

Metal-Hydride Clusters

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Co₆H₈(PⁱPr₃)₆: A Cobalt Octahedron with Face-Capping Hydrides

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Abstract: A square-planar Co_4 amide cluster, $Co_4\{N(SiMe_3)_2\}_4$ (2), and an octahedral Co_6 hydride cluster, $Co_6H_8(P^iPr_3)_6$ (4), were obtained from metathesis-type amide to hydride exchange reactions of a Co^{II} amide complex with pinacolborane (HBpin) in the absence/presence of P^iPr_3 . The crystal structure of 4 revealed face-capping hydrides on each triangular [Co_3] face, while the formal $Co^{II}_2CoI_4$ oxidation state of 4 indicated a reduction of the cobalt centers during the assembly process. Cluster 4 catalyzes the hydrosilylation of 2-cyclohexen-1-one favoring the conjugate reduction. Generation of the catalytically reactive Co cluster species was indicated by a trapping experiment with a chiral chelating agent.

Reactive molecular transition metal clusters are attractive for synthetic chemists, as they may facilitate redox processes and potentially allow the use of multiple metals in a reaction, which can lead to an efficient activation of small molecules.^[1] For example, trinuclear hydride clusters of Ru and Ti with auxiliary cyclopentadienyl ligands use all three metal centers to activate C-H, C-C, Si-H, and N-N bonds,^[2] while arenesupported Ru hydride clusters have been applied as hydrogenation catalysts for aromatic compounds.^[3] In these cases, hydride ligands protect the metal centers until the approach of the substrates, and subsequently they are transferred to the substrates or released in the form of H₂. An analogous role for hydrides has been proposed in the context of the FeMocofactor, which is a naturally occurring metal-sulfur cluster that catalyzes the biological reduction of atmospheric N₂. Spectroscopic studies of the active state (E_4 state) of the

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FeMo-cofactor revealed the presence of Fe-bridging hydrides,^[4] and it was proposed that the subsequent uptake of N₂ should occur via concomitant liberation of H₂.^[5] Studies on the synthesis and reactivity of new classes of such hydride-supported transition metal clusters should thus expand their scope of stoichiometric and catalytic applications of hydride clusters.

Typically, transition metal hydride complexes are obtained from salt metathesis-type reactions of metal halides with hydride reagents, from the addition of H₂ or protons to low-valent metal complexes, or from the β-elimination or hydrogenolysis of metal alkyls.^[6] Here, we examined less common metathesis-type reactions of a Co^{II} amide complex, $[Co{N(SiMe_3)_2}_2]_2$ (1),^[7] with pinacolborane (HBpin) in the presence/absence of PⁱPr₃. Replacement of a bulky N(SiMe₃)₂ moiety with a small hydride ligand upon treatment with HBpin furnished low-coordinate cobalt-hydride species, which should assemble through hydride (or amide) bridges to provide cobalt clusters. In some cases, such assembly processes are anticipated to accompany the reductive elimination of H₂ from intermediates carrying multiple hydrides followed by a further assembly of cobalt; disproportionation of Co^{II} hydrides into Co^I/Co^{III} species may also occur. We have previously reported a similar reaction between Cp*FeN-(SiMe₃)₂ and HBpin, which resulted in the concomitant formation of an Fe-hydride species and (Me₃Si)₂N-Bpin.^[8] Other related approaches include the borylation of N_2 on a dinuclear Ta complex,^[9] the in situ generation of Ca- and Mn-hydrides from amide complexes and boranes,^[10a] the synthesis of s-block hydride clusters from the reactions of amide/alkyl-supported Mg/alkali-metal complexes with PhSiH₃,^[10b] and the synthesis of nanoparticles from metalamide complexes.^[11] Herein, we describe the synthesis and structural characterization of a new square-planar Co₄ amide cluster, $Co_4 [N(SiMe_3)_2]_4$ (2), and of an octahedral Co_6 hydride cluster, $Co_6H_8(P^iPr_3)_6$ (4). As far as catalytic applications are concerned, we found that **4** is able to mediate the conjugate hydrosilylation of 2-cyclohexen-1-one.

