A key step in the formation of acrylic acid from CO_2 and ethylene: the transformation of a nickelalactone into a nickel-acrylate complex†

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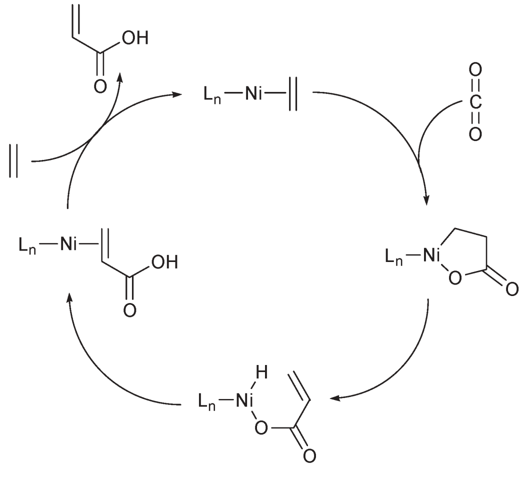
Received (in Cambridge, UK) 8th March 2006, Accepted 20th April 2006
First published as an Advance Article on the web 9th May 2006
DOI: 10.1039/b603540j

The reaction of a nickelalactone with dppm, resulting in the formation of a stable binuclear Ni(I) complex with an acrylate, a Ph_2P^- and a dppm bridge, models a key step in the formation of acrylic acid from CO_2 and ethylene.

Metallacyclic nickel carboxylates ("nickelalactones") are not only interesting building blocks for the formation of macrocycles by self-assembly[1] and for the short-route synthesis of fine chemicals and drugs,[2] but are also discussed as possible intermediates in the formation of acrylic acid from CO_2 and ethylene—a reaction which would be of great interest because of the use of CO_2 as feedstock. In a hypothetical catalytic cycle (Scheme 1), the oxidative coupling of these substrates to form nickelalactones, followed by a ß-hydride elimination to generate Ni-acrylate or Ni-bound acrylic acid, and replacement of the latter by ethylene/CO_2 are discussed as being the essential steps.

Although, to date, this catalytic reaction has never been experimentally realized, the stoichiometric formation of metallalactones from ethylene and CO_2 was observed,[3] and the mechanism of the Ni(0)-assisted reaction was recently investigated by means of DFT calculations.[4] Some years ago, Carmona *et al.* found that some Mo and W complexes formed hydrido-acrylate metal complexes from ethylene and CO_2,[5] and suggested that this reaction proceeds *via* metallalactones as (non-isolated) intermediates. Very recently, Schubert and Papai supported this with a theoretical study.[6]

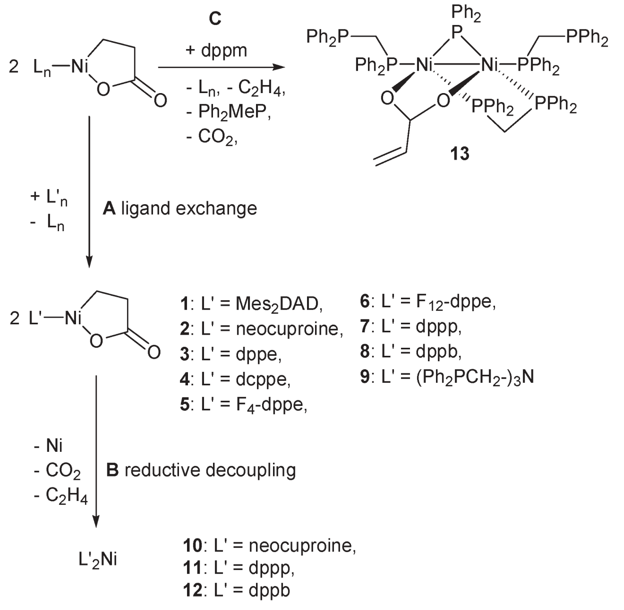


Scheme 1 Hypothetical catalytic cycle leading to the formation of acrylic acid from CO_2 and ethylene.

However, the key step of the above-discussed catalytic cycle, the reaction of a defined metallalactone under β-hydride transfer to generate an acrylate complex, has still to be discovered. To address this problem, we reacted the nickelalactones $[(L)_2Ni(C_2H_4COO)]$ (L_2 = tmeda or 2-pyridine)[7] and their deuterium-labelled derivatives with numerous ligands as potential activators for this reaction, and herein report the synthesis and characterization of compound **13**; the first complex resulting from a β-H elimination of a defined metallalactone.

