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Self-Assembled Organometallic Nickel Complexes as Catalysts for Selective Dimerization of Ethylene into 1-Butene

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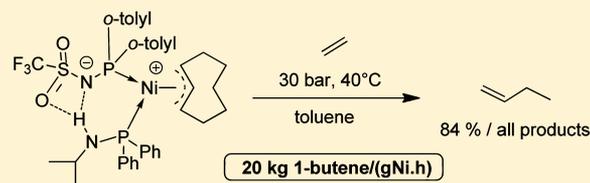
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Supporting Information

ABSTRACT: Sulfonamido-phosphorus and aminophosphine ligands self-assemble to readily form active and stable nickel catalysts that are highly selective for the dimerization of ethylene to 1-butene. The self-assembled allyl-nickel complexes are zwitterionic and are stabilized by hydrogen bond interactions between the two ligands. These organometallic *cis*-diphosphine complexes rearrange under an ethylene atmosphere to give *trans*-diphosphine catalysts, with one monoanionic P,O METAMORPhos ligand and an aminophosphine.



Since the discovery by Keim and co-workers that nickel complexes can be highly active catalysts for the oligomerization of ethylene (A in Figure 1),^{1,2} this reaction

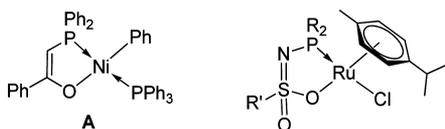


Figure 1. Representative anionic P,O ligand that forms the active nickel based SHOP catalyst (left) and a typical coordination mode of METAMORPhos, an adaptive sulfonamido-phosphorus ligand (right).

has been one of the showcase examples of homogeneous catalysis, leading to key industrial processes such as the Shell Higher Olefin Process (SHOP).³ Due to the commercial success of these processes, the nickel-catalyzed ethylene oligomerization reaction was studied in detail at the fundamental level.⁴ When traditional nickel catalysts giving a broad Schulz–Flory product distribution are employed, 1-butene is only a minor product and its production directly depends on the market for the higher linear α -olefins. Therefore, proposing on-purpose ethylene dimerization processes is of prime importance to serve the growing demand for 1-butene (global demand in 2011, 1.6 million metric tons; estimated demand in 2025, 3.5 million metric tons).⁵ Several nickel complexes have been reported to produce 1-butene, but these catalysts either also produce 2-butene (via isomerization) or only produce small amounts of 1-butene because of activity and/or lifetime issues. As such, re-exploring nickel-based catalysts with a different approach is scientifically and industrially challenging.

Sulfonamido-phosphorus ligands (METAMORPhos) were recently introduced as a family of highly versatile building blocks for late-transition-metal complexes (Figure 1).^{6–11} They display interesting adaptive coordination behavior, as they coordinate in P and P,O chelating forms and in both neutral and anionic states of the ligand. Tuning of the substituents allows the optimization of specific catalytic properties: e.g., a more acidic character of $R^1-SO_2-NH-R^2$ is anticipated to facilitate complex formation and to disfavor the reductive elimination reaction, leading to the neutral ligand and catalyst deactivation, resulting in an improved catalyst lifetime. Moreover, these ligands proved to be particularly suited to construct supramolecular bidentate or tridentate complexes through hydrogen bonding. As it is known that the additional PPh_3 ligand coordinated to the SHOP catalyst A displayed in Figure 1 has a great influence on catalyst stability and product distribution,^{4a,b} we anticipated that nickel complexes based on METAMORPhos and aminophosphine ligands would form supramolecular pincer ligands that due to the reversible nature of the supramolecular bonds in the complexes would favor the catalyst stability but at the same time retain the vacant site required for adequate catalytic activity. While self-assembled ligands by hydrogen bonding, metal–ligand, ionic, and stacking interactions have successfully been developed for noble transition metals such as rhodium, palladium, and platinum and have been applied in various catalytic transformations,¹² this approach has hardly been applied for first-row transition metals. To the best of our knowledge, the in situ generated Ni(0) complex that was used as a catalyst in the hydrocyanation

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reaction reported by Breit et al. is the only example.¹³ Considering the frequent use of nickel for industrial catalytic transformations, there is, however, still a great deal of potential for the use of self-assembled ligands. We report here such a supramolecular ligand approach for the formation of stable nickel complexes based on hydrogen bonds. In the presence of a nickel precursor as a template, METAMORPhos and aminophosphine ligands form a complex in which the ligands are organized via a hydrogen bond between the two ligands. The organometallic nickel complexes are remarkably stable and very active and can be tuned to favor selective ethylene dimerization to 1-butene.