Treatment of **1** with HBpin (1 equiv with respect to Co) in hexane resulted in the formation of a black solution, from which the tetrameric Co^I amide **2** could be isolated in 9% yield (Scheme 1). The low isolated yield of **2** is partly due to the formation of the Co₇ amide/hydride cluster byproduct $Co_7H_6[N(SiMe_3)_2]_6$ (**3**), which was crystallographically identified but not isolated. Notably, a recent DFT evaluation showed that the formation of **2** from Co{N(SiMe_3)_2}₂ (the monomeric form of **1**) through putative homolysis of one of the Co–N bonds followed by the formation of HN(SiMe_3)_2 via hydrogen abstraction from ether should be highly endergonic (154 kJmol⁻¹),^[12] and the spontaneous decomposition of **1** into **2** should thus be severely hampered. Nevertheless,

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Scheme 1. Synthesis of clusters 2-4.

the substitution of one of the amide ligands in $Co{N(SiMe_3)_2}_2$ by a hydride may offer a facile route to reduce Co^{II} to Co^I, probably via the release of 0.5 equiv of H₂ per cobalt atom (Scheme 1). Similar to the synthesis of 2, the octahedral Co_6 cluster 4 was obtained in the form of greenish black crystals in 42% yield from 1, $P'Pr_3$ (1 equiv with respect to Co), and HBpin (2 equiv with respect to Co). The clusters 2 and 4 are paramagnetic, and exhibited broad ¹H NMR signals in C_6D_6 at $\delta = -21.8$ and 20.8 ppm (SiMe₃ in 2), as well as at $\delta = -0.9$ and 149.9 ppm (Pr in 4) (Figures S1 and S2 in the Supporting Information). However, the appearance of two $SiMe_3$ signals for **2** is inconsistent with the solid-state structure (see below) wherein all cobalt and nitrogen atoms adopt a coplanar arrangement, indicating a slightly different solution structure. Variable-temperature ¹H NMR measurements of **2** in [D₈]toluene did not show any coalescense of the two SiMe₃ signals but led to decomposition at around 100 °C (Figure S3). Although an NMR assignment of the hydrides in 4 was unsuccessful, the chemical formulas of clusters 2 and 4 are supported by their electro-spray ionization mass (ESI-MS) spectra, wherein signals were observed at m/z = 876.0 ([2]⁺) and 1322.5 ($[4]^+$) (Figure 1). The cationic species $[2]^+$ and $[4]^+$ were probably generated in the spectrometer upon exposure to the applied potential. The tentative facile electronic oxidation of 4 is supported by its cyclic voltammogram in THF, which revealed, besides the rest potential, a redox couple for quasi-reversible 1e oxidation at $E_{1/2} = -1.53$ V (vs. Fc/Fc^+ ; Figure S8), while the cyclic voltammogram of 2 indicated a quasi-reversible reduction process at $E_{1/2}$ = -2.29 V (Figure S7). In addition to these quasi-reversible processes, other irreversible oxidation and reduction processes were found for both 2 and 4.



Figure 1. ESI-MS spectra for 2 (left) and 4 (right) in THF.

Some transition metal hydride clusters undergo H/D exchange between hydride ligands and deuterated solvents via reversible C-H(D) bond cleavage.^[2a] An analogous C-H(D) bond cleavage of the solvent (and $P^{i}Pr_{3}$) was suggested during the synthesis of 4. The m/z values of deuterated 4 observed in the ESI-MS increased in the order of samples obtained a) in the presence of DBpin in toluene, b) in the presence of HBpin in C₆D₆, and c) in the presence of DBpin in C₆D₆ (Figure S6). These results indicate that the incorporated deuterium stems from both DBpin and C₆D₆. The highest m/z value observed for sample (c) was even larger than that calculated for $Co_6D_8(P'Pr_3)_3$, suggesting additional incorporation of deuterium into P'Pr₃. Conversely, the isolated cluster 4 exhibited no evidence for H/D exchange in C_6D_6 at room temperature, indicating that the H/D exchange should occur in an intermediary cobalt hydride species.

