 2C), 28.4 (vt, $J_{PC} = 7.2$ Hz, C(CH₃)₃, 6C), 28.0 (vt, $J_{PC} = 4.4$ Hz, C(CH₃)₃, 6C), 22.1 (s, CH₂CH₂CH₂, 1C). $^{31}P\{^1H\}$ NMR (C_6D_6): 173.9 δ (s).

2.5. Reaction of 3 with CO. Formation of trans-[Ni(C(O)OH){cis-1,3-Bis-(di-tert-butylphosphinito)cyclohexane}] (**4**)

Complex **3** was dissolved in C_6D_6 (0.6 mL) in a J. Young tube, and the tube was pressurized with approximately 2 atm CO. The sample was stored at RT for 3 days, until **4** was observed as the only significant compound by means of NMR-spectroscopy. Further storage at RT afforded fine, light yellow, X-ray quality crystals. ^1H NMR (C_6D_6): δ 3.55–3.50 (m, CH₂CHO, 2H), 2.07–2.04 (m, CH₂CH₂CHO, 2H), 1.65 (t, $J_{PH} = 11.5$ Hz, HC-Ni, 1H), 1.57–1.52 (m, CH₂CH₂CH₂, 1H), 1.40 (vt, $J = 13.5$ Hz, ^tBu, 18H), 1.37 (vt, $J = 13.5$ Hz, ^tBu, 18H), 1.09–0.90 (m, CH₂CH₂CHO, 2H and CH₂CH₂CH₂, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 228 (s, Ni-COOH, 1C), 85.8 (vt, $J_{PC} = 14.2$ Hz, CH₂CHO, 2C), 68.6 (t, $J_{PC} = 26.9$ Hz, HC-Ni, 1C), 40.4 (vt, $J_{PC} = 15.8$ Hz, C(CH₃)₃, 2C), 38.5 (vt, $J_{PC} = 20.7$ Hz, C(CH₃)₃, 2C), 33.9 (vt, $J_{PC} = 12.1$ Hz, CH₂CH₂CHO, 2C), 28.6 (vt, $J_{PC} = 5.5$ Hz, C(CH₃)₃, 6C), 28.3 (vt, $J_{PC} = 5.3$ Hz, C(CH₃)₃, 6C), 22.4 (s, CH₂CH₂CH₂, 1C). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 193.4 (s).

2.6. Reaction of 3 with CO₂. Formation of trans-[Ni(OC(O)OH){cis-1,3-Bis-(di-tert-butylphosphinito)cyclohexane}] (**5**) and [{(cis-1,3-Bis-(di-tert-butylphosphinito)cyclohexane)Ni}₂(μ-CO₃)] (**6**)

A degassed hexane solution (7 mL) of **3** (35 mg, 0.073 mmol) was treated with 1 atm CO₂, and a fine yellow precipitate appeared within seconds. After 4 h of stirring at RT the reaction mixture was treated with toluene (1.5 mL) to afford a clear solution. Slow evaporation of the solvents afforded **5** as yellow X-ray quality crystals. Running the reaction in C_6D_6 under 4 atm CO₂ gave **5** as the predominant species in solution within 3 h, and full conversion of **3**. Removal of the C_6D_6 in vacuo afforded a solid residue that was fully soluble in hexane, and storage of a concentrated hexane solution at −30 °C for several days yielded X-ray quality crystals of **6**.

Complex **5**: ^1H NMR (C_6D_6): δ 12.4 (br s, Ni-OC(O)OH, 1H), 3.47–3.42 (m, CH₂CHO, 2H), 1.81–1.77 (m, CH₂CH₂CHO, 2H), 1.75 (t, $J_{PH} = 11.0$ Hz, HC-Ni, 1H), 1.48 (vt, $J = 12.5$ Hz, ^tBu, 36H), 1.37–1.33 (m, CH₂CH₂CH₂, 1H), 0.93–0.87 (m, CH₂CH₂CHO, 2H and CH₂CH₂CH₂, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 161.50 (br s, Ni-OCOOH, 1C), 87.50 (vt, $J_{PC} = 15.5$ Hz, CH₂CHO, 2C), 53.54 (t, $J_{PC} = 29.4$ Hz, HC-Ni, 1C), 39.48 (vt, $J_{PC} = 10.9$ Hz, C(CH₃)₃, 2C), 37.72 (vt, $J_{PC} = 16.3$ Hz, C(CH₃)₃, 2C), 33.48 (vt, $J_{PC} = 10.9$ Hz, CH₂CH₂CHO, 2C), 28.10 (vt, $J_{PC} = 6.5$ Hz, C(CH₃)₃, 6C), 27.79 (vt, $J_{PC} = 6.2$ Hz, C(CH₃)₃, 6C), 21.55 (s, CH₂CH₂CH₂, 1C). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 178.2 (s). IR (ATR): $\nu_{as}(CO_2) = 1615$ cm^{-1}, $\nu_s(CO_2) = 1369$ cm^{-1}.

Complex **6**: ^1H NMR (C_6D_6): δ 3.50–3.45 (m, CH₂CHO, 4H), 1.93–1.89 (m, CH₂CH₂CHO, 4H), 1.65 (vt, $J = 13.5$ Hz, ^tBu, 36H), 1.60 (vt, $J = 13.0$ Hz, ^tBu, 36H), 1.65–1.58 (HC-Ni, 2H), 1.36–1.32 (m, CH₂CH₂-