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Outer-sphere reactivity shift of secondary phosphine oxide-based nickel complexes : From ethylene hydrophosphinylation to oligomerization

Rudy Lhermet,[a] Emile Moser,[a] Erwann Jeanneau,[b] Hélène Olivier-Bourbigou,[a] and Pierre-Alain R. Breuil*[a]

Abstract: A new dimension for secondary phosphine oxide (SPOs) ligands is described in this article. Demonstrated on original π-allylic nickel structures, these self-assembled complexes trigger catalytic hydrophosphinylation reactions. Addition of a Lewis acid as $B(C_6F_5)_3$ switches the reactivity towards migratory insertion and thus ethylene oligomerisation through an unprecedented outer-sphere interaction with the coordinated SPO ligand. NMR experiments and X ray analyses allowed to observe the zwitterionic active species formed as well as its degradation pathway.

While tertiary phosphines are among the most commonly used ligands for transition metal homogeneous catalysis,[1] the potential of the air- and moisture-stable secondary phosphine oxides (SPOs) has been considered only recently although the first example of SPO-based metal complex was disclosed in 1983 for the platinum-catalysed hydroformylation of terminal alkenes.[2] The ligands generated from SPOs present a great range of electronic properties thanks to their modularity (monodentate or bidentate, neutral or anionic, see Figure 1) that still needs to be assessed in catalysis.[3] They are considered for gold nanoparticles stabilisation,[4] for effective asymmetric noble metal-catalysed transformations as hydrogenation,[5] or for coupling reactions.[6] By contrast, when considering catalyst design and access to well-defined species, examples with first-row and low-cost transition metals such as nickel remain more than sporadic despite their unique properties compared to noble metals as palladium. To the best of our knowledge, only Kläui followed by Walther and Hartung reported such isolated structures, without further reactivity studies.[7] More recently, Han and coworkers disclosed the nickel-catalyzed hydrophosphinylation of terminal alkynes with a mixture of $[Ni(PPh_2Me)_4]$ and $Ph_2P(O)H$,[8] generating *in situ* a five-coordinated hydrido phosphinito nickel complex (**D**, Figure 1), characterized by ^1H NMR spectroscopy but not isolated.

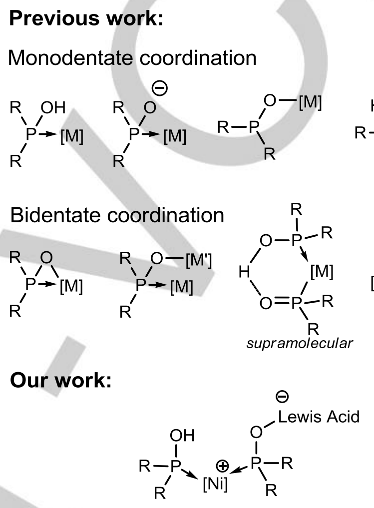

Figure 1. SPO modularity in coordination chemistry.

Although prone to promote hydrophosphinylation reactions, we anticipated that structures presenting a cationic nickel(II) species bearing metal-hydride or metal-carbon bonds could be of interest for migratory insertion of olefins to produce oligomers or polymers.[9] However, due to their high reactivity and their instability, these organonickel compounds are usually generated *in situ* from a nickel(II) halide precatalyst and an excess of aluminum activator rather than isolated.[10] Herein, we describe a family of supramolecular organonickel complexes and their reactivity shift from hydrophosphinylation towards ethylene oligomerization using unprecedented outer-sphere interactions of Lewis acids with SPOs.

We reported recently that bis(cyclooctadiene)nickel(0) $[Ni(COD)_2]$ reacts with sulfonamido-phosphines in the presence of a second phosphine ligand, leading to a self-assembled supramolecular organometallic species.[11] We thus wondered if similar structure could be reached starting from simple SPO preligands. Walther and Hartung described the reaction between $[Ni(COD)_2]$ and two equivalents of diphenylphosphine oxide in THF and identified $[Ni(Ph_2PO)_2(COD)]$ as resulting complex, after concomitant release of hydrogen and COD.[7] Interestingly, performing this reaction in toluene, we isolated the diamagnetic π-allylic nickel **1a** bearing a phosphinito-phosphinous acid system as a yellow solid in 96% yield (Scheme 1). The structure of complex **1a** was confirmed by X ray diffraction on monocrystal as well as ^1H, ^{13}C, ^{31}P NMR spectroscopies and elemental analysis.