Mixing equimolar amounts of nickel(0) bis(1,5-cyclooctadiene) ($\text{Ni}(\text{COD})_2$), $\text{Ph}_2\text{P-NH-}i\text{Pr}$, and 1-NEt_3 (or **2**) in chlorobenzene solution led to the selective formation of nickel(II) complex **3** (or **4**), in which METAMORPhos coordinates as an anionic ligand. During the formation of the complex, the COD ligand was converted to the π -allyl species (Figure 2). Such complexes can be formed after oxidative

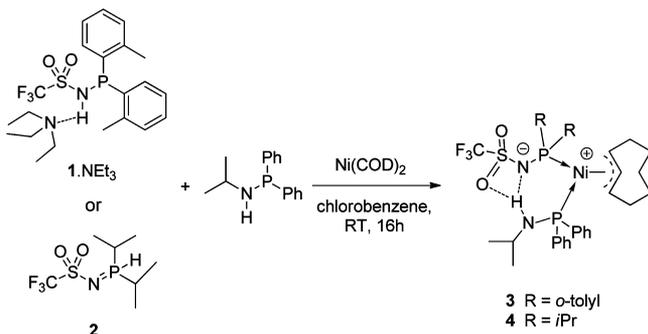


Figure 2. Synthesis of supramolecular nickel complexes **3** and **4**.

addition of the acidic sulfonamide ligand and subsequent insertion of the hydride in the double bond of the COD fragment. The supramolecular nickel complexes were isolated as yellow powders (yields up to 57%) and characterized by ^1H , ^{13}C , and ^{31}P NMR and the molecular structures were confirmed by X-ray analyses (see the Supporting Information).

Crystals of complexes **3** and **4** suitable for X-ray analysis were obtained by slow diffusion of pentane in a toluene solution of the complex. The complexes **3** and **4**, displayed in Figures 3 and 4, adopt a square-planar coordination geometry, with the phosphorus ligands in *cis* positions with respect to one another. The nickel atom is formally cationic, whereas the negative charge is delocalized on the NSO fragment of the METAMORPhos ligand, as is also clear from the P–N and N–S bond lengths (intermediate between single and double bonds) and the S–N–P angles (typically between sp^2 - and sp^1 -hybridized nitrogen: 131.0° for **3** and 134.17° for **4**). The anionic NSO site forms a good hydrogen bond acceptor, and indeed there is a hydrogen bond formed with the NHP of the adjacent ligand. Interestingly, for complex **3** the nitrogen–hydrogen bond distance is significantly longer (2.994 Å) in comparison to that found in complex **4** (N2–H...N1 bond of 2.190 Å, consistent with the literature),⁹ suggesting that there is a weaker interaction between the ligands in complex **3**. The difference in steric bulk between the two METAMORPhos ligands likely accounts for this. Inspection of the structures reveals that in complex **4** the two isopropyl substituents are transversal to the coordination plane, whereas in complex **3** the *o*-tolyl substituents are opposite to the allyl moiety. The latter

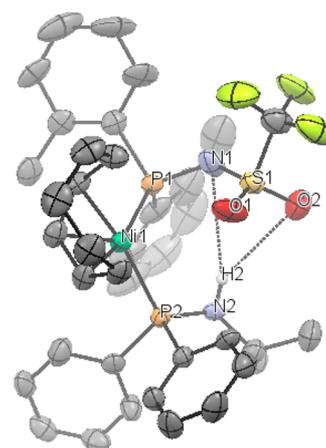


Figure 3. ORTEP plot (50% probability displacement ellipsoids) of complex **3**. Hydrogen atoms have been omitted for clarity (except for the NH moiety). Selected bond lengths (Å) and angles (deg): Ni1–P1, 2.222(2); Ni1–P2, 2.206(2); N2–H2, 0.859; N1...H2, 2.994; O1...H2, 2.844; P2–Ni1–P1, 104.55(9).

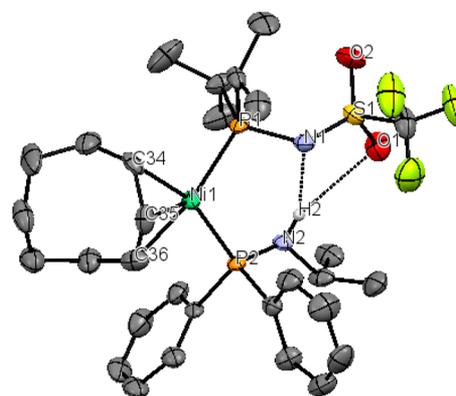


Figure 4. ORTEP plot (50% probability displacement ellipsoids) of complex **4**. Hydrogen atoms have been omitted for clarity (except for the NH moiety). Selected bond lengths (Å) and angles (deg): Ni1–P1, 2.2165(17); Ni1–P2, 2.2007(13); N2–H2, 0.852; N1...H2, 2.190; O1...H2, 2.588; P2–Ni1–P1, 103.96(6).

geometry results in a rotation of the sulfonamido fragment, increasing the distance to the hydrogen bond donor. This geometry difference in the two complexes is further supported by the switch of the dihedral angle P–Ni–P–N_{METAMORPhos} from 28.5° for **4** to 79.3° for **3**.

