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Facile synthesis of a tricyclohexylphosphine-stabilized η^3-allyl-carboxylato Ni(II) complex and its relevance in electrochemical butadiene carbon dioxide coupling

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With the reaction of bis(1,5-cyclooctadiene)nickel(0) and *trans*-penta-2,4-dienoic acid in the presence of tricyclohexylphosphine, a new more general method was developed to synthesize cyclic π^3-allyl-carboxylato Ni(II) complexes, which are known to be intermediates in the C–C coupling of butadiene and CO_2. The cyclic π^3-allyl-carboxylato Ni(II) complex obtained is tested as a mediator in the electrochemical coupling reaction of butadiene and carbon dioxide. We also demonstrate the dependency on the coordination sphere by using platinum instead of nickel as the metal center. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: allylic coordination; cyclic carboxylates, nickel complexes; platinum complexes, butadiene, carbon dioxide, electrochemistry

INTRODUCTION

The palladium-catalyzed C–C coupling of butadiene and CO_2 yields the δ-lactone 2-ethyliden-6-hepten-5-olide, where the ratio of butadiene and CO_2 is 2 : 1.[1–4]

The stoichiometric reaction of dienes and CO_2 with zero-valent nickel leads to a cyclic π^3-allyl-carboxylato Ni(II) complex, where the ratio of diene and CO_2 is 1 : 1[5–12] (Scheme 1). With additional CO_2 the nickel allylcarboxylates react after hydrolysis to afford the dicarboxylic acid hex-3-enedioic acid.[13] With an excess of additional allylchloride or in the presence of oxygen, deca-3,7-dienedioic acid was formed by intermolecular C–C coupling at the nickel-atom-coordinated C_5O chains.[14]

With respect to the noteworthy research activities in the 1 : 1 coupling of butadiene derivatives and CO_2 mediated by nickel(0) complexes,[15] only a few nickel-containing intermediates were isolated. Thus, the 1 : 1 coupling of 2,3-dimethylbutadiene and CO_2 in the presence of bis(1,5-cyclooctadiene)nickel(0) ([Ni(COD)$_2$]) and *N,N,N′N′*-tetramethylethylenediamine (TMEDA) leads to the TMEDA-stabilized π^3-allyl-carboxylato Ni(II) complex **1** (Scheme 1).[6] Complex **1** has a square-planar orientation that is formed by the two terminal allylic carbon atoms, one carboxylic oxygen atom and one nitrogen atom of the TMEDA ligand. The second nitrogen atom is only weakly coordinated to nickel.

RESULTS AND DISCUSSION

To study the chemistry of the cyclic π^3-allyl-carboxylato Ni(II) complexes, which are intermediates in the coupling of butadiene and carbon dioxide, we developed a more general approach to these complexes on the basis of an oxidative addition reaction. In contrast to the oxidative coupling of butadiene and CO_2 at zero-valent nickel centers, this reaction is easy to handle and allows the use not only of nickel but also of platinum as the metal center. Furthermore, the formation of phosphine-stabilized π^3-allyl-carboxylato Ni(II) complexes can be carried out in one step, unlike the established reaction where a ligand exchange of TMEDA against the phosphine as a second step is inevitable.

Adding stoichiometric amounts of penta-2,4-dienoic acid and tricyclohexylphosphine to a THF solution of [Ni(COD)$_2$]

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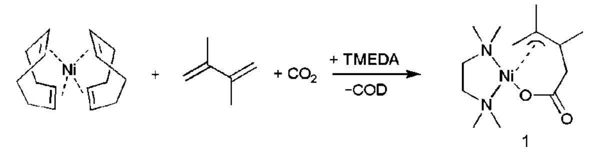
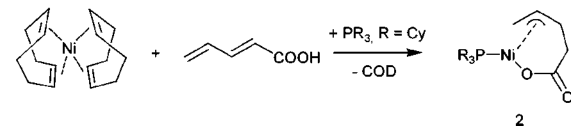
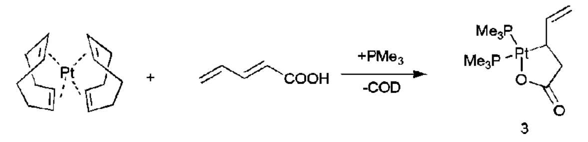


Scheme 1. Reaction of $[Ni(COD)_2]$ with 1,3-dimethylbutadiene and carbon dioxide.