A detailed examination of reactions between the nickelalactones and neutral ligands showed that three different reactions occurred (Scheme 2).

Most of the ligands reacted in a simple ligand exchange reaction (route A), resulting in new nickelalactones **1–9**, in which the altered electronic and steric properties might open up new applications as building blocks for organic syntheses. In some cases, a reductive decoupling to form low-valent Ni complexes (**10–12**), Ni, CO_2 and



Scheme 2 Reactions of $[(L)_2Ni(C_2H_4COO)]$ (L_2 = tmeda or 2-pyridine) with N- and P-donor ligands.

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† Electronic supplementary information (ESI) available: (a) Synthesis and characterization of the complexes **1–17** and their crystallographic summary data (except for **7**). (b) Crystallographic data for **1–6** and **8–17** in CIF or other electronic format (CCDC 600545–600559 and 600812). See DOI: 10.1039/b603540j

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C_2H_4, following the ligand exchange reaction, was observed (route B). **1–12** were thoroughly characterized.†

Investigations with bisphosphine ligands of the type $R_2P–(CH_2)_n–PR_2$ demonstrated that the reaction route is strongly dependent on the chain length of these ligands. For example, reactions of bisphosphines (where $n = 2$) resulted in the formation of thermally-stable five-membered chelate complexes (**3–6**), while the homologous phosphines (where $n = 3, 4$) gave unstable nickelalactones **7** and **8**, which easily underwent a reductive decoupling to form Ni(0) complexes **11** and **12** (route B) when warmed up.

Of particular interest, however, was the reaction of the smallest bisphosphine, bis(diphenylphosphino)methane (dppm, $n = 1$), which was found to be the only ligand to react in a complete different way, affording new compound **13** in high yield (route C, Scheme 2). Compound **13** is a deep-green crystalline product and was characterized in solution by NMR spectroscopy and in the solid state by elemental analyses and single-crystal X-ray analysis (Fig. 1).

In complex **13**, the two Ni(I) centres are linked by a Ni–Ni single bond (256.3(1) pm) and three different bridging ligands (dppm, the carboxylato group of acrylate and a diphenylphosphido bridge). Additionally, each Ni atom coordinates a monodentate dppm ligand. The bond lengths and angles lie within the range usually observed for Ni–OCO and Ni–P bonds.

To gain a deeper insight into the course of the reaction to form **13**, the following additional experiments were carried out:

(i) Monitoring the reaction between dppm and $[(tmeda)Ni(C_2H_4COO)]$ (2 : 1 mixture) by ^{31}P NMR spectroscopy indicated the formation of Ph_2PCH_3 ($\delta_P = -25.4$)

(ii) The deuterium-labelled nickelalactones reacted significantly more slowly than the "normal" nickelalactone, suggesting that the β-H–C activation is the rate-determining step for the formation of **13**. $[(tmeda)Ni(C_2D_4COO)]$ reacted under formation of the deuterium-labelled complex **13**. The same product was formed when the reaction was carried out in the presence of a two-fold excess of ethylene (C_2H_4). Since, under these conditions, the unlabelled complex **13** could not be detected by ^1H NMR spectroscopy, a C_2H_4/C_2D_4 exchange during the reaction can be excluded. Reaction of the deuterium-labelled pyridine complex with dppm (molar ratio = 1 : 1) resulted in a yellow product mixture, in which **13** could not be identified. Recrystallisation from THF/ether gave some crystals of the Ni(0) complex $[(\eta^1\text{-dppm})_2(\eta^2\text{-dppm})Ni]$ (**14**), resulting from the reductive decoupling reaction of the nickelalactone.