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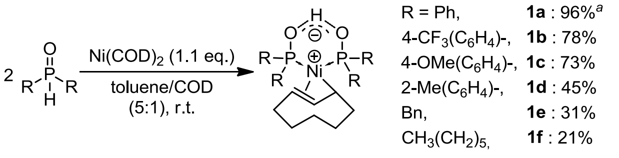


Scheme 1. Synthesis of supramolecular SPO complexes. [a] Reaction carried without COD.

Complex **1a** adopts a square-planar coordination geometry with P-O bond lengths (1.553 and 1.559 Å) half way between single and double bonds (1.500-1.630 Å), traducing the negative charge delocalization (Figure 2). Equivalence of the two phosphorus atoms is supported by ^{31}P NMR, with a sole singlet at 101 ppm. This proton exchange equilibrium is also pointed out by the great O-H-O angle (175.24°), the short O-O distance (2.431 Å) and the deshielded phosphinous acid proton (16.1 ppm). Using a related protocol, complexes **1b**-**1f** were synthesized from the corresponding SPOs (Scheme 1). Nevertheless, an additional amount of COD was necessary to prevent metallic nickel formation. All these compounds are diamagnetic and were characterized by NMR analyses. They also present two equivalent phosphorus atoms with a single signal between 98 and 110 ppm as well as a deshielded phosphinous acid protons (see SI). Crystals of complex **1b**, suitable for X-ray analysis, were grown in toluene. **1b** structure displays similar square planar features to **1a** (Figure 3), with an almost flat O-H-O angle (167.58°) and a short O-O distance (2.425 Å).

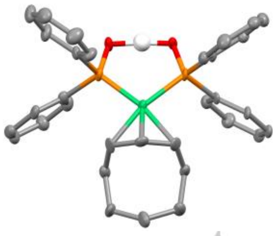


Figure 2. ORTEP plot (50% probability displacement ellipsoids) of complex **1a**. Hydrogen atoms have been omitted for clarity (except for the OHO moiety).

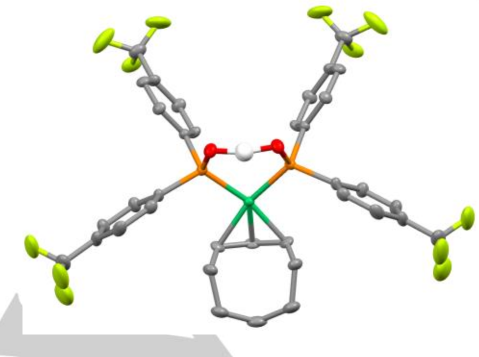


Figure 3. ORTEP plot (50% probability displacement ellipsoids) of complex **1b**. Hydrogen atoms have been omitted for clarity (except for the OHO moiety).

Under ethylene pressure and at 40°C, complexes **1a**-**1f** conduct to the formation of traces of tertiary ethyl phosphine oxides and vinylcyclooctene, confirmed by GC/MS, ^{1}H and ^{31}P NMR spectroscopies, along with complex degradation. We postulated an activation of complexes **1** under ethylene pressure, leading to the zwitterionic alkylnickel intermediates **2** after departure of the vinylcyclooctene (Figure 4). These species probably coexist with their neutral form **2'** through a P($\sigma^4\lambda^5$)-P($\sigma^3\lambda^3$) equilibrium. In agreement with phosphorylation reactions, the formation of these tertiary ethyl phosphine oxide species can result from reductive elimination from Ni-ethyl intermediate **2'**.[8,12]