Scheme 2. Reaction of $[Ni(COD)_2]$ with PCy_3 and pentadieneoic acid.

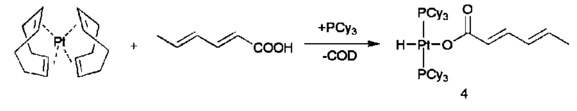


Scheme 3. Reaction of $[Pt(COD)_2]$ with PMe_3 and pentadieneoic acid.

results quantitatively in the formation of (3,4,5-η^3-3-pentenylato)-(tricyclohexylphosphine) -nickel(II) complex **2** (Scheme 2).

To obtain a platinum-containing complex, the reaction was carried out with $[Pt(COD)_2]$ as a source for the zero-valent metal species. The use of trimethylphosphine as a stabilizing ligand leads to the formation of (3-σ-pent-4-enylato)-[bis(trimethylphosphine)]-platin(II) complex **3** (Scheme 3), which is equivalent to the above-mentioned nickel complex **2**. It is again a metal-containing cyclic ether but the coordination of the allylic group to the metal center is not a η^3-coordination but a η^1-coordination.

Replacing the sterically undemanding trimethylphosphine ligand by the bulky tricyclohexylphosphine ligand prevents the formation of the cyclic ether. Oxidative addition of the acid at the zero-valent platinum center takes place, but the reaction is aborted after the formation of hydride complex **4** [*trans*-bis(tricyclohexylphosphine)-hexadieneoate-hydrido-platinum(II)] (Scheme 4). The platinum-containing complex **4** shows no interaction between the olefin bonds and the platinum center; correspondingly, there are no significant changes in the NMR data of the olefinic protons and the carbon atoms. The ^{1}H-NMR spectrum of complex **4** clearly shows the presence of a Pt–H bond. Accordingly, the signal of the hydride is observed as a triplet at −22.7 ppm, with platinum satellites ($^2J_{H\text{-}P} = 14.1$ Hz; $^1J_{H\text{-}Pt} = 1122.4$ Hz). The change from penta-2,4-dienoic acid (which was used for the oxidative addition at the nickel center) to hexa-2,4-dienoic acid is unproblematic with respect to the chemical properties and was accomplished to improve the solubility of the product and because of the higher thermal stability of hexa-2,4-dienoic acid.



Scheme 4. Reaction of $[Pt(COD)_2]$ with hexadieneoic acid and PCy_3.

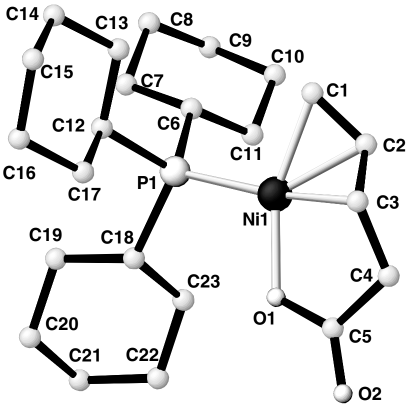


Figure 1. View of the molecular structure of complex **2** in the crystal.

Table 1. Product yield for the electrochemical coupling reaction between butadiene and CO_2

	Yield (%)			
	0 : 2[a]	1 : 1[b]	2 : 1[c]	2 : 2[d]
No mediator	55.3	3.9	18.6	22.2
Complex **2**	35.1	1.6	21.9	41.5

[a] 4-Ethenyl-cyclohexene, cyclooctadiene.
[b] Isomers of carboxylic acid ($C_5H_8O_2$).
[c] Isomers of dicarboxylic acids ($C_6H_8O_4$).
[d] Isomers of dicarboxylic acids ($C_{10}H_{14}O_4$).

