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Acetylacetonate and Acetate Complexes of Nickel(II) Catalyse the Air Oxidation of Phosphines

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Abstract: The polymeric complex *trans*-[Ni(acac)$_2$(μ_2-dppe)]$_n$.2MeCN (**1a**, dppe=1,2-ethylenebis(diphenylphosphine) is sometimes transiently deposited from the reaction of [Ni(acac)$_2$] with dppe in MeCN prior to its facile onwards air oxidation to final crystallization of a doubly-oxygenated relative, *cis*-[Ni(acac)$_2$(μ_2-dppeO$_2$)]$_n$ (**2**, dppeO$_2$= 1,2-ethylenebis(diphenylphosphineoxide). A similar unsolvated phase of the initial polymer, *trans*-[Ni(acac)$_2$(μ_2-dppe)]$_n$ (**1b**), can be isolated from toluene. The oxidation of dppe by O$_2$ is catalytic and dppeO$_2$ was isolated in close to stoichiometric yields from solutions containing 5 % Ni(acac)$_2$ relative to dppe. The reaction rate slows after a few turnovers due to inhibition by the product. The relative yields of dppeO$_2$ are higher than those from catalytic air oxidation of methyldiphenylphosphine and triphenylphosphine and we speculate that a pathway for this reaction involves a dimetallic cooperativity enabled specifically by dppe.

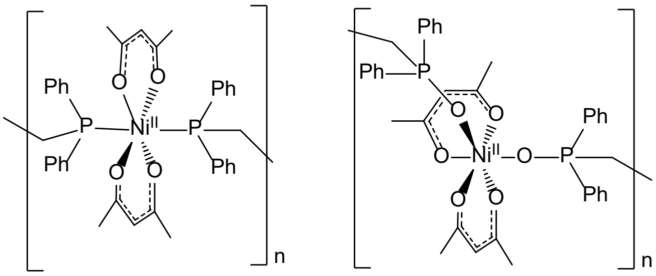
Introduction

Oxidation of otherwise air-stable tertiary phosphines by O$_2$ is well known to be promoted by metal ions to yield phosphine oxide complexes commonly in stoichiometric reactions.[1] The reactivity can however be catalytic. Methylrheniumtrioxide[2] catalyses oxidation of PPh$_3$ by O$_2$ and transfer of an O atom to the phosphine substrate occurs with consequent reduction of the complex. O$_2$ then re-oxidizes the CH$_3$Re^{V}O$_2$ generated to close a catalytic cycle. High catalyst loading (10%) and only a few turnovers were reported. Similarly trimesityl iridium, where in situ Ir^{V}O(mes)$_3$ is generated from oxidation by O$_2$, is proposed to be the O atom donor for the catalysis of PPh$_3$ oxidation by O$_2$.[3] In a mechanistic contrast the substrate phosphine is proposed to effect displacement of Pt(II)coordinated peroxide generated by oxidative addition of O$_2$ to a Pt(0)phosphine complex and the liberated peroxide is then the active reagent.[4] A related mechanism is suggested for Vaska's complex, IrX(CO)(PPh$_3$)$_2$, with yields influenced by the halide ligand (X).[5] An oxo-peroxo Mo(VI) complex transfers an O atom to PMe$_3$ and the complex is regenerated by O$_2$ to close a catalytic cycle.[6] Ruthenium complexes also catalyse O$_2$ oxidations of phosphines.[7] The O$_2$ activation activities of the more geometrical- and spin-state-flexible first row transition metal complexes is less understood, but are highly relevant to essential O$_2$ activation pathways used in nature. The mechanisms of PPh$_3$ oxidation by O$_2$ catalyzed by Fe(II)[8], Fe(III)[9] and Co(II)[10] are uncertain, however Fe(II)[8] and Co(II)[11] complexes are well known to activate O$_2$. We demonstrate here that the simple Ni(II) compounds, Ni(acac)$_2$ and Ni(OAc)$_2$, are unrecognized examples of first row transition metal catalysts for the O$_2$ of air-stable tertiary phosphines. This activity is surprising in light of the facile preparation of the Ni(II) dihalides of bis-monodentate and bidentate tertiary phosphines which can be carried out in air without observing any oxidation of the tertiary phosphine.[12] Ni(II) halide phosphine complexes can even be oxidized to the Ni(III) state (e.g. [NiBr$_3$(dppe)][13]) without oxygenation of the phosphine donor.[12c, 14]

Results and Discussion

Synthesis

The reaction of Ni(acac)$_2$ with dppe in toluene layered with n-hexane results in the rapid precipitation of a pale blue crystalline solid (**1b** Figure S1). A mononuclear formulation, *cis*-[Ni(acac)$_2$dppe] for this material was previously ruled out on the basis of solid state ^{13}C NMR spectroscopy (SSNMR), since the relatively simple spectrum for this paramagnetic material suggested high symmetry. A *trans* orientation of the phosphine donors with retention of the square plane of the Ni(acac)$_2$ unit was concluded.[15] This prediction is now confirmed using single crystal X-ray diffraction analysis which shows the 1D polymeric *trans*-[Ni(acac)$_2$dppe]$_n$ (**1b**, Figures 1, 2). If the reaction is performed in acetonitrile, the same 1D polymer occasionally crystallizes as pale green needles in a solvated phase, *trans*-[Ni(acac)$_2$(μ_2-dppe)]$_n$.2MeCN (**1a,** Figure S1). Compound **1a** must be removed quickly from the mother liquor in order to avoid its subsequent dissolution which will occur within minutes in the yellow-hued reaction mixture. Over the course of a few hours under ambient conditions the solution colour changes to green and pale green crystals of *cis*-[Ni(acac)$_2$(μ_2-dppeO$_2$)]$_n$ (**2**, Figure S1) are deposited.



