Hydrocarbon-Soluble Nanocatalysts with No Bulk Phase: Coplanar, Two-Coordinate Arrays of the Base Metals

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S *Supporting Information*

ABSTRACT: A structurally unique class of hydrocarbon-soluble, ancillary-ligand-free, tetrametallic Co(I) and Ni(I) clusters is reported. The highly unsaturated complexes are supported by simple, sterically bulky phosphoranimide ligands, one per metal. The electron-rich nitrogen centers are strongly bridging but sterically limited to bimetallic interactions. The hydrocarbon-soluble clusters consist of four coplanar metal centers, mutually bridged by single nitrogen atoms. Each metal center is monovalent, rigorously linear, and two-coordinate. The clusters are in essence two-dimensional atomic-scale "molecular squares," a structural motif adapted from supramolecular chemistry. Both clusters exhibit high solution-phase magnetic susceptibility at room temperature, suggesting the potential for applications in molecular electronics. Designed to be catalyst precursors, both clusters exhibit high activity for catalytic hydrogenation of unsaturated hydrocarbons at low pressure and temperature.

Figure 1. Trialkylphosphoranimidometal(I) tetramers.

The use of molecular metal clusters as soluble surrogates for heterogeneous-catalyst active sites was introduced more than three decades ago and continues to be a fertile ground for research in transition-metal catalysis.[1] The synthesis of discrete, catalytically active molecular clusters of the transition metals is plagued by, inter alia, uncontrolled redox disproportionation and poor control over the metal coordination environment. In most of the literature examples, the metal ions suffer from coordinative saturation, ligand-imposed steric inaccessibility, or both.[2] Such attributes limit the utility of many polymetallic complexes as either catalysts or model systems for studying metal−metal cooperativity, both of which require the generation and investigation of coordinatively unsaturated metal centers.[2,3]

Recent investigations have clearly demonstrated that the ligand architecture plays a critical role in controlling the metal coordination environment in polymetallic assemblies of the late first-row transition metals.[3] Cleverly designed polydentate ligand scaffolds nucleate multiple transition-metal ions within mutual bonding distance and simultaneously impose coordinative unsaturation at the metal to allow for metal−metal cooperativity.[3]

Here we report the preparation and characterization of the homoleptic trialkylphosphoranimide clusters $[M(\mu_2-NP^tBu_3)]_4$ [M = Co(I) (**1**), Ni(I) (**2**)] (Figure 1), in which the four metal centers are coplanar and extremely low-coordinate. In addition,

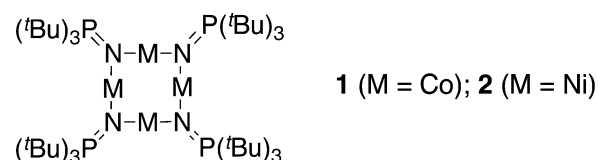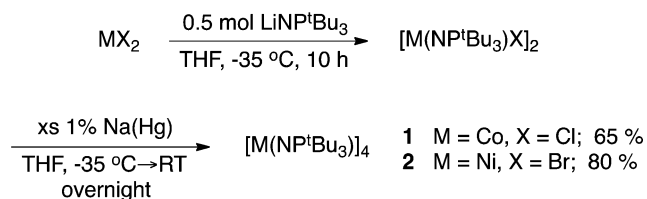we demonstrate that both clusters catalyze alkene and alkyne hydrogenation under mild conditions.

Complexes **1** and **2** constitute the first polymetallic d^8 and d^9 coordination compounds in which each of the metal centers is linear and two-coordinate.[4] Two-coordinate complexes of late first-row transition metals are challenging synthetic targets. About 80 two-coordinate compounds, mostly mononuclear, have been structurally characterized, all relying largely on steric isolation as a design motif.[5]

In this work, sterically large trialkylphosphoranimide ligands were used to control the metal coordination and impart thermodynamic stability, taking advantage of characteristically strong internal bonds, variable electronic character, and considerable *but spatially displaced* steric protection, the latter a function of the bulky phosphorus substituents.[6] The structures of tetrametallic complexes **1** and **2** are unique in many ways; both comprise nearly ideal models for investigating metal−metal cooperativity, as they contain metal centers with extremely low coordination numbers and multiple metal ions located within mutual bonding distance. The synthesis of such discrete, low-valent, and terminally low-coordinate polymetallic complexes is exceptionally rare; the literature is limited largely to dinuclear and trinuclear systems.[3,7]