The molecular structures of clusters 2-4 were determined by single-crystal X-ray diffraction analysis (Figure 2), even though the quality of crystals of 2 was low (R1/wR2 = 0.11/wR2 =0.38). The solid-state structures revealed that each edge of the $[Co_4]$ square in 2 is bridged by $N(SiMe_3)_2$ ligands, similar to the corresponding nickel and copper congeners M4{N- $(SiMe_3)_2$ (M = Ni, Cu).^[12,13] These congeners share the same space group (P2/n) and exhibit comparable crystal parameters. The Co-Co distances in 2 (2.566(2)-2.591(3) Å)are longer than the corresponding distances in the Ni congener (2.4328(4), 2.4347(5) Å), but shorter than those in the Cu congener (2.6770(7), 2.6937(7) Å). The Co-N(bridge) distances in 2 (1.938(7)-1.973(6) Å) are longer than those in the Ni (1.9127(2)–1.9189(2) Å) and Cu (1.917(3)–1.925(4) Å) complexes. These Co-N(bridge) distances are shorter than the corresponding distance in Co^{II} complex 1 (2.062(4) Å), even though the ionic radius of Co^I should be larger than that of Co^{II}.

The planar Co₇ cluster **3** reveals a hexagonal arrangement of six Co atoms around a central Co atom. Each Co₃ triangle around the central Co atom is capped by a μ_3 -hydride ligand, which faces in alternate directions across the Co₃ triangles. Although refinement of hydrides by X-ray crystallography is not always reliable, these hydrides should coordinate efficiently to the central cobalt atom, and the Co–(μ_3 -H) distances (1.69(3)–1.75(3) Å) fall into the previously reported range for cobalt clusters with triply-bridging hydrides (1.56-(4)–1.82(2) Å).^[14] Moreover, a planar Rh₇ hydride cluster [Rh₇(μ_3 -H)₆]²⁺, containing an analogous [Rh₇(μ_3 -H)₆]

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2

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Figure 2. Molecular structures of **2**–4 with atomic displacement parameters set at the 50% probability. Only selected atoms are labeled, and hydrogen atoms, except for the hydride ligands, are omitted for clarity. Selected bond distances (Å) and angles (°) for **2**: Co–Co 2.566(2)–2.591(3), Co–N 1.938(7)–1.973(6); Co-N-Co 81.7(3)–83.5(4); **3**: Co–Co 2.5231(2)–2.5288(3), Co–N 2.0476(17)–2.0703(18), Co–H 1.69(3)–1.75(3); Co-N-Co 75.72(6)–75.60(6); **4**: Co–Co 2.4667(6)–2.4684(5), Co–P 2.3173(5), Co–H 1.810(17)–1.86(3).

core,^[15] and a planar Co₇ cluster supported by pyridinylmethoxide^[16] have previously been reported. Based on the molecular structure, the oxidation state of the cobalt atoms should be assigned either as $\text{Co}^{II}_5\text{Co}^{I}_2$ or as $\text{Co}^{II}_6\text{Co}^0$. Considering the observed narrow range of Co–Co distances (2.5231(2)–2.5288(3) Å), we tentatively assigned an averaged oxidation state, Co(+1.71).