These diamagnetic complexes also form in solution, as is clear from the ^{31}P NMR and ^1H NMR spectra. The two doublets observed in ^{31}P NMR are shifted downfield with respect to the corresponding ligands, and the small coupling constant is in agreement with a *cis* geometry ($J_{\text{PP}} = 30$ Hz). In the ^1H NMR spectra the signals for the π -allyl fragment are clearly observed at δ (ppm, C_6D_6) 3.71 (2H) and 5.09 (1H) for complex **3** and 3.36 (1H), 4.19 (1H), and 4.48 (1H) for complex **4**. Moreover, the NH proton of the coligand $\text{Ph}_2\text{P-NH-}i\text{Pr}$, initially appearing at 1.56 ppm (C_6D_6), was shifted to 2.85 ppm for complex **3** and to 5.85 ppm for complex **4**, in agreement with a H-bonding interaction between the two ligands.

To clarify the role of hydrogen bonding in the complex, we performed control experiments in which we replaced $\text{Ph}_2\text{P-NH-}i\text{Pr}$ by similar ligands that do not have a H-donor group. When the ligand $\text{Ph}_2\text{P-N}(i\text{Pr})_2$ or PPh_3 was stirred in a

solution with $\text{Ni}(\text{COD})_2$ and METAMORPhos **2**, the reaction mixture instantly turned black, indicating complex decomposition. These control experiments support the importance of hydrogen bonding between the two ligands, as it improves complex stability, allowing isolation.

These complexes were evaluated as catalysts in the ethylene oligomerization reaction at 40 °C under an ethylene pressure of 30 bar, in the absence of any additional activator. The reactions ran for 90 min, which allowed the accumulation of significant amounts of oligomers (>10 g), to confirm the productivity per gram of nickel and stability of the catalyst. In addition, at large production a proper mass balance (>90%) can be reached, leading to very reproducible catalytic results. High selectivity for the formation of 1-butene (up to 84 wt %/all products) and good productivity (24 $\text{kg}_{\text{oligo}}/(\text{g}_{\text{Ni}}\cdot\text{h})$) were obtained with steady ethylene uptake over a period of 90 min for complex **3** (Table 1; see also the Supporting Information). On the basis of

Table 1. Catalytic Evaluation of Complexes 3, 4, and A^a

complex	n_{Ni} (μmol)	T (°C)	prod ^b	product distribution ^c			
				C_4	C_6	C_8^+	1- C_4 ^d
3	10	40	24	85	13	2	99.0
4	10	40	12	35	28	37	99.7
A	50	50	5	1	2	97	76.7
3^e	10	80	63	73	21	6	97.6

^aTest conditions unless specified otherwise: 30 bar of C_2H_4 , solvent toluene (55 mL), 90 min. ^bProductivity in $\text{kg}_{\text{oligo}}/(\text{g}_{\text{Ni}}\cdot\text{h})$. ^cIn wt %, determined by GC. ^d1- C_4 wt % in C_4 fraction, determined by GC. ^eSolvent toluene (100 mL).

these results, we formed a new class of nickel complexes which are, to our knowledge, the most robust and efficient organometallic nickel catalysts for 1-butene formation.^{4,14–21} The high selectivity for short terminal olefins (1- C_4 >99.0%), i.e. little isomerization, was also observed when complex **4** was applied as the catalyst; however, a lower productivity and a clear shift in selectivity to a larger linear α -olefin distribution (Schulz–Flory with $K_{\text{SF}} = 0.45$) was, however, observed. The difference in selectivity observed between catalysts **3** and **4** is likely caused by the difference in electron density at the P atom of the METAMORPhos. In comparison, the representative benchmark complex (**A**; Figure 1) required higher concentration to produce a significant amount of oligomers and slightly higher temperature for activation (50 °C). Under these reaction conditions, this complex led to a very large Schulz–Flory distribution with a low productivity ($K_{\text{SF}} > 0.90$). Moreover, a break in the ethylene consumption curve for the benchmark complex after 40 min, representative of catalyst deactivation, reinforces the importance of hydrogen bonding to the catalyst lifetime in complexes **3** and **4**, for which stable activities were noticed over 90 min. At 80 °C, an important exotherm was observed with catalyst **3** at the beginning of the reaction (up to 123 °C; see the Supporting Information) despite an increased volume of toluene for a better heat dispersion. The temperature is rapidly stabilized at 80 °C, and then a remarkable steady ethylene consumption was observed over more than 1 h. The global productivity is high (63 $\text{kg}_{\text{oligo}}/(\text{g}_{\text{Ni}}\cdot\text{h})$), as is the activity after temperature control (35 $\text{kg}_{\text{C}_4\text{H}_8}/(\text{g}_{\text{Ni}}\cdot\text{h})$; see the Supporting Information). Not surprisingly, at higher temperature, as the ethylene concentration decreases,²² side reactions such as codimerization and slight isomerization