Comparable results were observed by Yamamoto *et al.*, with monounsaturated acids being used instead of double unsaturated acids.[16]

The reaction with $[Ni(COD)_2]$ does not terminate at the hydride complex as the platinum-containing complex but is followed by a hydrogen migration from the nickel atom to the α-C atom of the carboxylate to yield the π^3-allyl-carboxylato Ni(II) complex **2**. The four electrons of the two double bonds and the three remaining carbon atoms of the former butadiene unit form a η^3-allylic structure with the nickel atom. These findings were confirmed by the results from an X-ray analysis performed on a crystal of complex **2** obtained by extraction with pentane (Fig. 1).

The molecular structure shows the monodentate coordination of the carboxylic group to the metal with an Ni–O distance of 189.7(1) pm, which is short compared with Ni–O distances of other nickel-carboxylato complexes, which are in the range 201–211 pm.[17–21]

The C1, C2 and C3 carbon atoms build an allylic coordination to the nickel center with Ni–C distances in the range 195–201 pm. These values for the allylic coordination agree with those of other non-ionic nickel allyl complexes stabilized by tertiary phosphine ligands.[22]

Assuming the coordination sphere of the nickel atom to be formed by C1, C3, O1 and P1 as ligands, the geometry of complex **2** in the crystal may be described as slightly distorted square-planar.

The NMR spectroscopic data of complex **2** confirm the crystallographic findings and are consistent with the literature data.[23] The monodentate coordination of the carboxylic group in complex **2** is furthermore reflected in its IR spectrum, where the $\nu_a(CO_2^-)$ absorption is observed at 1644 cm^{-1} and the Δ value $[\nu_a(CO_2^-) - \nu_s(CO_2^-)]$ at 201 cm^{-1} is larger than the ionic value for free carboxylates (161 cm^{-1}).[24]

To investigate if complex **2** is not only an intermediate in the C–C coupling reaction of butadiene and CO_2 but is also a catalytically active species, complex **2** was appointed as mediator in the electrochemical coupling reaction between butadiene and CO_2 (Table 1). The experiments were carried out under the same conditions as in Ref. 25. It was found that by the use of complex **2** as mediator a slight increase of 2 : 2 butadiene–CO_2 coupling products and a decrease of butadiene dimerization occurs. However, complex **2** is not a suitable catalyst because it decomposes and a variety of coupling products were formed.

In conclusion, we report here a new reaction type in organometallic chemistry: the oxidative addition of a double unsaturated acid to a Ni(0) center, involving a hydrogen migration step in the presence of a phosphine ligand as stabilizing ligand. This reaction is an easy and efficient synthesis towards a cyclic π^3-allyl-carboxylato Ni(II) complex that shows the same structural features as the coupling product of 1,3-dimethylbutadiene and carbon dioxide at a nickel(0) center. Using the tricyclohexylphosphine-stabilized π^3-allyl-carboxylato Ni(II) complex **2** as mediator in the electrocatalytic butadiene–CO_2 coupling reaction has shown an improvement in the product selectivity. Owing to the general application of the synthesis, general access to nickel-containing π^3-allyl-carboxylato complexes with varying stabilizing ligands was found. This, finally, should lead to more detailed investigations on the reactivity and electronic properties of these complexes, with the aim of developing a catalytic synthesis of unsaturated dicarboxylic acids.

