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Mild electrochemical synthesis of metal phosphides with dibenzo-7-phosphanorbornadiene derivatives: mechanistic insights and application to proton reduction in water†

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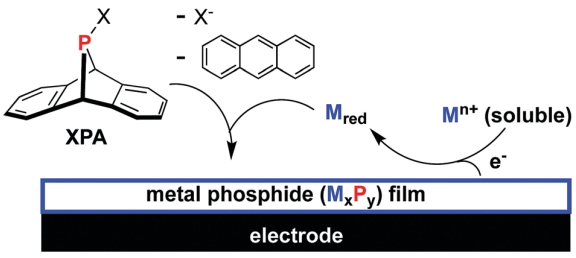
Transition metal phosphide films were synthesized using a mild electrochemical method. Dibenzo-7-phosphanorbornadiene derivatives (XPA) are introduced as versatile precursors to amorphous metal phosphide electrocatalysts for proton reduction in acidic water. Homogeneous model reactions reveal distinct reactivity between XPA and nickel in different oxidation states, with Ni(0) resulting in Ni_xP_y formation.

With aqueous proton reduction catalysis emerging as a strategy for the storage of solar energy in the form of chemical bonds, facile synthesis of high performance, robust, and inexpensive electrocatalysts is desirable.[1] Toward practical electrocatalysts based on earth abundant elements, transition metal phosphides have been demonstrated to have high activity for the hydrogen evolution reaction (HER) at low overpotentials.[2] Despite a growing interest in metal phosphides for applications including HER, oxygen reduction reaction (ORR),[3] and batteries,[4] conventional methods of synthesis typically require high temperatures and hazardous starting materials.[5a] These conditions limit the structural diversity of the obtained materials; critically, the forcing conditions required for generating these phosphides results in thermodynamic control of the products as opposed to the potentially more reactive and synthetically useful materials generated by kinetic control. Furthermore, limited mechanistic insight is available for the typical methodologies of metal phosphide preparation. The synthesis of metal phosphides at relatively low temperatures is rare.[6] Toward large scale applications of metal phosphide materials, the development of reliable and safe protocols that allow for control of the material's properties through varied composition and structure is desirable. Starting with mechanistic insight derived from well-defined homogeneous metal complexes, we report herein the development of a mild electrochemical method for the synthesis of transition metal phosphides active for HER. Moreover, we report a new type of precursor for the synthesis of metal phosphide materials.

$P(SiMe_3)_3$, PH_3, trialkyl phosphines, and P_4 are the typical P-sources employed in the synthesis of metal phosphides.[5a] NaH_2PO_2 has been used for the electrodeposition of metal phosphides from aqueous solution,[6b–e] although contamination with metal(0) and metal oxide has been reported under these conditions.[6b] We sought to employ alternate P-sources suitable for the electrochemical synthesis of high purity metal phosphides. In homogeneous synthetic chemistry, NaOCP has also been demonstrated as a P source, upon CO extrusion.[5b–e] Similarly, metal coordinated 7-phosphanorbornadiene derivatives have been utilized as phosphinidene precursors, generating transient metal phosphinidene fragments with concomitant arene elimination.[7] Cummins and coworkers recently reported the facile synthesis of dibenzo-7-phosphanorbornadiene derivatives (XPA, Scheme 1) in one or two steps from commercially available precursors and demonstrated that such species can serve as a source of phosphinidene upon mild thermolysis.[8] ClPA was recently employed in the synthesis of a molecular terminal molybdenum phosphide.[9] In that process, a *para*-terphenyl diphosphine-supported Mo(0) precursor undergoes a



Scheme 1 Conceptual representation of the electrochemical synthesis of metal phosphides *via* metal salt reduction and subsequent reaction with XPA (X = Cl for ClPA; X = NMe_2 for Me_2NPA).