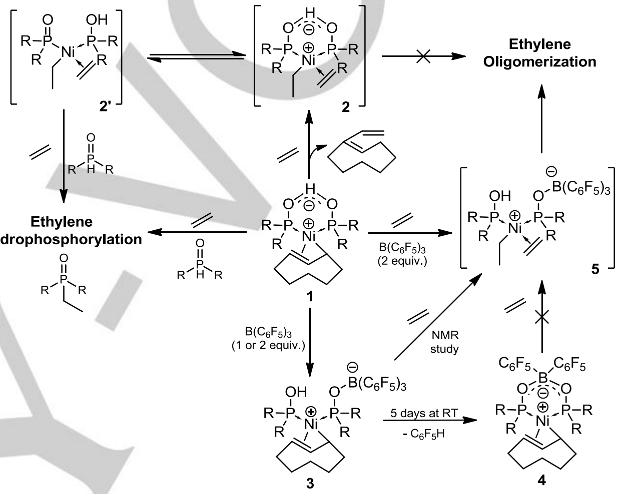
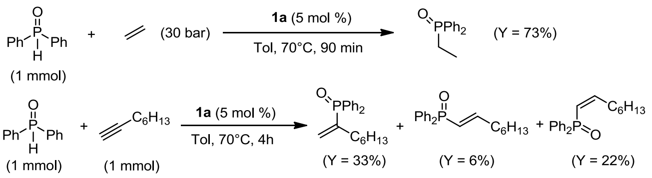


Figure 4. Reactivity path of SPO-based nickel complexes.

The catalytic feature of complex **1a** for hydrophosphinylation transformations was demonstrated with ethylene or 1-octyne and Ph$_2$P(O)H. Under catalytic conditions (5 mol % of Ni, 30 bar of C$_2$H$_4$ and 70°C), complex **1a** efficiently coupled Ph$_2$P(O)H and C$_2$H$_4$ in toluene to form Ph$_2$P(O)Et with up to 73% yield. When focusing on 1-octyne, well-defined species **1a** led at 70°C in toluene to a mixture of branched and linear regio-isomers with 33% and 28% yield, respectively.



Scheme 1. Nickel-catalyzed hydrophosphinylation reactions.

We hypothesized that addition of Lewis acids may allow an outer-sphere modulation of the complex electronics and hamper

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in this example contribution of structure **2'**, preventing P(III)-P(V) rearrangement which favors phosphorylation reactions and moreover, preserve the electro-deficient character of the nickel center profitable to ethylene oligomerization reactions.[9,13] The proof-of-concept was established with tris(pentafluorophenyl)borane as a remote activator (Table 2). Indeed, mixing precursor **1a** with $B(C_6F_5)_3$ (2 equivalents) under ethylene pressure triggered the ethylene consumption, leading to short-chain linear olefins (C_4 to C_8), with up to 98.9% for 1-butene in the C_4 fraction, although deactivation was noticed after 1 hour of reaction (see SI). In similar conditions, complex **1b** provided a more active and stable catalyst (6467 $g_{oligo}/(g_{Ni}.h)$), while no activity was noticed with complex **1c** at 40°C, 60°C being required for a weak reaction initiation, highlighting the induction of SPO electronic properties (*para*-CF_3 in **1b** and *para*-OMe in **1c**). Introducing steric hindrance on the SPOs as in complex **1d** allows the access to a wider product distribution ($K_{SCHULZ\text{-}FLORY}$~0.7). Similarly to **1c**, solely a slight reactivity could be detected with benzyl substituted SPO complex **1e** at 60°C. This detrimental effect of electron-rich SPOs was confirmed with the alkyl analog **1f**, inert even at 60°C. Interestingly, replacement of $B(C_6F_5)_3$ with $GaCl_3$ afforded a much more active system in the case of **1a**, with a selectivity of 93.6% towards butenes. With *para*-CF_3 SPO-based complex **1b**, ethylene uptake was lower than expected, with a butene selectivity up to 94.8%. Surprisingly, a 1:1 ratio between complex **1a** and borane (50 µmol) also resulted in an absence of activity. In addition, when adding few equivalents of $Ph_2P(O)H$ to **1a** and $B(C_6F_5)_3$ under ethylene, $Ph_2P(O)Et$ is obtained as the hydrophosphinylation product. The control of the olefin distribution brought by inner-sphere and outer-sphere modifications, through the nature of the SPO pre-ligand or the Lewis acid, respectively, lies in the heart of the industrial developments to meet the flexibility requirements of the LAO markets.