1a, 1b

2

Figure 1. Chemical drawings of the monomeric units in *trans*-[Ni(acac)$_2$(μ_2-dppe)]$_n$ (**1a, 1b**) and *cis*-[Ni(acac)$_2$(μ_2-dppeO$_2$)]$_n$ (**2**).

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In **2** the oxidized dppe ligand, dppeO$_2$, acts as a bidentate *O,O'*-donor ligand bridging the adjacent Ni(II) atoms (Figure 1, 3). The oxidation reaction is accelerated by heating and the intermediate precipitation of **1a** is not always observed. Controls show that dppe is not oxidized by air, in acetonitrile or chloroform, in the absence of Ni(acac)$_2$ (Figure S15, S16). Controls using other Ni(II) sources revealed that dppe is also oxidized in the presence of Ni(OAc)$_2$, however no dppeO$_2$ adduct was isolated.

Structures of 1D polymers of *trans*-[Ni(acac)$_2$(μ_2-dppe)]$_n$ and *cis*-[Ni(acac)$_2$(μ_2-dppeO$_2$)]$_n$

The Ni(II) complexes of **1a** and **1b** crystallize in the monoclinic space group $P2_1/c$ and triclinic space group $P\overline{1}$ respectively (Figure 1a, b, Table S1). Selected bond distances and angles (Table S2) for donor atoms around the Ni(II) ion show no significant differences between the structures of **1a** and **1b**. The Ni(II) ion of **1b** (Figure 2b) lies on a center of symmetry, and the mid-point of the ethyl bond of the dppe sits on a second inversion center. The dppe ligand bridges pairs of nickel ions, generating 1D polymeric chains running parallel to the *a* axis (Figure 1d). There are several interchain interactions; an (aryl)C-H···O$_{acac}$ H-bond, an edge-to-edge π overlap and two (aryl)C-H···π interactions that link the chains in three dimensions (Figure 2d, S2 and S4, Table S4). The structure of **1b** is isomorphous with the iron(II) analog *trans*-[Fe(acac)$_2$(μ_2-dppe)]$_n$ which must be prepared under strictly anaerobic conditions.[16]

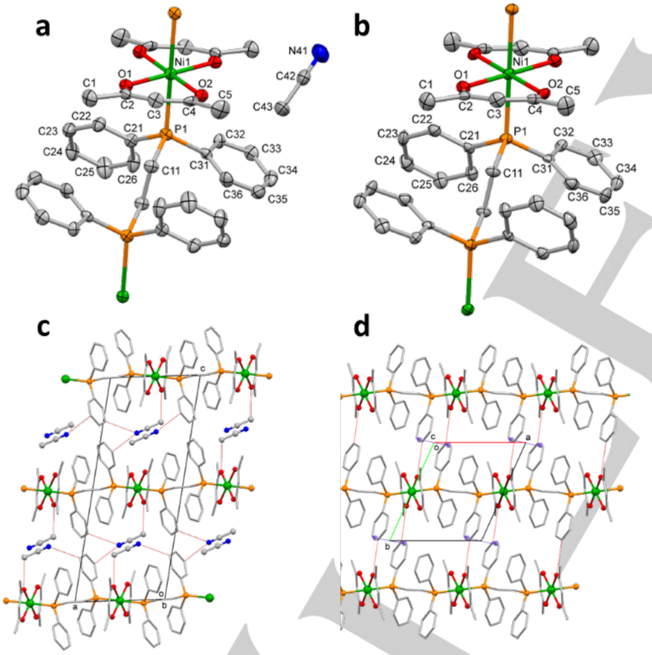

Figure 2. Top: Molecular structures of **(a)** *trans*-[Ni(acac)$_2$(μ_2-dppe)]$_n$.2MeCN (**1a**), and **(b)** *trans*-[Ni(acac)$_2$(μ_2-dppe)]$_n$ (**1b**). Anisotropic displacement parameters are drawn at the 50% probability level, atomic labels are shown for one asymmetric unit and hydrogen atoms are omitted for clarity. Bottom: **(c)** Packing diagram of *trans*-[Ni(acac)$_2$(μ_2-dppe)]$_n$.2MeCN (**1a**) viewed along the *b* axis and **(d)** *trans*-[Ni(acac)$_2$(μ_2-dppe)]$_n$ (**1b**) viewed along the *c* axis showing the relationship between the two phases. Red dashed lines represent C-H····O or C-H····N interactions, purple dots indicate bond centroids and dashed purple lines show π-π interaction.