Tri-*tert*-butylphosphoranimidometal complexes **1** and **2** were synthesized by a two-step strategy involving low-temperature anionic ligand metathesis followed by chemical reduction (Scheme 1). Tetrametallic cobalt cluster **1** was obtained by treatment of a cold suspension of $CoCl_2$ in tetrahydrofuran (THF) with substoichiometric $LiNP^tBu_3$ at −35 °C followed by in situ reduction using sodium amalgam at room temperature. The air-sensitive, pentane-soluble product was isolated in 65% yield after precipitation at −35 °C.

The salt metathesis was originally demonstrated by Stephen and co-workers.[6b] The reaction is highly sensitive to the reaction conditions but upon optimization provides a straightforward and general alternative to the more limited

Scheme 1. Synthesis of $[M(NP^tBu_3)]_4$

$$MX_2 \xrightarrow[\text{THF, -35 °C, 10 h}]{\text{0.5 mol LiNP}^t\text{Bu}_3} [M(NP^tBu_3)X]_2$$

$$\xrightarrow[\substack{\text{THF, -35 °C→RT} \\ \text{overnight}}]{\text{xs 1\% Na(Hg)}} [M(NP^tBu_3)]_4 \quad \begin{array}{l} \textbf{1} \;\; M = Co, \; X = Cl; \; 65\;\% \\ \textbf{2} \;\; M = Ni, \; X = Br; \; 80\;\% \end{array}$$

thermal process pioneered by Dehnicke et al.[6d] The latter requires that the reaction be conducted in excess molten trimethylsilylphosphoranimide at very high temperature, a procedure that is neither scalable nor amenable to the use of higher-molecular-weight phosphoranimides. The anionic exchange using tri-*tert*-butylphosphoranimide and $CoCl_2$ in THF at -35 °C yielded the phosphoranimide-bridged dimer $[CoCl(\mu_2\text{-NP}^tBu_3)(THF)]_2$ (**3**), which was readily isolated and purified by recrystallization (Figure 2). The solid-state

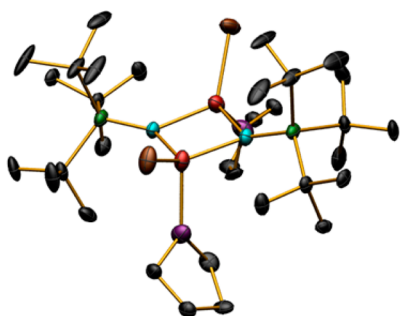**Figure 2.** ORTEP diagram for $[CoCl(\mu_2\text{-NP}^tBu_3)(THF)]_2$ (**3**). See the Supporting Information (SI) for structural parameters.

structure of **3** features a dinuclear Co(II) core with doubly bridging phosphoranimide ligands. Each metal center is further solvated by a THF molecule and decorated with a residual chloride. Interestingly, the halide functionalities adopt a cis orientation with respect to the diamond-shaped Co_2N_2 plane.

Reduction of dimer **3** using Na/Hg afforded a dark-brown, pentane-soluble material that crystallized, surprisingly, from THF at -35 °C. This complex, **1**, was characterized in the solid state by X-ray crystallography (Figure 3), in solution by magnetic susceptibility measurements (Evans' method), and by elemental analysis.

The solid-state structure of **1** revealed the coplanar tetrametallic framework, with each Co(I) center bonded to two doubly bridging phosphoranimide ligands (Figure 3). The
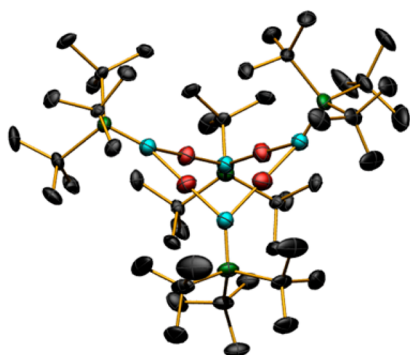

Figure 3. ORTEP diagram for **1**. See the SI for structural parameters.