Table 2. Catalytic evaluation of complexes **1a-f** associated with $B(C_6F_5)_3$ and $GaCl_3$.[a]

Complex	T (°C)	m_{oligo} (g) [b]	Prod. [c]	Product distribution (%) [d]		
				C_4 (1-C_4[e])	C_6	C_8^+
1a[f]	40	8.6	3919	56.1 (98.9)	25.1	18.8
1b	40	14.2	6467	67.4 (91.9)	22.8	9.8
1c	60	<1	<500	59.0 (96.3)	20.3	20.7
1d	40	19.3	8778	14.5 (83.7)	6.2	79.3
1e	60	<1	<500	31.8 (86.9)	14.1	54.1
1f	60	-	-	-	-	-
1a[f,g]	40	15.9	7224	93.6 (59.7)	4.8	1.6
1b[g]	40	5.2	2340	94.8 (78.5)	4.8	1.0

[a] Ni complex (25 µmol), $B(C_6F_5)_3$ (50 µmol), toluene (30 mL), 30 bars of C_2H_4, 90 min. [b] Mass of oligomers formed during the reaction in grams. [c] Productivity in $g_{oligo}/(g_{Ni}.h)$. [d] In wt%, determined by GC. [e] 1-Butene wt% in C_4 fraction, determined by GC. [f] **1a** solubilized in CH_2Cl_2 (2 mL). [g] $B(C_6F_5)_3$ replaced by $GaCl_3$ (2 eq.).

To gain mechanistic insights, **1a** was mixed in CD_2Cl_2 with one equivalent of $B(C_6F_5)_3$ and monitored by phosphorus decoupled proton NMR spectroscopy. Within ten minutes, disappearance of the phosphinito-phosphinous acid system signal at 101 ppm was observed. The rise of two new doublets indicated a disymmetrization of the system. Cis configuration of the P atoms was preserved, as evidenced by a weak ^{31}P coupling constant (J_{PP} = 32 Hz). Taking a closer look at the signal at 110 ppm revealed a doublet of septuplet, due to a close interaction of one phosphorus with the six *ortho* fluorine atoms of $B(C_6F_5)_3$ (J_{PF} = 5 Hz, Figure 5). Moreover, a new broad singlet on the proton NMR spectra rose in the allylic area, attributed to a P-OH signal. All these observations support formation of the zwitterionic dissymmetric borate adduct **3a** (Figure 4).

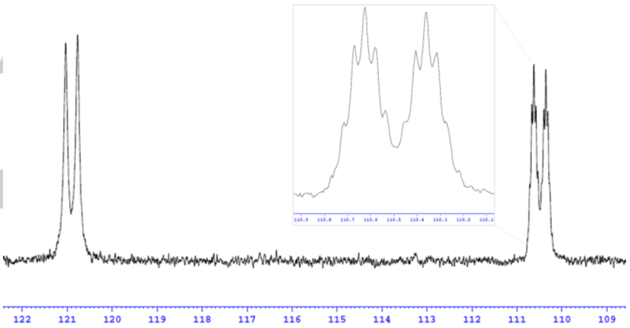

Figure 5. ^{31}P NMR spectroscopy of complex **3** highlighting the interaction between one phosphorus and $B(C_6F_5)_3$.