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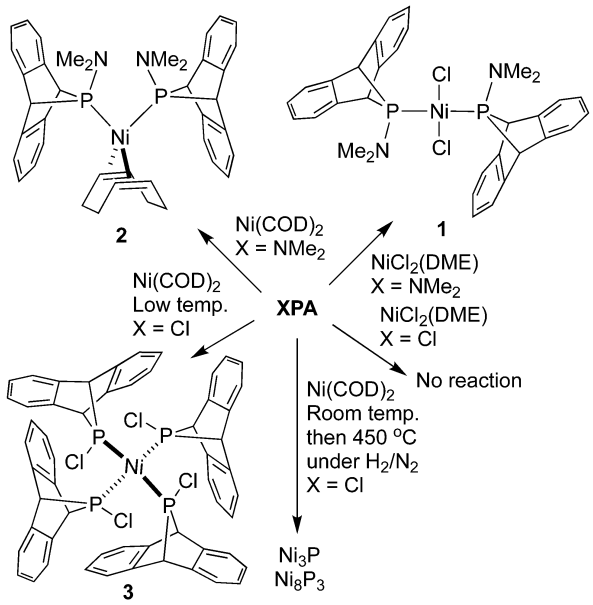
4e$^-$ oxidation upon reaction with ClPA, to generate anthracene and a Mo(IV) phosphide chloride under mild conditions, even below room temperature. This multielectron redox process requires a low oxidation state metal precursor for P-atom transfer.

Encouraged by the aforementioned precedent in solution-state molecular chemistry, we targeted the synthesis of solid-state metal phosphides at low temperatures using the XPA family of compounds as the P-atom source. Conceptually, starting with common metal salts is desirable not only due to their availability and low cost, but also because of a lower propensity to undergo oxidation and group transfer with XPA (Scheme 1). To localize the metal phosphide deposition on the electrode, a reactive, low oxidation state metal species is generated electrochemically. The reduced metal species must perform the P-group transfer efficiently upon formation at the electrode surface to avoid reactivity and subsequent precipitation away from the electrode. Furthermore, the P-transfer reagent should not react by itself on the electrode, to avoid the deposition of P-rich materials. If these conditions are satisfied, a film of metal phosphide is generated on the electrode, allowing for direct subsequent use for electrocatalytic applications.

Toward selecting the most suitable XPA reagent, we studied the solution reactivity of ClPA and Me_2NPA with Ni precursors. Reactions of Ni(II) and Ni(0) with XPA were conducted using $NiCl_2$(DME) (DME = 1,2-dimethoxyethane) and $Ni(COD)_2$ (COD = 1,4-cyclooctadiene), respectively (Scheme 2). The addition of Me_2NPA to a pale yellow solution of $NiCl_2$(DME) in THF results in a color change to red, corresponding to the formation of the diphosphine complex $NiCl_2[P(NMe_2)A]_2$ (**1**, Fig. 1), as confirmed by single crystal X-ray diffraction (XRD). No reaction is observed spectroscopically upon treatment of $NiCl_2$(DME) with ClPA, as indicated by observation of free ClPA by $^{31}P\{^1H\}$ NMR spectroscopy; however, electrochemical studies are consistent with some interaction between ClPA and $NiCl_2$(DME) (*vide infra*). The ability of Me_2NPA to bind Ni(II), in contrast to ClPA, is likely a consequence of the more electron rich nature of the aminophosphine. As expected, Ni(II) reagents do not promote oxidative group transfer; only coordination is observed. This behavior makes the Ni(II) reagent suitable for use in the electrochemical protocol.



Scheme 2 Reactions of XPA with Ni(II) and Ni(0) complexes.

The reactivity of XPA with $Ni(COD)_2$ (Scheme 2, bottom), a surrogate for an electrochemically generated low oxidation state metal center, was explored. Addition of Me_2NPA to a solution of $Ni(COD)_2$ at room temperature, results in a color change from yellow to orange. ^1H NMR spectroscopy indicates the clean formation of new species, confirmed by XRD to be $Ni(COD)[P(NMe_2)A]_2$ (**2**, Fig. 1). In contrast, a black precipitate forms upon addition of ClPA to a $Ni(COD)_2$ solution. These solids were insoluble in common organic solvents. Powder X-ray diffraction (PXRD) studies indicate that this precipitate is amorphous. Thermal annealing at 450 °C under forming gas promotes reorganization to a material consistent with Ni_3P and Ni_8P_3, as evidenced by PXRD (Fig. S10, ESI†). Energy-dispersive X-ray spectroscopy (EDX) studies indicate the presence of both Ni and P, before and after the annealing, in roughly 3 : 1 ratio (Fig. S11 and S12, ESI†). The fast formation of a heterogeneous nickel phosphide from Ni(0) and ClPA points to this reagent as a good candidate for metal phosphide synthesis by electrodeposition.