The structure of acetonitrile solvate **1a** (Figure 2a) has the same molecular symmetry as **1b** and the polymer chains in **1a** and **1b** are superimposable (Figure S5). The chains in **1a** again lie parallel to the *a* axis of the larger, monoclinic cell (Figure 2c). The chains are further apart than in **1a** to accommodate the MeCN molecules that lie in between them in layers parallel to the *ab* plane (at approx. z=0.25 and z=0.75). The only notable links between chains in **1a** are *via* the MeCN molecules; there are two (aryl)C-H···N and one (alkyl)C-H···O$_{acac}$ hydrogen bonds (Figure 1c, S3, Table S3). Thus, in contrast to the structure of **1b** there are no significant direct links between polymer chains as the π-interactions are lost with the increased chain separation. Once **1a** is removed from solution the crystals show diminishing diffraction indicating rapid loss of crystallinity over just a few minutes under ambient conditions. Given the weak but significant hydrogen bonding between the polymeric layers of **1a** *via* the MeCN molecules, loss of these upon spontaneous desolvation is a likely explanation for the deterioration of the crystalline material after **1a** is removed from the mother liquor (Table S3). Retention of crystal integrity for **1a** depends on prevention of desolvation, either by immersion in MeCN or by sealing the crystals (e.g. by coating in oil). No C-N stretch (expected 2200-2300 cm^{-1}) is observed in the IR spectrum of even very fresh samples of **1a**, confirming that the MeCN is lost rapidly (Figure S9). Adequate data for the single crystal structural determination were obtained by mounting a crystal very rapidly under the cryostream after removal from the mother liquor and coating it with cryogenic oil. However, the diffraction data obtained were still not high quality due to the rapid loss of crystallization solvent (Table S1). A PXRD diffractogram measured on a slurry of **1a** in the mother liquor (Figure S8e), is different from the diffractogram of the **1a** measured 3h after being removed from the mother liquor (Figure S8d) where Bragg peaks do not convincingly appear in the same positions as for sample **1b** (Figure S8b). The IR spectrum also shows minor differences to that for **1b** (Figure S9). It is therefore concluded that **1a** is not converted into **1b** when the guest acetonitrile solvate is desorbed. *Cis*-[Ni(acac)$_2$(μ_2-dppeO$_2$)]$_n$ (**2**) also crystallizes as a 1D polymer (Figure 3) but, in contrast to the *trans* geometry in **1a** and **1b**, the geometry at the metal ion is *cis*. The nickel ion in **2** lies on a 2-fold axis and there is an inversion center at the mid-point of the ethyl bond in the dppeO$_2$ ligand; the zig-zag polymer chain runs parallel to the *a* axis (Figure S6). There is an intrachain π-stacking interaction between two phenyl groups on different dppeO$_2$ ligands *cis* to one another (though the rings are not quite parallel) and intrachain (aryl)C-H···N and (alkyl)C-H···O hydrogen bonds (Table S5), as well as two (aryl)C-H···π intrachain interactions (Figure S7).

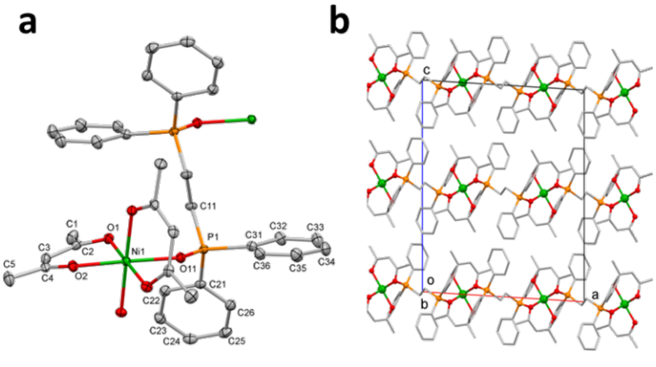

Figure 3. (a) Molecular structure of *cis*-[Ni(acac)$_2$(μ_2-dppeO$_2$)]$_n$ (**2**). Anisotropic displacement parameters are drawn at the 50% probability level, atomic labels are shown for one asymmetric unit and hydrogen atoms are omitted for clarity. **(b)** Packing diagram viewed down the *b* axis.

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The few known complexes of dppeO_2 have been predominantly prepared by the coordination reaction of preformed dppeO_2.[17] Only in some cases is *in situ* oxidation of dppe the source of dppeO_2. This occurs in copper,[18],[19] lead,[20] molybdenum,[21] zinc,[22] nickel[23], and cobalt[24] complexes. Recently $[Ni(acac)_2(dmpeO_2)]_n$ dmpeO_2 = ethylenebis-(dimethylphosphinedioxide), which is a homologous to **2**, was prepared using dmpe and $Ni(acac)_2$ as a starting material.[25] In contrast to **2** the structure of $[Ni(acac)_2(dmpeO_2)]$ shows a *trans* orientation of the phosphine oxide donors. Interestingly Smolko *et al.*[24d] found the semi-oxygenated [2-ethylene(diphenylphosphino)]diphenylphosphine oxide, (dppeO) in a minor product, $[Co(dppeO_2)Br_2Co(dppeO)Br_2]_n$, where the major product is $[CoBr_2(dppeO_2)]_n$. None of these reactions were shown to be catalytic. Indeed, O_2 as the source of O atoms was not definitively demonstrated in any of these cases.