diffraction data set, however, suggested partial substitution of the Co(I) centers by Na^+ cations in the selected crystal.[8] The structure, coupled with the results of magnetic susceptibility experiments, suggests an effective electron count of 12 for each metal center. The N−Co−N bond angles and Co−N bond distances, ranging from 176.0(3) to 179.3(3)° and 1.840(4) to 1.863(4) Å, respectively, are comparable to those of other two-coordinate and quasi-two-coordinate complexes of Co(II).[4a] The slight deviation from perfect linearity could be due to very weak bonding interactions between adjacent Co centers or, at least equally probable, crystal packing forces in the solid state. Linear two-coordinate complexes of Co(I), to the best of our knowledge, remain exceptionally rare, if not unprecedented.[5b] The average distance of 2.41 Å between adjacent Co(I) centers lies within the range of internuclear distances reported for complexes known to have Co−Co single bonds.[9] Solution magnetic susceptibility measurements revealed that the cluster is an 8-electron paramagnet ($\mu_{eff} = 8.98\mu_B$); each metal center has two unpaired electrons, consistent with a high-spin electron configuration for each d^8 Co atom. Under the assumption that the cluster remains intact in solution, the spin state suggests that the metals do not engage in significant Co−Co bonding, despite the short interatomic distances enforced by the "single-atom" nitrogen bridges.

Taken together, these structural features make clusters **1** and **2** possibly *the simplest conceivable manifestation of a ligand-supported "surface-mimetic" metallic array*. In this design, however, the metal support is a vaguely toroidal, nanometer-scale hydrocarbon shell encircling the metal−nitrogen array rather than a quasi-planar surface upon which the metal centers bind. Topologically, these clusters display two equivalent reactive "surfaces" to the external environment.

The analogous Ni(I) tetramer **2** was vastly easier to obtain as high-purity single crystals (Scheme 1). The complex, subsequently identified as $[Ni(NP^tBu_3)]_4$, was prepared using a similar salt metathesis/reduction procedure starting with the soluble Ni(II) precursor $NiBr_2$(dme). Subsequent reduction produced a dark-green, pentane-soluble product from which X-ray quality crystals could be obtained, again from THF at -35 °C in 80% yield.[10] The solid-state structure (Figure 4) reveals
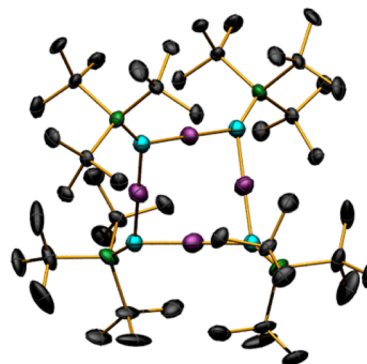

Figure 4. ORTEP diagram for **2**. See the SI for structural parameters.

that **2** is isostructural to cobalt complex **1** but has 13-electron Ni(I) centers. The measured N−Ni−N bond angles range from 178.31(18) to 179.6(3)° for the four metal centers.

A few structurally linear, homoleptic first-row transition metal complexes have been characterized.[5b] The range of Ni−N distances in cluster **2**, 1.864(4)−1.876(4) Å, is comparable to the Ni−N distances in the groundbreaking Ni(I) amido

complexes prepared by Hillhouse[5d] [1.865(2) Å for (NHC)-Ni(NR$_2$)]. The average Ni–Ni distance of 2.38 Å is within the range of several reported Ni–Ni single bonds,[9] but the possibility of significant Ni–Ni bonding is not supported by solution magnetic susceptibility measurements. The cluster is paramagnetic at temperatures as low as −80 °C, and the magnetic susceptibility at 27 °C gave an effective magnetic moment of 4.40μ_B, revealing that cluster **2** is a 3.50-electron paramagnet. The magnetic properties of both clusters suggest that this high-symmetry structural motif will serve as an excellent template for generating extremely low-coordinate high-spin clusters in which the intermetallic distances should allow for metal–metal communication and cooperative effects. Thorough investigations of the solution and solid-state electronic and magnetic properties will be reported in a full account.