Further insight into the process of group transfer from ClPA to Ni was sought by performing the reaction at low temperatures. Upon mixing thawing toluene solutions of the reagents (Ni(0) and ClPA) and carefully warming to −35 °C, formation of the black precipitate was not observed. Vapor diffusion of pentane into the reaction solution at −35 °C afforded single crystals of $Ni(PClA)_4$ (**3**). Isolation of **3** indicates that coordination of ClPA to Ni through P may precede group transfer chemistry and metal phosphide generation. The thermal stability of isolated **1–3** was evaluated by variable temperature (VT) NMR spectroscopy. Ni(II) adduct **1** was stable at 40 °C. In contrast, Ni(0) complex **2** decomposes slowly in solution at room temperature, a process that accelerates upon warming to 40 °C, as measured by the release of anthracene and observation of free COD ($t_{1/2} \approx 152$ min at 25 °C, 55 min at 40 °C). The formation of anthracene is consistent with a group transfer process. Surprisingly, **3** was stable even at 40 °C. This thermal stability of **3** suggests that it is not an intermediate in the fast formation of Ni_3P and Ni_8P_3 upon the room temperature addition of ClPA to $Ni(COD)_2$. More reactive lower coordination number Ni(0) complexes of ClPA, $Ni(ClPA)_n$ (n = 1, 2 or 3) generated *in situ* may be responsible for the observed facile group transfer. The reactivity observed between the two XPA derivatives and both Ni(0) and Ni(II) precursors suggests that ClPA is the most suitable reagent for electrochemical deposition of nickel phosphide due to the fast reaction with Ni(0) to engender P-atom transfer.

To investigate the behavior of XPA derivatives under electrochemical conditions, cyclic voltammograms (CVs) were measured. No reduction of XPA is observed at potentials as negative as −2.2 V (Me_2NPA) and −2.0 V (ClPA), respectively (Fig. 2ai and ii). The CV of $NiCl_2$(DME) shows an irreversible reduction wave (Fig. 2aiii), that remains unchanged after 10 cycles (Fig. 2b), with no evidence of film formation on the electrode.

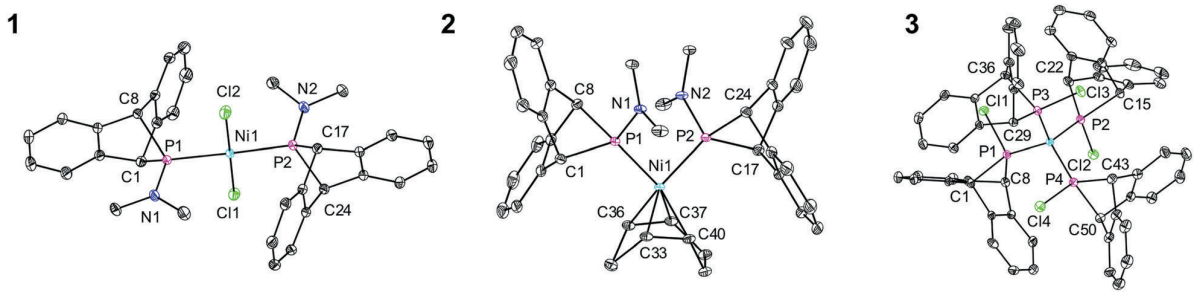


Fig. 1 Solid-state structures of **1–3** with anisotropic displacement ellipsoids shown at the 50% probability level. Solvate molecules and hydrogen atoms are omitted for clarity.