Spectroscopic characterization, O atom source

Although it would seem likely that the origin of the O atoms in *cis*-$[Ni(acac)_2(\mu_2\text{-}dppeO_2)]_n$ is expected to come from O_2 from air it cannot be assumed. Especially considering that water as the O atom donor with concurrent reduction of Ni(II) in $Ni(acac)_2$ to a Ni(0) species has been suggested as the mechanism by Ananikov *et al.* for the production of tertiary phosphine oxide biproducts in a procedure for making Ni(0) species.[26] The FT-IR spectrum of a crushed single crystal of **2** shows a band at 1174 cm^{-1} assigned to the P=O stretch for the coordinated phosphine oxide[27] and this band shifts to 1153 cm^{-1} when the preparation is carried out under an atmosphere of 99% $^{18}O_2$ (Figure 4, S10). In addition, a new band at 1093 cm^{-1} in the partially ^{18}O labelled **2** appears to be related to the 1103 cm^{-1} band in ^{16}O-**2**. In conclusion, the origin of the O atoms in the dppeO_2 ligand is O_2 from air is indisputable.

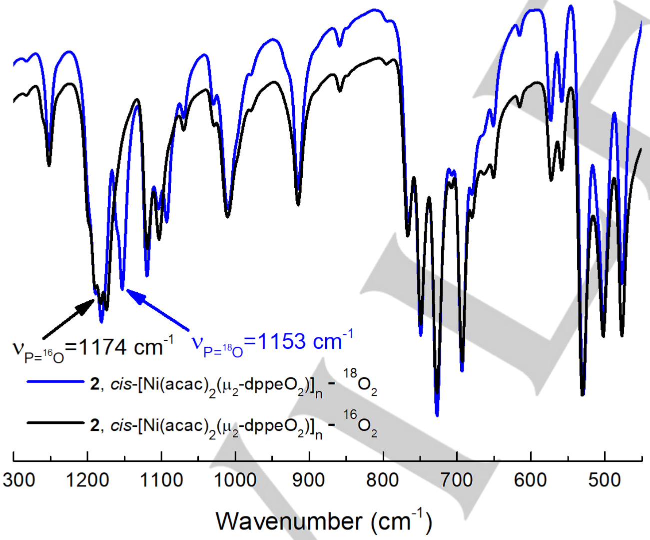

Figure 4. FT-IR spectrum of crystal of **2** showing the isotopically sensitive ($\nu_{P=^{16}O}$ vs $\nu_{P=^{18}O}$) phosphorus oxide stretches in ^{16}O-**2** and ^{18}O-**2**.

Despite the polymeric nature of the complexes, electrospray ionization (ESI) mass spectrometry can be used to identify charged fragments produced by depolymerization of **1a**, **1b** and **2** in acetonitrile (Figure S11, S12). The mass spectrum of the sample of **2** prepared under $^{18}O_2$ (in the presence of excess dppe) shows ions that can be assigned to both ^{18}O- and ^{16}O-labelled fragments $[dppeO_2H]^+$, $[Na(dppeO_2)]^+$, $[Ni(acac)(dppeO_2)]^+$, and $[Na(dppeO_2)]^+$ indicating that the polymeric solid state contained both ^{18}O-**2** and ^{16}O-**2**. Significantly $^{18}O^{16}$O-**2** was not detected. Closer inspection of the IR spectrum of "^{18}O-**2**" (Figure 4) suggests also traces of ^{16}O-**2**. The only explanation for the presence of ^{16}O-**2** was that dppe was air oxidized in an *oxidation with catalytic turnover*. This was concluded since after observing what appeared to be a good yield of the pale green crystals of "^{18}O-**2**", the reaction was assumed to be complete. The flask was then disconnected from the $^{18}O_2$ cylinder and allowed to stand open to air overnight. During this time the small excess of dppe remaining in the reaction mixture was oxidised by unlabelled O_2 from the air.