EXPERIMENTAL

Crystal and intensity data for complex **2**: yellow crystal, $C_{23}H_{39}NiO_2P$, $M = 437.22$, monoclinic, $a = 13.0350(9)$, $b = 10.2723(7)$, $c = 16.9843(12)$ Å, $\beta = 97.159(1)°$, $V = 2256.5(3)$ Å^3, $T = 200(2)$ K, space group $P2(1)/c$ (No. 14), $Z = 4$, absorption coefficient = 0.946 mm^{-1}, 23 361 reflections measured, 5498 unique ($R_{\text{int}} = 0.0348$) that were used in all calculations. The final wR_2 was 0.0808 (all data).

In the crystal structure, the two CH carbon atoms C2 and C3 of the allylic unit are disordered with a 60 : 40 probability resulting in the two different enantiomers of the η^3-allyl-carboxylato complex **2**. The C–C–C angles in the allyl groups differ slightly for the two isomers and were determined as 118.9(4)° and 123.8(6)°. These values are consistent with corresponding data of other d^8-transition metal η^3-allyl complexes.[24]

The crystallographic data were deposited as supplementary publication no. CCDC 179680 at the Cambridge Crystallographic Data Centre and are available on request from: CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

The NMR spectra were recorded on a Bruker Avance 250 MHz spectrometer and MS-ESI spectra were recorded on an HP Series 1100 MSD (eluent: 5 mmol of NH_4OAc solution).

Complex **2**. ^{1}H-NMR data (C_6D_6): δ(ppm) = 5.0 (br, 1H, H2), 3.53 (br, 1H, H3), 3.17 (br, 1H, H4), 2.99 (br, 1H, H4′), 2.19 (br, 1H, H1syn), 1.22 (br, 1H, H1anti′), 1.0–2.2 (m, 33H, Cy). ^{31}P{^{1}H}-NMR (C_6D_6): 35.55. ^{13}C{^{1}H}-NMR (C_6D_6): 185.2 ($^3J_{\text{C-P}} = 11.5$ Hz; C-5), 111.1 (C-2), 83.0 ($^2J_{\text{C-P}} = 10.3$ Hz; C-3), 39.5 (C-1), 38.3 ($^3J_{\text{C-P}} = 4.6$ Hz; C-4), 33.4 ($^1J_{\text{C-P}} = 18.4$ Hz; Cy), 30.1 ($^2J_{\text{C-P}} = 14.9$ Hz; Cy), 27.5 ($^3J_{\text{C-P}} = 11.5$ Hz; Cy), 26.4 (Cy). IR (KBr pellet): 2925 (vs), 2848 (s), 1644 (vs), 1443 (s), 1274 (s), 1228 (m), 1100 (w), 1006 (m), 890 (m), 849 (m), 741 (w), 517(m), 494 (w). MS-ESI (m/z): 437 (M + 1), 297 ($Cy_3P + NH_3$), 281 ($Cy_3P + 1$). Analytical data for complex **2**: calc. for $C_{23}H_{39}NiO_2P$: C, 63.18%; H, 8.99%; found: C, 62.57%; H, 8.91%.