A CV of a $NiCl_2$(DME)/Me_2NPA mixture shows a reductive event at a more negative potential compared to $NiCl_2$(DME), likely due to *in situ* formation of **1**; the increased electron density at nickel upon Me_2NPA binding shifts the reduction cathodically (Fig. 2c, blue trace). The reduction wave of a $NiCl_2$(DME)/ClPA mixture appeared at slightly more positive potential than that of $NiCl_2$DME (Fig. 2d, blue trace), consistent with some interaction between ClPA and $NiCl_2$(DME). Notably, while the voltammogram was unchanged after 10 cycles in the presence of Me_2NPA (Fig. 2c), successive changes were observed in the presence of ClPA (Fig. 2d). The gradual change of the CV of the $NiCl_2$(DME)/ClPA mixture is attributed to the deposition of a nickel phosphide film, generated by the reaction of reduced nickel species with ClPA at the electrode. In contrast, for the $NiCl_2$(DME)/Me_2NPA mixture, the lower propensity to lose anthracene and the formation of soluble species (**2**) prevent deposition onto the electrode and result in no change in the CV upon cycling. For comparison, commercially available PCl_3 was examined as a potential precursor for electrochemical reduction. As the precursor to XPA synthesis, low-cost PCl_3 is an attractive P-atom source for electrochemical deposition. However, it shows a reduction onset around −1.1 V *vs.* Fc/Fc^+ (Fig. S16, ESI†), significantly more positive than that of XPA, and more cathodically shifted than that of $NiCl_2$(DME). Additionally, reduction of PCl_3 leaves an insulating film on the electrode surface after the first reduction cycle. Although there is a report of chemical reduction of PCl_3 and $NiCl_2$ by sodium metal upon heating to 330 °C in an autoclave, PCl_3 is not a suitable P-source in the present methodology. Overall, both homogeneous and electrochemical studies indicate that ClPA is the most suitable phosphorus source of those studied, offering the advantage of rapidly delivering a single P-atom under mild conditions.

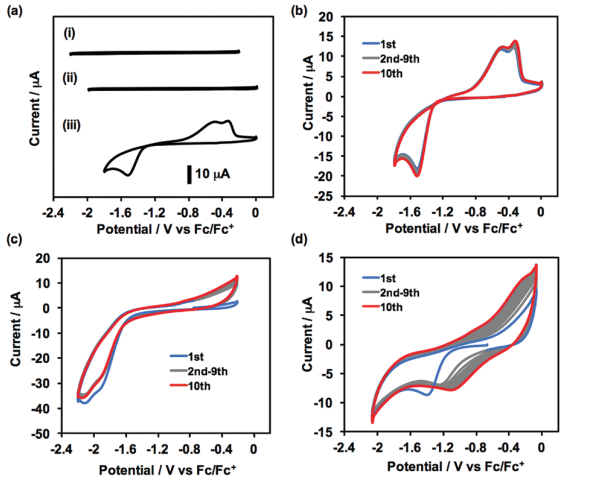


Fig. 2 CVs recorded in 0.1 M $^nBu_4NPF_6$ in THF at a scan rate of 100 mV s^{-1}. (a) (i) 5 mM Me_2NPA, (ii) 5 mM ClPA, (iii) 2.5 mM $NiCl_2$DME. (b–d) CV for 10 scans in (b) 2.5 mM $NiCl_2$DME, (c) 2.5 mM $NiCl_2$DME + 5 mM Me_2NPA, (d) 2.5 mM $NiCl_2$DME + 5 mM ClPA.

With ClPA selected as reagent of choice, the synthesis of nickel phosphide (Ni–P) by constant potential electrolysis was conducted. Due to its higher solubility in THF, $NiBr_2$(DME) was employed as a nickel source instead of the chloride salt. Using a titanium foil working electrode, a constant potential (−1.7 V *vs.* Fc/Fc^+) was applied for 60 min while stirring the solution. Following electrolysis, a black film was left on the working electrode, which was carefully washed with THF and subsequently used for characterization and HER.

PXRD of the obtained electrode showed identical peaks to the underlying Ti foil, indicating the amorphous nature of the material. The morphology and elemental composition were analyzed by scanning electron microscopy (SEM) (Fig. 3a), indicating formation of a uniform Ni–P film covering the entire electrode surface (Fig. 3a). EDX analysis demonstrated the incorporation of both Ni and P and their colocalization into the film (Ni/P = 1.6 to 3 in atomic ratio, Fig. 3b and Fig. S18, ESI†). X-ray photoelectron spectroscopy (XPS) data of the Ni 2p region (Fig. 3c) shows a Ni $2p_{3/2}$ peak at 853.3 eV, close to reported Ni–P (852.9 eV for Ni_2P and 852.7 eV for Ni_3P) or metallic nickel (852.7 eV).[10] The phosphorus 2p region showed a lower energy 2p signal that was fitted to two peaks derived from $2p_{3/2}$ and $2p_{1/2}$ (Fig. 3d). The $2p_{3/2}$ peak at 129.6 eV corresponds to that of reported Ni–P (129.45 eV for Ni_2P, 129.53 eV for Ni_3P),[10] demonstrating the presence of anionic phosphorus ($P^{\delta-}$). The broad peak at 132.3 eV was assigned to orthophosphate,[6b] which presumably forms *via* surface oxidation upon exposure to air.