The structure of adduct **3a** was finally confirmed by elemental analysis and X ray analysis on monocrystal, obtained by slow diffusion of pentane in a toluene solution (Figure 6). Similarly, addition of two equivalents of $B(C_6F_5)_3$ to **1a** led only to adduct **3** on the ^{31}P NMR spectra, in solution with free borane detected by ^{19}F NMR (see SI). Keeping the solution five days at room temperature resulted in the complete conversion of **3a** into a new symmetrical compound **4a**, fully characterized by NMR spectroscopies and elemental analysis. This preferred reaction path is in line with preliminary DFT calculations (wB97XD) from the structures determined by XRD. The formation of the boron adduct **3** from complex **1a** is thermodynamically favored by 34.3 $kcal.mol^{-1}$. In addition, the degradation path of adduct **3**, leading to the stable complex **4a** and the departure of C_6F_5H is also confirmed to be exergonic (ΔG = -15.0 $kcal.mol^{-1}$). Compound **4a** displayed two equivalent phosphorous atoms but no deshielded proton. Monocrystals could be obtained by slow diffusion of pentane in a toluene solution (Figure 7), confirming the bridging borane moiety through XRD.[14] Complex **4a** is not active towards ethylene at 40°C, even in the presence of additional $B(C_6F_5)_3$. Thus, the requirement of two equivalents of borane during catalysis remains unclear. *In situ* ^{31}P NMR study of **1a** under ethylene with 1 or 2 equivalents of $B(C_6F_5)_3$, suggests that with one equivalent of borane, the decoordination of the SPO ligands occurs while with 2 equivalents, the ligands coordination is longer preserved, sustaining an enhanced catalyst lifetime (see SI).

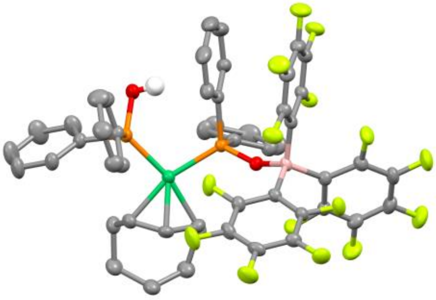

Figure 6. ORTEP plot (50% probability displacement ellipsoids) of complex **3a**. Hydrogen atoms have been omitted for clarity.

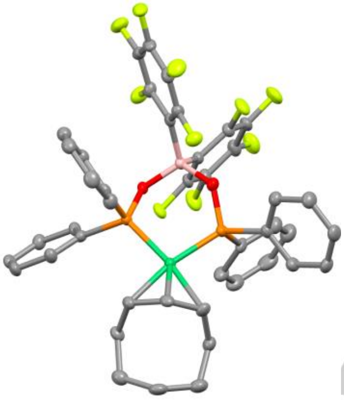

Figure 7. ORTEP plot (50% probability displacement ellipsoids) of complex **4a**. Hydrogen atoms have been omitted for clarity.

In conclusion, we synthesized and fully characterized a new family of supramolecular phosphinito-phosphinous acid π-allylic nickel complexes. We highlight a unique remote control of the metallic center and its electro-density through SPO ligands to switch the complex reactivity towards elementary migratory insertion and ethylene oligomerization and selectivity. Ultimately, NMR experiments and X ray analyses provided crucial information on the Lewis acid interaction generating zwitterionic active species as well as its degradation pathway. Such outer-sphere interaction on the broad class of SPO ligands opens an unprecedented opportunity for the electronic steering in transition metal (asymmetric) catalysis.

Experimental Section

Ligand and complex syntheses and characterizations, crystal structure determinations, DFT calculations and reactivity study are detailed in the supporting information file. This material is available free of charge via the Internet.

Acknowledgements

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Keywords: Secondary phosphine oxide ligand • nickel • Lewis acid interaction • outer-sphere coordination • homogeneous catalysis

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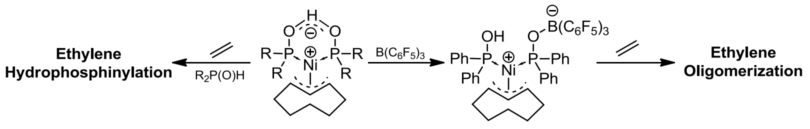

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