In cluster 4, the $[Co_6]$ core adopts an octahedral geometry with face-capping μ_3 -hydrides. The presence of eight hydrides is in agreement with the observed ESI-MS signals, while the Co–(μ_3 -H) distances in **4** (1.810(17)–1.86(3) Å) are slightly longer than the corresponding distances in previously reported Co clusters.^[14] Even though the formal oxidation state of **4** is Co^{II}₂Co^I₄, the six cobalt atoms are crystallographically equivalent and the Co-Co distances (2.4667(6)-2.4684(5) Å) are also almost identical, which suggests an averaged oxidation state of Co(+1.33) for each cobalt atom. The Co-P distances in 4 (2.3173(5) Å) are longer than those reported for phosphine-supported hydride complexes of Co^{II} and $\text{Co}^{\text{I}} (\leq 2.291(3) \text{ Å}),^{[17]}$ indicating steric repulsion between the $P'Pr_3$ ligands. Interestingly, 4 exhibits a structural analogy to Stryker's reagent, Cu₆H₆(PPh₃)₆, which mediates chemoselective conjugate reductions of α , β -unsaturated carbonyl compounds. ${}^{[1\tilde{8},\,1\tilde{9}]}$ The crystallographically analyzed analogues $Cu_6H_6(PR_3)_6$ (R = for example, NMe₂, p-tolyl, p-anisyl) contain face-capping hydrides on six of the eight [Cu₃] faces.^[20] In contrast to the virtually identical Co-Co distances determined for 4, the $Cu_6H_6(PR_3)_6$ copper clusters exhibited short (av. 2.47–2.52 Å; Cu₃(µ₃-H) faces) and long (av. 2.68–2.80 Å; Cu₃ without hydride faces) Cu-Cu distances. The Co-P distances in 4 are longer than the Cu–P distances in $Cu_6H_6(PR_3)_6$ (2.196(1)-2.315(2) Å).

In solution at 298 K, the magnetic moments of **2** (10.0-(5) μ B) and **4** (14.5(7) μ B) are close to the spin-only S = 4.5 (9.9 μ B) and S = 7 (15.0 μ B) states. In order to assess their magnetism and the Co–Co interactions, theoretical analyses of these clusters were carried out by density functional theory (DFT), using the solution magnetism for selecting their spin states (see the Supporting Information). For the calculation of

2, we chose the S = 4 state, as it possesses an even number of d-electrons, while the S=7 state was applied for the calculation of 4. The fully optimized structures of 2 and 4 are in good agreement with their X-ray structures (Figures S15 and S16). The unpaired electrons in 2 are mainly localized on Co, affording a spin density of 7.8 µB for all Co atoms. In contrast, 4 reveals a significant spin delocalization over the P atoms and the hydrides, resulting in a calculated spin density of 11.8 µB for all Co atoms. To get some insights for the metal-metal bonding, natural bond orbital (NBO) analysis was performed for 2 and 4. The Co-Co NBOs between the neighboring Co atoms were found for both Co₄ and Co₆ systems (see the Supporting Information), while assignment of the exact bond order numbers was difficult with complex data from open-shell systems. Also importantly, no diagonal Co-Co bond was found in the analysis.

The aforementioned analogy between cluster 4 and Stryker's reagent prompted us to examine the potential of 4 for the catalytic hydrosilylation of 2-cyclohexen-1-one (Table 1). Addition of 150 equiv of 2-cyclohexen-1-one and PhSiH₃ to a benzene solution of 4 resulted mainly in the conjugate reduction. The subsequent workup afforded cyclo-

+ PhSiH ₃ + (1.0 mmol)		Co catalyst benzene	+	OH +	OH
		then TBAF, H ⁺	a	0	C
Entry	Catalyst	sub:Si:cat ^[b]	Product yields [%] ^[c]		

Table 1	Reduction of 2	cvclohexen-1-one	catalyzed by	cobalt clusters ^[a]
TUDIC I.	Reduction of Z		catalyzeu Dy	Coball Clusters.

Entry	Catalyst	sub:Si:cat ^[b]	Product yields [%] ^[c]		
			а	Ь	С
1	4	150:150:1	83	4	11
2	1	50:50:1	9	38	8
3	2	100:100:1	12	78	8

[a] TBAF = tetrabutylammonium fluoride. [a] sub = cyclohexenone, Si = PhSiH₃, cat = catalyst. The substrate/Co-atom ratio was 25:1 in all entries. [b] Yields were estimated by GC analyses.