Catalysis

The hypothesis of actual catalytic turnover (Eq. 1) of the air oxidation of dppe was tested by stirring a mixture of $Ni(acac)_2$ (5% relative to dppe) in MeCN open to air. After 3 hrs the MeCN was removed and the residue was analyzed by ^{31}P NMR spectroscopy ($CDCl_3$). This experiment showed 71% conversion of dppe to dppeO_2 (Table 1, Figure S13), confirming our suspicion based on the ESI-MS and FT-IR data. An identical experiment run for 24 hours produces a higher yield of dppeO_2 and the conversion is quantitative after a couple of days. The reaction was followed over 3 hrs in $CDCl_3$ using ^{31}P NMR (Figure 5) with a lower overall yield compared to the reaction in MeCN. The difference in yield suggests that coordinating MeCN facilitates dissociative mechanisms and therefore catalysis. The $CDCl_3$ experiment shows the conversion is fastest within the first 40 mins, after which time the rate slows significantly suggesting that a product inhibits the reaction. This is consistent with isolation of the polymeric Ni(II) complex of the product dppeO_2. Ni–OPR_3 bonds will be more stable in $CDCl_3$ compared to nucleophilic MeCN. DppeO is also detected in some reactions (Table 1, Figure S14).

$$O_2 + (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2 \xrightarrow{Ni(acac)_2} (C_6H_5)_2P(O)CH_2CH_2P(O)(C_6H_5)_2 \quad (1)$$

Table 1. Yields of oxygenated phosphine from the $M(acac)_2$ and $M(OAc)_2$ M = Ni, Cu, Zn catalyzed air oxidations of dppe performed in MeCN.

Catalyst	[M]:[dppe]	Time (h)	dppeO_2 (%)	dppeO (%)	Unreacted dppe (%)
None	-	3	1	3	96
$Ni(acac)_2(OH_2)_2$	1:20	3	71	29	0
		24	83	17	0
	1:10	3	95	0	5
$Ni(OAc)_2{\cdot}4H_2O$	1:20	3	90	0	10
		24	94	6	0
	1:10	3	82	18	0
$Zn(acac)_2(OH_2)$	1:10	3	2	2	96
$Zn(OCOCH_3)_2{\cdot}2H_2O$	1:10	3	1	3	96
$Cu(acac)_2$	1:10	3	1	2	97
$Cu(OCOCH_3)_2{\cdot}H_2O$	1:10	3	10	13	77

As controls, the analogous Cu(II) and Zn(II) bis-acac complexes, and Ni(II), Cu(II), Zn(II) acetates were tested for their ability to catalyze the air oxidation of dppe (Table 1) under closely similar conditions. $Zn(acac)_2$, $Zn(OAc)_2$ and $Cu(acac)_2$ show minimal promotion of the air oxidation of dppe. $Cu(OAc)_2$ shows activity but with significantly lower yields. $Ni(OAc)_2$ is as effective as $Ni(acac)_2$ in catalyzing the reaction, however the product dppeO_2 does not remain coordinated to nickel. The orange hue of the reaction mixture of $Ni(OAc)_2$ with 10 eq. of dppe in MeCN suggests that the solution speciation of the Ni(II) might be the

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square planar Ni(dppe)(OAc)$_2$, where the two acetates are constrained to monodentate and *cis* coordination. The conclusion is that nickel acetate shows a lower affinity for dppeO$_2$ than does Ni(acac)$_2$ in MeCN solution and therefore the reaction may be less inhibited by the product; however, we have not followed the evolution of this reaction.

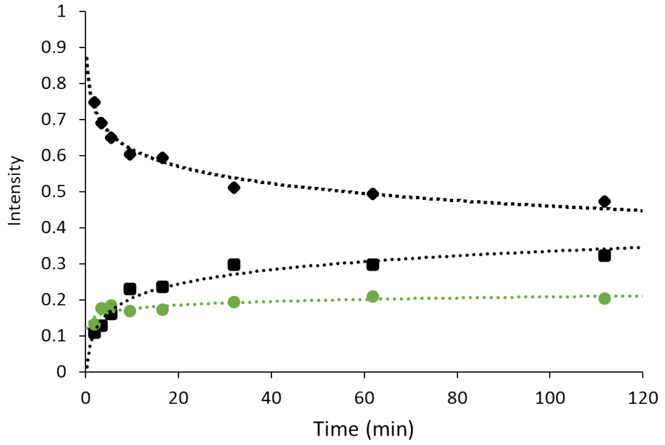

Figure 5. Catalysis of air oxidation of dppe by Ni(acac)$_2$ (1Ni:20dppe, 1 atm, rt, 3 hr) in CDCl$_3$ followed by ^{31}P NMR spectroscopy (◆ dppe ● dppeO ■ dppeO$_2$). Plot of the devolution of dppe (δ = -12.5 ppm) and evolution of dppeO$_2$ (δ = 32.5 ppm) and dppeO (δ = 32.71 ppm (d, J = 48.8 Hz) and δ = -11.96 ppm (d, J = 48.9 Hz)).

A hint of bimetallic cooperativity

Low valent Ni(0) and Ni(I) complexes are expected to react with O$_2$. Ni(II) activation of O$_2$ is also known[28] and high valent Ni(III) and Ni(IV) oxides are known to transfer O atoms[29]. We therefore hypothesized that the catalysis we observe might be rationalized through spectroscopic identification of a transient Ni(I), Ni(III) or Ni(IV) species. The solution changes colour from yellow to green (the colour of **2**) during the Ni(acac)$_2$-catalyzed air oxidation reaction. Time resolved UV-Visible spectroscopy shows the absorbance at 430 nm of the yellow solution devolving during the process (Figure 6) however no intermediate is detected.