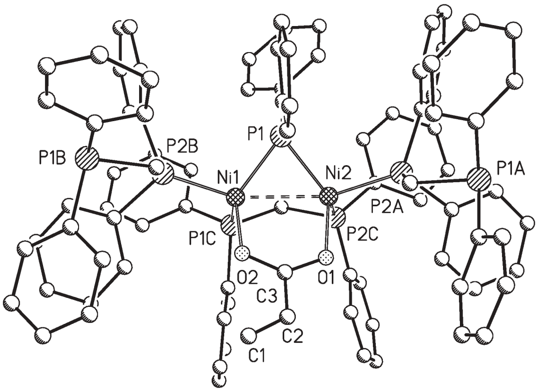


Fig. 1 Molecular structure of complex **13** (H-atoms are omitted for clarity). Selected bond distances (Å) and bond angles (°): Ni1–Ni2 2.563(1), Ni1–P1 2.124(2), Ni1–P2B 2.176(2), Ni1–P1C 2.208(2), Ni1–O2 2.070(4), Ni2–P1 2.128(2), Ni2–P2A 2.193(2), Ni2–P2C 2.205(2), Ni2–O1 2.056(4), O1–C3 1.251(8), O2–C3 1.267(8), C3–C2 1.485(10), C2–C1 1.262(12), Ni1–P1–Ni2 74.14(6), P1–Ni1–P1C 119.15(7), P1–Ni1–P2B 104.15(7), P1–Ni1–O2 113.1(1), P1C–Ni1–P2B 109.91(7), P1C–Ni1–O2 112.6(1), P2B–Ni1–O2 94.7(1), P1–Ni2–P2C 104.85(7), P1–Ni2–P2A 104.85(7), P1–Ni2–O1 118.8(1), P2C–Ni2–P2A 109.03(7), P2C–Ni2–O1 111.3(1), P2A–Ni2–O1 93.5(1).

An X-ray crystal structure determination of **14** (Fig. 2) revealed that the Ni atom is tetrahedrally surrounded by four P atoms of the ligands. Two of them are bound in a monodentate fashion, the third and fourth act as part of a chelating ligand, yielding a four-membered chelate ring. In addition, a ^{31}P NMR study showed that there is an equilibrium between **14** and $(dppm)_2Ni$ (**15**).[8] Complex **15** could also be synthesized (together with **13**) from the reaction between dppm, $Ni(cod)_2$ and succinic anhydride (molar ratio = 6 : 3 : 2) under the same conditions that usually result in the formation of nickelalactones. The hitherto unknown crystal structure of **15**, determined by X-ray analysis, shows that the two dppm ligands form four-membered chelate rings with Ni(0).†

(iii) When the reaction was carried with a 1 : 2 mixture of dppm and $[(py)_2Ni(C_2H_4COO)]$ in a solution of DMF, the mixed complex $[(py)(dppm)Ni(C_2H_4COO)]$ (**16**) was isolated as yellow needles upon partial evaporation of the solvent. Its ^1H NMR spectrum showed that **16** was stable during the measurement at rt. A small quantity of single crystals were isolated from the mother liquor, and an X-ray crystallographic study revealed that **16** co-crystallizes with its partially oxidized product (**17**), in which the free P-atom is oxidized to a PO group, in an approximately 75 : 25 ratio. The nickelalactone ring is intact and the dppm ligand is coordinated in a monodentate fashion. **16** can be considered as the first reaction product on the way to the binuclear complex **13**.

A possible pathway for the formation of **13**, based on these results, is shown in Scheme 3.

In a stepwise reaction (*via* **16**) $[(dppm)_2Ni(CH_2CH_2COO)]$ is formed. This reactive intermediate then undergoes two reactions: (a) reductive decoupling to form CO_2, ethylene and the Ni(0) species $(dppm)_3Ni$ (**14**), in equilibrium with $(dppm)_2Ni$ (**15**), and (b) β-H elimination to form a reactive hydrido-Ni(II)-acrylate.