The Ni–P film was tested for HER electrocatalysis. The overpotentials (η) at 10 mA cm^{-2} and 20 mA cm^{-2} are −171 mV

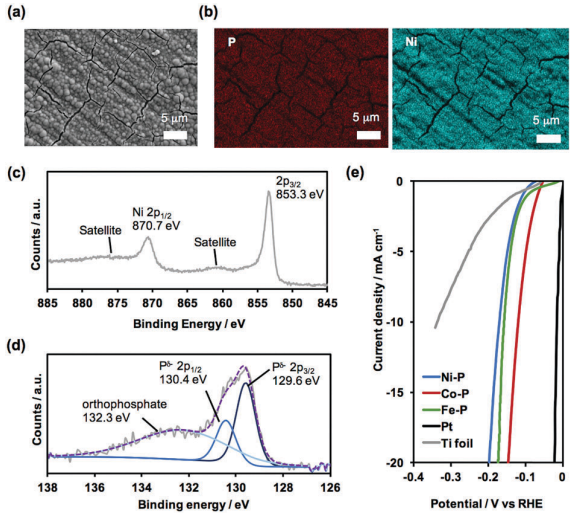


Fig. 3 (a) SEM image of Ni–P film. (b) Elemental mapping of P and Ni on Ni–P film. (c and d) XPS spectra of Ni 2p and P 2p regions. (e) Polarization data for Ni–P, Co–P and Fe–P modified electrode in 0.5 M H_2SO_4 at a scan rate of 3 mV s^{-1}. Data for Pt and Ti foil electrode are included for comparison.

and −199 mV, respectively. These values are much more positive than those of bare Ti foil, demonstrating that the obtained amorphous metal phosphide is a competent HER catalyst, operating at similar overpotentials to Ni–P catalysts reported to date.[2a,c]

To examine the scope of this electrodeposition methodology, cobalt phosphide (Co–P) and iron phosphide (Fe–P) were also fabricated under similar conditions, using ClPA as the P-source and CoI_2 and FeI_2, respectively, as the metal salts. After the electrolysis, black amorphous films were deposited on the electrodes, which were characterized by PXRD, SEM/EDX and XPS (Fig. S21 and S23, ESI†). These measurements support the formation of the corresponding amorphous metal phosphide films with a metal- phosphorous ratio of Co/P = 1.9 and Fe/P = 0.77. Both Co–P ($\eta_{10\,mA\,cm^{-2}} = -121$ mV, $\eta_{20\,mA\,cm^{-2}} = -147$ mV) and Fe–P ($\eta_{10\,mA\,cm^{-2}} = -158$ mV, $\eta_{20\,mA\,cm^{-2}} = -173$ mV) films are competent HER electrocatalysts, with overpotentials in the range reported for these materials.[2a] Previously reported electrosyntheses of metal phosphides (Ni–P[6d] and Co–P[6b,c]) under mild conditions were performed in aqueous media, using $NaPH_2O_2$ as the P-source and resulted in low incorporation of phosphorus (Co/P = 20[6b] and 7[6c] atomic ratio) and contamination with metal oxide in the as-prepared film. The much higher phosphorous content observed here with ClPA demonstrates its efficacy as a versatile P-source for electrochemical metal phosphide synthesis.

In summary, based on mechanistic insight derived from molecular chemistry, we report a new method for the synthesis of a variety of amorphous transition metal phosphide films on electrodes under mild conditions. The XPA compounds, established to perform group transfer in solution chemistry, are introduced as versatile precursors for the synthesis of solid-state metal phosphides. Solution characterization of the reactivity of XPA reagents and their complexes with Ni pointed to ClPA as the most suitable precursor for the present methodology. While unreactive toward Ni(II), ClPA performs group transfer efficiently with low oxidation Ni species generated upon reduction at the electrode. The scope of this method was demonstrated through the synthesis of Co–P and Fe–P films under similar conditions. All transition metal phosphides are electrocatalysts for HER. Current studies are focused on applications of this methodology to the controlled synthesis of complex architectures of phosphide materials.

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Conflicts of interest

There are no conflicts to declare.

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