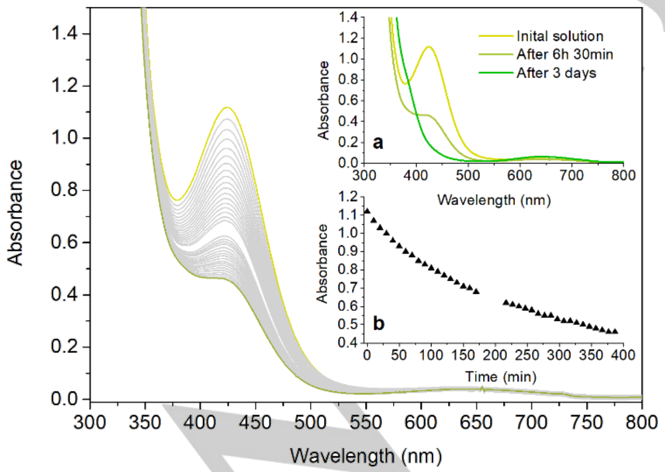

Figure 6. Time-resolved UV-vis spectra of an acetonitrile solution of equimolar dppe and Ni(acac)$_2$ that had been heated to 50°C for 5 mins then subsequently diluted with acetonitrile to 1.25 mM for the T=0 measurement. The UV-vis spectrum recorded over 6.5 hrs at rt during which time the colour changes from yellow to green. Insets **(a)** change over three days. **(b)** Decrease in absorbance at 425 nm.

Although scope has not been the focus of the present study it was relevant to test the possible importance of bidenticity, and the ability of the dppe, dppeO and dppeO$_2$ to bridge between metal ions, for their influence on this catalytic reaction. We therefore tested the monophosphine most closely related to dppe, methyldiphenylphosphine and PPh$_3$ as substrates. Catalysis also occurs however the yields are significantly lower (Table 2) compared to the reactions using dppe as substrate under the same Ni:P ratios and conditions. The significantly lower yields for the oxides of the monophosphine substrates give impetus to the idea of a concerted bimetallic O$_2$ activation. Pertinently the reaction of O$_2$ with dinickel complexes is known.[28a, 30] We speculate that the O$_2$ activation could, for example, be facilitated by a fleeting [(acac)$_2$Ni(μ$_2$-dppe)Ni(acac)$_2$] species which might support a second μ-O$_2$ ligand. Ni(II) is geometrically flexible in terms of geometry and spin state and will accommodate these dynamics. In the absence of spectroscopic evidence for O$_2$ sensitive Ni(I), high valent Ni(III)- or Ni(IV)-oxygen species or evidence to the contrary, that the O$_2$ activation does not engage nickel redox activity, a proposed mechanism cannot be elucidated. SI Figure S17, however presents a candidate which uses two high-spin Ni(II) to polarise a bridging O$_2$ with a supporting substrate dppe strapping between nickel ions. The *trans* and *cis* orientation of the dppe and dppeO$_2$ ligands respectively in the isolated 1D polymers do not imply any steric orientation relevant for an oxygen activation or O transfer pathway for the labile solution state complexes in reaction mixtures. Rather, these orientations are presumably determined by favourable crystal packing forces. The insolubility of the dppeO$_2$ complex is the reason for inhibition of the catalysis after a few turnovers.

Table 2. Air oxidation of tertiary phosphines catalysed by Ni, Cu, Zn acac and acetate complexes. [M = Ni, Cu, Zn]:[P] = 1:20. 3 hrs exposure to air. T = 21° C. Solvent MeCN.

Catalyst	Unreacted substrate	Product
	CH_3PPh_2 (%)	$CH_3P(O)Ph_2$ (%)
None	98	2
Ni(acac)$_2$(OH$_2$)$_2$	84	16
Cu(acac)$_2$	98	2
Zn(acac)$_2$(OH$_2$)	88	12
Ni(OCOCH$_3$)$_2$·4H$_2$O	90	10
Cu(OCOCH$_3$)$_2$·H$_2$O	94	6
Zn(OCOCH$_3$)$_2$·2H$_2$O	92	8
	PPh_3 (%)	$OPPh_3$ (%)
Ni(acac)$_2$(OH$_2$)$_2$	96	4

Conclusion

The discovery of simple non-noble metal catalysts for new greener methods to activate O$_2$ from air is an important step towards finding technologies to replace otherwise very polluting oxidation chemistry.[31] While air oxidation of tertiary phosphines in the presence of many types of metal complexes is well known in stoichiometric chemistry to give phosphine oxide complexes, it is much more rarely reported in turnover catalytic reactions. It was therefore surprising to discover that simple Ni(II) complexes of acetate and acac ligands catalyse this reaction. In the case of Ni(acac)$_2$ the reaction is inhibited by the product dppeO$_2$ because of the formation of an insoluble polymer when dppeO$_2$ accumulates. Potentially this could be overcome by in-stream

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product removal to realize a robust catalytic system using O_2 as the direct terminal oxidant.