Complex **3**. ^{1}H-NMR (THF-d_8, −40 °C): δ(ppm) = 6.00 (ddd; $^3J_{4\text{-}5(\text{E})} = 17, 1$ Hz; $^3J_{4\text{-}5(\text{Z})} = 10, 1$ Hz; $^3J_{4\text{-}3} = 6, 55$ Hz; $^3J_{\text{H-Pt}} = 8.7$ Hz; 1H; H-4), 4.67 (d; $^3J_{5\text{-}4} = 17.1$ Hz; $^4J_{\text{H-Pt}} = 17.1$ Hz; 1H; H-5), 4.44 (d; $^3J_{5'\text{-}4} = 10.1$ Hz; $^4J_{\text{H-Pt}} = 10.1$ Hz; 1H; H-5′), 2.69 (dd; $^3J_{3\text{-}4} = 6.55$ Hz; $^3J_{3\text{-}2} = 15.2$ Hz; 1H; H-2exo), 2.34 (m; 2H; H-2endo, H-3); 1.6 (d; $^2J_{\text{H-P}} = 10.7$ Hz; $^3J_{\text{H-Pt}} = 41$ Hz; 9H; PMe_3), 1.46 (d; $^2J_{\text{H-P}} = 9.4$ Hz; $^3J_{\text{H-Pt}} = 17.7$ Hz; 9H; PMe_3). ^{13}C{^{1}H}-NMR (THF-d_8, −40 °C): $\delta = 187.6$ ($^3J_{\text{C-P}} = 16$ Hz; C-1), 146.4 ($^3J_{\text{C-P}} = 8$ Hz; $^2J_{\text{C-Pt}} = 52$ Hz; C-4), 103.3 ($^4J_{\text{C-P}} = 6.9$ Hz; $^3J_{\text{C-Pt}} = 41.4$ Hz; C-5), 40.9 ($^3J_{\text{C-P}} = 6.9$ Hz; $^2J_{\text{C-Pt}} = 50$ Hz; C-2), 32.7 ($^2J_{\text{C-P(trans)}} = 79.3$ Hz; $^2J_{\text{C-P(cis)}} = 3.4$ Hz; $^1J_{\text{C-Pt}} = 430$ Hz; C-3); 15.5 ($^1J_{\text{C-P}} = 79.3$ Hz; $^3J_{\text{C-P}} = 3.5$ Hz; $^2J_{\text{C-Pt}} = 50$ Hz; PMe_3), 14.5 ($^1J_{\text{C-P}} = 28.7$ Hz; $^2J_{\text{C-Pt}} = 19.5$ Hz). ^{31}P{^{1}H}-NMR (THF- d_8, −40 °C): $\delta = -11.2$ ($^2J_{\text{P-P}} = 14.8$ Hz; $^1J_{\text{P-Pt}} = 1801$ Hz; P-8), −34.8 ($^2J_{\text{P-P}} = 14.8$ Hz; $^1J_{\text{P-Pt}} = 3427$ Hz; P-9). IR (KBr pellet): δ(cm^{-1}) = 2963 (w), 2907 (w), 1624 (vs), 1419 (m), 1337 (s), 1288 (m), 1278 (m), 1251 (w), 976 (s), 948 (s), 913 (w), 871 (w), 737 (w), 686 (w), 675 (w). MS-ESI (m/z): 446 (M + 1), 418 (M-C_2H_3), 406 (M-C_3H_4), 347 (M-$C_5H_6O_2$).

Complex 4. ^{1}H-NMR (THF-d_8): $\delta = 6.58$ (dd; $^3J_{\text{H-H}} = 14.6$ Hz; $^3J_{\text{H-H}} = 11.4$ Hz; 1H; CH), 5.81 (pt; $^3J_{\text{H-H}} = 11.4$ Hz; 1H; CH), 5.50 (m; 1H; CH-CH$_3$), 5.47 (d; $^3J_{\text{H-H}} = 14.6$ Hz; CH−COO), 1.70 (d; $^3J_{\text{H-H}} = 11.4$ Hz; 3H; CH$_3$), −22.7 (t; $^2J_{\text{H-P}} = 14.1$ Hz; $^1J_{\text{H-Pt}} = 1122.4$ Hz; 1H; Pt-H). ^{13}C{^{1}H}-NMR (THF-d_8): $\delta = 171.6$ (COO), 141.2, 138.2, 130.2, 125.2 (CH), 21.2 (CH$_3$). ^{31}P{^{1}H}-NMR (THF-d_8): $\delta = 38.8$ (s; $^1J_{\text{P-Pt}} = 2927$ Hz). IR (KBr pellet): 2926 (vs), 2850 (vs), 2230 (m), 2217 (m), 2203 (m), 1621 (s), 1446 (s), 1348 (s), 1266 (m), 1195 (w), 1175 (w), 998 (m), 888 (vw), 848 (w), 740 (w), 512 (w), 491 (vw). MS-ESI (m/z): 756 ([Pt(PCy$_3$)$_2$] + 1).

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