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hexanone (**a**) in 83 % yield, 2-cyclohexen-1-ol (**b**) in 4% yield, and cylcohexanol (**c**) in 11% yield (entry 1); the chemoselectivity was found to vary with the silanes (Table S1). A similar silane-dependent selectivity was observed for the conjugate reduction of 1-phenyl-1-buten-3-one mediated by Cu^{I} fluoride.^[21] The chemoselectivity decreased in THF (Table S3), which may be due to the slow and partial degradation of **4** through the coordination of THF. The corresponding hydrosilylation catalyzed by Co^{I} amide cluster **2** using the same total amount of cobalt favored the 1,2-reduction, affording **a**, **b**, and **c** in 12%, 78%, and 8% yields, respectively (entry 3).

In the presence of additives such as chiral diphosphines, fragmentation of Stryker's reagent into catalytically active monomeric copper-hydride species has been proposed,^[22] and the reaction of Cu₆H₆(PPh₃)₆ with PPh₃ and Ph₃SiH was reported to furnish the monomeric complex (Ph₃P)₃Cu(SiPh₃) in 82% yield.^[23] In light of the suggested fragmentation of $Cu_6H_6(PPh_3)_{62}$, we tried to gain further insight into the possibility of generating monomeric cobalt species from 4. As the detection of cobalt species in the catalytic reaction mixture by ESI-MS was unsuccessful, we attempted a trapping experiment with a chelating agent. Nishiyama et al. reported that a catalytic amount (5 mol%) of cobalt complex bearing a chiral *N*,*N*,*N*-bis(oxazolinylphenyl)amine ligand (Bopa) mediates the enantioselective hydrosilylation of 4-ⁿBuC₆H₄COMe with (EtO)₂MeSiH at 40°C (48 h) in THF to afford the reduced product in 99% yield and 98% ee.^[24] We used this reaction as a reference, and observed that 4 catalyzed the same hydrosilylation in the presence of 6 equiv Bopa (1 equiv with respect to Co), when using the same total amount of cobalt as in the reference reaction (Scheme 2). In the presence of Bopa, the reduction product was obtained in 98% yield and 28% ee, while the racemic product was obtained in the absence of Bopa (84% yield). Although the Bopa ligand improved the product yield by 14% and induced some enantioselectivity, the low ee (28%) suggests a limited contribution of monomeric cobalt species to the catalysis. Possible partial degradation of 4 in THF may also contribute to the generation of a part of Bopa-supported Co species. Thus, the results shown in Scheme 2 indicate that Co cluster(s) are the predominant catalytically active



Scheme 2. Attempted trapping of catalytically active monomeric Co species.

component(s). However, at this stage, the results remain preliminary and require further investigations.

In summary, we synthesized the reactive cobalt clusters $Co_4[N(SiMe_3)_2]_4$ (2) and $Co_6H_8(P'Pr_3)_6$ (4) through metathesis reactions of $[Co\{N(SiMe_3)_2\}_2]_2$ (1) with HBpin in the presence or absence, respectively, of P'Pr_3. We demonstrated that the obtained octahedral Co_6 -hydride cluster is able to catalyze the hydrosilylation of 2-cyclohexen-1-one, and that the Co cluster(s) most likely represent the predominant catalytic component(s).

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Communications

Metal–Hydride Clusters

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 $Co_6H_8(P^iPr_3)_6\colon A$ Cobalt Octahedron with Face-Capping Hydrides



Reactive cobalt clusters: The octahedral Co_6 -hydride cluster $Co_6H_8(P^iPr_3)_6$ and the square-planar Co_4 cluster $Co_4\{N-(SiMe_3)_2\}_4$ were synthesized from the reactions of a Co^{11} amide complex with pinacolborane in the presence and absence of P^iPr_3 , respectively. The Co_6 -hydride cluster catalyzes the conjugate hydrosilylation of 2-cyclohexen-1-one.

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