Experimental Section

[Ni(acac)$_2$] was prepared by dehydrating [Ni(acac)$_2$(H$_2$O)$_2$] at 130 °C.[32] Cu(acac)$_2$[33] and Zn(acac)$_2$[34] were prepared according to literature references. Other chemicals used as supplied.

***catena*-poly[[bis-(1,3-dimethylpropane-1,3-dionato-*κO,O'*)nickel(II)]-*μ*-1,2-ethylenebis(diphenylphosphine)-*κP,P'*] acetonitrile solvate, *trans*-[Ni(acac)$_2$(μ_2-dppe)]$_n$.2MeCN (1a)**

1,2-ethylenebis(diphenylphosphine) (dppe) (100 mg, 0.25 mmol) and [Ni(acac)$_2$] (66 mg, 0.26 mmol) were mixed in acetonitrile (10 mL) to give a pale-yellow solution. Within 1 min, *trans*-[Ni(acac)$_2$(μ_2-dppe)]$_n$.2MeCN crystallized as pale green needle crystals. These were collected within 30 min by suction filtration, during this process the crystals collapse losing visible crystallinity (105 mg, 57%). The crystal used for single crystal X-ray diffraction was selected directly from the mother liquor, mounted and immediately flash cooled in a 150 K cold nitrogen gas stream. IR (FT-ATR diamond anvil) v/cm^{-1} = 3062 (vw), 2987 (vw), 2914 (vw), 1583 (s), 1513 (s), 1484 (w), 1456 (m), 1432 (m), 1401 (s), 1356 (m), 1326 (w), 1256 (m), 1192 (m), 1179 (m), 1104 (w), 1071 (vw), 1015 (m), 921 (m), 853 (w), 761 (m), 740 (s), 717 (m), 694 (s), 652 (m), 619 (w), 572 (m), 561 (m), 512 (s), 488 (m), 438 (w), 417 (s).

***catena*-poly[[bis-(1,3-dimethylpropane-1,3-dionato-*κO,O'*)nickel(II)]-*μ*-1,2-ethylenebis(diphenylphosphine)-*κP,P'*], *trans*-[Ni(acac)$_2$(μ_2-dppe)]$_n$ (1b)**

1,2-Ethylenebisdiphenylphosphine (dppe) (159 mg, 0.4 mmol) and [Ni(acac)$_2$] (102 mg, 0.4 mmol) were dissolved in toluene (3 mL). n-Hexane (4 mL) was layered on top of the solution and within an hour pale blue crystals of *trans*-[Ni(acac)$_2$(dppe)]$_n$ deposited. Yield: 0.190 g (76%). Anal. calcd. for $C_{36}H_{38}NiP_2O_4\cdot½(C_7H_8)$: C, 67.65; H, 6.04.. Found: C, 67.73; H, 5.98. IR (FT-ATR diamond anvil) v/cm^{-1} = 3059 (vw), 2988 (vw), 2916 (vw), 1582 (s), 1514 (s), 1460 (m), 1431 (m), 1403 (s), 1359 (m), 1255 (m), 1197 (m), 1180 (m), 1122 (w), 1103 (w), 1092 (w), 1071 (w), 1017 (m), 924 (m), 853 (w), 760 (m), 743 (s), 718 (m), 695 (s), 676 (m), 653 (m), 618 (vw), 591 (vw), 571 (m), 569 (m), 532 (m), 513 (s), 488 (m), 437 (w), 420 (m).

***catena*-poly[[bis-(1,3-dimethylpropane-1,3-dionato-*κO,O'*)nickel(II)]-*μ*-ethylenebis(diphenylphosphine oxide)-*κO,O'*], *cis*-[Ni(acac)$_2$(μ_2-dppeO$_2$)]$_n$ (2)**

Instead of isolating *trans*-[Ni(acac)$_2$(μ_2-dppe)]$_n$.2MeCN after its preparation, the mixture of *trans*-[Ni(acac)$_2$(μ_2-dppe)]$_n$.2MeCN and mother liquor was heated gently until all the solids were dissolved. On standing in an open vessel the solution changes colour from yellow to green and after 4-6 hours pale green crystals of *cis*-[Ni(acac)$_2$(μ_2-dppeO$_2$)]$_n$ crystallised (35 mg, 20%). Anal. calcd. for $C_{36}H_{38}NiP_2O_6\cdot½(H_2O)$: 62.09; H, 5.64. Found: C, 61.98; H, 5.78. IR (FT-ATR diamond anvil) v/cm^{-1} = 3059 (vw), 3021 (vw), 2991 (vw), 2954 (vw), 2911 (vw), 2851 (vw), 1586 (m), 1513 (s), 1455 (m), 1437 (m), 1397 (s), 1355 (m), 1252 (m), 1182 (s), 1119 (m), 1103 (m), 1070 (vw), 1009 (m), 915 (m), 859 (vw), 796 (vw), 767 (m), 749 (s), 727 (s), 693 (s), 650 (m), 615 (vw), 573 (m), 558 (m), 530 (s), 502 (s), 477 (s), 411 (m).