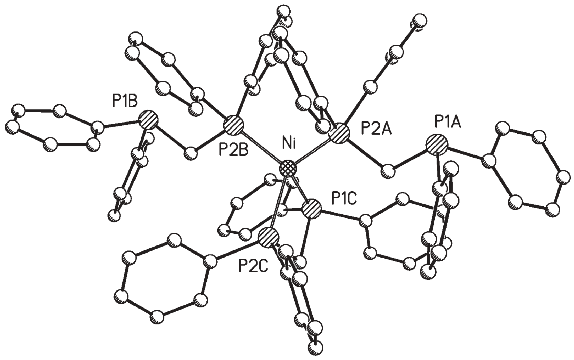
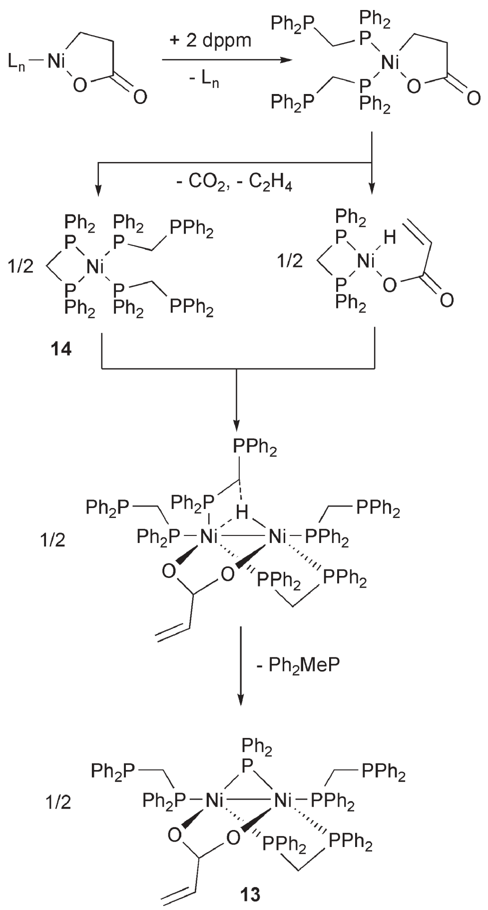


Fig. 2 Molecular structure of complex **14** (H-atoms are omitted for clarity). Selected bond distances (Å) and bond angles (°) : Ni–P1C 2.1950(6), Ni–P2C 2.1814(6), Ni–P2A 2.1627(6), Ni–P2B 2.1681(6), P1C–Ni–P2C 77.43(2), P1C–Ni–P2A 117.75(2), P1C–Ni–P2B 112.23(2), P2C–Ni–P2A 117.07(2), P2C–Ni–P2B 115.86(2), P2A–Ni–P2B 112.34(2).



Scheme 3 A possible pathway for the formation of **13**.

These two competition reactions may have comparable reaction rates. However, in the deuterium-labelled nickelalactone, the rate of the latter reaction is strongly decreased, and therefore reductive decoupling of the nickelalactone ring is favoured.

An alternative way, (c), would be that the ethylene formed by reductive decoupling subsequently reacts with the $(dppm)_n$Ni(0) under oxidative addition, generating a vinyl-Ni-hydride, which may then insert CO_2 to form the acrylate. However, the above reaction with $[(tmeda)Ni(C_2D_4COO)]$ in the presence of ethylene, in which the formation of the unlabelled complex **13** was not observed, may exclude this pathway.

In the last steps, reaction of $(dppm)_n$Ni(0) with the hydrido-Ni-acrylate intermediate may form a binuclear Ni(0)–Ni(II) species, connected *via* a dppm bridge (Scheme 3), followed by attack of the Ni–H bond on a dppm ligand to form the phosphido bridge and Ph_2PCH_3—in analogy to the splitting of the P–CH_2 bond by the Ni–H bond in the complex $[Ni_2Cl_2(\mu\text{-dcpm})(\mu\text{-H})]$ (dcpm = bis(dicyclohexyl-phosphino)methane).[9] The formation of the carboxylate bridge can then stabilize the Ni(I) complex **13**.

In conclusion, the formation of **13** illustrates that the key step of the hypothetical catalytic cycle to form acrylic acid from CO_2 and ethylene—the β-hydride elimination from a nickelalactone—can be activated if the "right" ligand is chosen. Among the great number of ligands investigated in this study, only one ligand (dppm) was able to promote this reaction. The main reason for the unique behaviour of dppm might be its high flexibility as a ligand, whereby it can act as a monodentate, chelating or bidentate bridging ligand during the formation of **13**. Further studies of model compounds for the above catalytic cycle and attempts to stabilize the hitherto unknown Ni(0)-acrylic acid complexes discussed above, as well as intermediates of this cycle, will be reported in a subsequent publication.

This research was supported by a grant from the Deutsche Bundesstiftung Umwelt and by the Deutsche Forschungsgemeinschaft (SFB 436).

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