The low-coordinate clusters are nucleated by strongly bridging phosphoranimide anions, and the tetrametallic assemblies are not easily disrupted. The robustness of the nickel cluster was challenged by treatment with strong neutral donor ligands. The intact Ni$_4$ cluster was recovered upon recrystallization from a THF solution of **2** treated with either phosphine or N-heterocyclic carbene (NHC) ligands. Anionic metathesis starting from the Ni(I)–NHC precursor [(IPr)Ni-(μ-Cl)]$_2$[5d] yielded **2** and unligated IPr.[11]

Low-coordinate dimeric Ni(I) complexes have been used to model the active sites of heterogeneous catalysts that mediate C–C and C–S bond cleavage reactions, which are fundamental transformations pertinent to petroleum hydrotreatment.[7a,12] The tetrameric clusters **1** and **2** constitute an electronically novel and topologically unique family of soluble surrogates that are particularly well-suited to modeling the cobalt and nickel sites present in commercial Co- or Ni-promoted MoS$_2$ and WS$_2$ hydrotreatment catalysts.[13]

From the perspective of reactivity and catalysis, clusters **1** and **2** arguably constitute the simplest possible homogeneous models for active metal surfaces, such as Raney nickel and other high-surface-area heterogeneous reagents and catalysts. More to the point, we also report that both **1** and **2** are active for a range of important catalytic transformations.

With an initial focus on reductive catalysis, our investigation of cluster reactivity began with simple hydrogenation reactions. To confirm that this minimalist design begets functional catalysis, the hydrogenation of alkenes and alkynes was briefly investigated. Both the cobalt and nickel nanocatalysts mediate hydrogenation under very mild conditions. Allylbenzene and diphenylacetylene, which are representative terminal alkene and internal alkyne substrates, respectively, were hydrogenated quantitatively at room temperature under 1 atm H$_2$ (Scheme 2).[14]

Scheme 2. Catalytic Hydrogenation Reactions
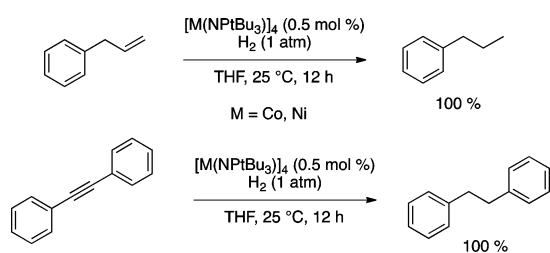
Exposure of the catalyst to hydrogen alone resulted in immediate darkening of the solution but no visible deposition of solid. The appearance of new IR stretches in the 2400–1600 cm^{-1} range was observed within 20 min after H$_2$ exposure. The IR bands are suggestive of terminal and bridging hydride ligands, pending more rigorous characterization of this material.[15] The solid recovered from this reaction did not crystallize under conditions that resulted in the crystallization of catalysts **1** and **2**, suggesting that the reaction with hydrogen is, unsurprisingly, irreversible. No precipitate or change in color was detected during the course of the hydrogenation reactions. The rates were unaffected by the presence of excess Hg^0, suggesting that the active catalyst is homogeneous.

Homogeneous hydrogenation using nickel complexes remains rare.[16] Most Ni-catalyzed hydrogenation catalysts are heterogeneous, including a range of Raney nickels[17] and Ziegler-type systems.[18] A handful of structurally characterized Ni(II) precatalysts, largely variants of bis(phosphine)nickel halides, do show hydrogenation activity upon prereduction, but the active catalysts remain uncharacterized and may be homogeneous or heterogeneous.[19] In contrast to nickel, cobalt is the most extensively developed first-row metal for applications to homogeneous hydrogenation.[20]

Homoleptic two-coordinate Ni(I) and Co(I) cluster complexes have thus been prepared and structurally characterized. The structures of these unique ancillary-ligand-free clusters situate each metal center in a highly unsaturated, rigorously linear coordination environment. The M$_4$N$_4$ core is coplanar rather than globular, creating a sterically open, self-supporting coordination array with potentially exploitable electronic and magnetic properties. Catalysis, however, remains our primary objective; to that end, a conceptually simple and potentially general new approach to the design of high-activity base-metal catalysts has been validated.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete experimental and crystal structure details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(8) The calculated yields of clusters **1** and **2** are based on the limiting reactant, LiNP^tBu_3. The crystal structure reported for **1** was derived from a crystal that returned a structure solution nearest to the tetracobalt stoichiometry, as determined by combustion analyses on numerous samples. Since the bulk product obtained from multigram-scale synthesis analyzed for the pure Co_4 cluster **1** by combustion, we proceeded with magnetic susceptibility and catalysis experiments.

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(11) Experimental procedures are provided in the SI. Mechanistic studies will be presented in a full account.

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