Catalysis

Dppe (50.5 μmol) and M(acac)$_2$ or M(OAc)$_2$ (M = Ni, Cu or Zn) (5 μmol) dissolved in MeCN (9.25 mL) were stirred open to the atmosphere at room temperature for 3 hours. The solvent was removed (rot. evap.) and the residue was analysed with ^{31}P NMR (CDCl$_3$) which was recorded using a reverse gated ^{1}H decoupling approach. The yields of the catalytic reactions are based on the integration of the signals for dppe (-12.54 ppm), dppeO$_2$ (32.55ppm) and dppeO (32.71, -11.96 ppm) by ^{31}P NMR spectroscopy. Dppe (50.5 μmol) was stirred in MeCN (9.25 mL) in the absence of catalyst open to the atmosphere for 3 hours. The solvent was removed (rot. evap.) and the residue dissolved in CDCl$_3$ and analysed by ^{31}P-NMR.

CH_3PPh_2 (102 μmol) and M(acac)$_2$ or M(OAc)$_2$ (M=Ni, Cu or Zn) (5 μmol) were dissolved in MeCN (9.25 mL) and stirred under air at rt conditions for 3 hours. Acetonitrile was removed by rotary evaporation and the crude product was analysed with ^{31}P NMR as described above. CH_3PPh_2 (102 μmol) was stirred in MeCN (9.5 mL) without presence of catalyst open to atmosphere for 3 hours and analysed by ^{31}P NMR.

Crystallography

Data for **1a** and **1b** were collected at 150(2) K on a Bruker-Nonius Apex II CCD diffractometer using Mo*K*α radiation (λ = 0.71073Å) and data for **2** were collected at 100(1) K on a Synergy, Dualflex, AtlasS2 diffractometer using Cu*K*α radiation (λ = 1.54184 Å). All three structures were solved by dual space methods (SHELXT[35]) and refined on F^2 using all the reflections (SHELXL-2017/1[36]). All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms were inserted at calculated positions using a riding model. Additional refinement details and figures are included in the supplementary material.

Crystal Data for 1a: $C_{40}H_{44}N_2NiO_4P_2$, monoclinic, $P2_1/c$, a = 8.536(5) Å, b = 10.279(6) Å, c = 21.562(12) Å, β = 100.75(2)°, V = 1858.5(18) Å^3, Z = 2, T = 150(2) K, μ(MoKα) = 0.651 mm^{-1}, 31655 refl measured, 3268 unique, R_{int} = 0.2825, $R1$ = 0.0754 (I > 2σ(I)), wR_2 = 0.1449 (all data).

Crystal Data for 1b: $C_{36}H_{38}NiO_4P_2$, triclinic, $P\overline{1}$, a = 8.5126(12) Å, b = 10.1655(15) Å, c = 10.351(3) Å, α = 101.604(11)°, β = 91.860(11)°, γ = 113.381(8)°, V = 799.0(3) Å^3, Z = 1, T = 150(2) K, μ(MoKα) = 0.746 mm^{-1}, 10034 refl measured, 2816 unique, R_{int} = 0.1153, $R1$ = 0.0528 (I > 2σ(I)), $wR2$ = 0.0900 (all data).

Crystal Data for 2: $C_{36}H_{38}NiO_6P_2$, monoclinic, I2/a, a = 15.49930(10) Å, b = 10.40120(10) Å, c = 20.22510(10) Å, β = 93.5410(10)°, V = 3254.29(4) Å^3, Z = 4, T = 100.00(10) K, μ(CuKα) = 2.164 mm^{-1}, 43565 refl measured, 3415 unique, R_{int} = 0.0198, $R1$ = 0.0273 (I > 2σ(I)), $wR2$ = 0.0696 (all data).

Supporting Information

CCDC 1979564-1979566 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. Additional information and PXRD, IR, ESIMS and NMR data can be found in link.

Keywords: β-diketonate • acetate • nickel • oxygen activation • phosphine oxidation

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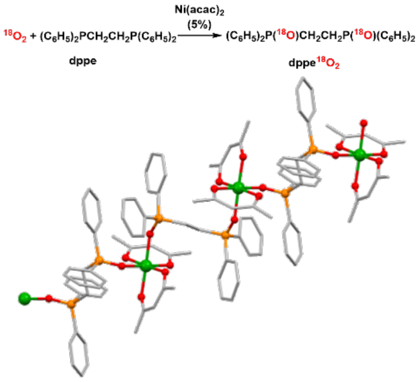
Acetylacetonate and Acetate Complexes of Nickel(II) Catalyze the Air Oxidation of Phosphines



Dppe is air-oxidized in turnover reactions catalyzed by $Ni(acac)_2$ and $Ni(OAc)_2$. The metastable 1D polymeric *trans*-$[Ni(acac)_2(\mu_2\text{-dppe})]_n$.2MeCN and *cis*-$[Ni(acac)_2(\mu_2\text{-dppeO}_2)]_n$ are isolated at the start and end of the reaction respectively. Higher yields compared to reactions using the analogous monophosphine suggest a dimetallic O_2 activation process.

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