of 1-butene (from 99.0% at 40 °C to 97.6% at 80 °C) are favored.

More information on the active species was obtained from in situ NMR, revealing the rearrangement of both complexes under ethylene pressure. Indeed, at room temperature and under 5 bar of ethylene, the original complex **3** solution turned from orange to green and a new complex formed with two phosphines in trans positions, as evidenced by the large coupling ³¹P NMR (55.5 ppm (d, $J = 271$ Hz); 69.2 ppm (d, $J = 271$ Hz)). In the ¹H NMR no hydride was observed. Similar reactivity was observed with nickel complex **4**, leading to a new species (53.5 ppm (d, $J = 275$ Hz); 89.8 ppm (d, $J = 275$ Hz)). GC and GC/MS analyses of the NMR solution revealed the presence of short-chain olefins (butenes and hexenes) and vinylcyclooctene. According to these experiments, we propose as a mechanism for catalyst rearrangement the ethylene insertion in catalyst precursor **3** (and **4**) with subsequent β -H elimination or β -H transfer with ethylene, leading to vinylcyclooctene and the nickel–ethyl complex as the resting state (see Figure 5). Concomitantly, the rearrangement of the METAMORPhos ligand under the monoanionic P,O chelating ligand is proposed.

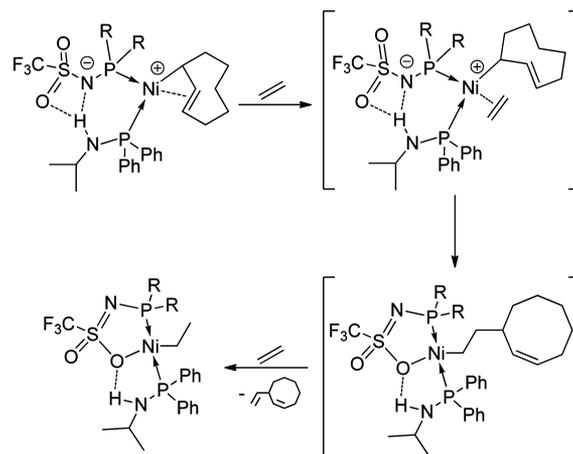


Figure 5. Suggested mechanism for catalyst rearrangement.

In conclusion, we have reported the synthesis and detailed characterization of stable nickel complexes supported by supramolecular bidentate ligands based on sulfonamido-phosphorus and aminophosphine ligands. The hydrogen bond between the ligands in the zwitterionic nickel complexes was unambiguously proven in two X-ray structures. It was established that the hydrogen bond is essential for the stability of the complex during ethylene dimerization reactions. Importantly, this novel class of complexes provides highly active catalysts that display unprecedented selectivity (1- C_4 >99.0% in the C_4 fraction). The lifetime of these catalysts is excellent, even at high temperature, and these species form during ethylene oligomerization mainly 1-butene (up to 84 wt %) along with small amounts of hexenes and octenes. This high selectivity for short linear α -olefins is interesting, considering the market demand for such products, and as such these results may renew interest in the development of a new generations of nickel catalysts. In situ NMR experiments under ethylene pressure suggest the rearrangement of these structures to the proposed nickel complex as the resting state chelated by a monoanionic P,O ligand, which may explain the specific

properties displayed by the catalyst. Complementary studies are underway to understand more precisely what governs the oligomerization selectivity. This provides a good starting point for further development and a detailed understanding of this new class of nickel catalysts.

■ ASSOCIATED CONTENT

■ Supporting Information

Text, figures, tables, and CIF files giving details of ligand and complex syntheses, crystal structure determinations for complexes **3** and **4** and ligand **1**, NMR spectra, and catalytic studies. This material is available free of charge via the Internet at <http://pubs.acs.org>. CIF files have also been deposited with the CCDC and can be obtained on request free of charge, by quoting the publication citation and deposition numbers 1029754–1029756.

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Notes

The authors declare no competing financial interest.

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