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Stable Dihydrogen Complexes of Cobalt(−I) Suggest an Inverse *trans*-Influence of Lewis Acidic Group 13 Metalloligands

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Supporting Information

ABSTRACT: A triad of d^{10} cobalt dihydrogen complexes was synthesized by utilizing Lewis acidic group 13 metalloligands, $M[N((o\text{-}C_6H_4)NCH_2P^iPr_2)_3]$, where M = Al, Ga, and In. These complexes have formal Co(−I) oxidation states, representing the only coordination complexes in which dihydrogen is bound to a subvalent transition metal center. Single-crystal X-ray diffraction and NMR studies support the assignment of these complexes as nonclassical dihydrogen adducts of Co(−I).

Nonclassical dihydrogen adducts of transition metals, $M(\eta^2\text{-}H_2)$, are ubiquitous intermediates in the transfer of H_2 to a variety of substrates.[1] Isolable $M(\eta^2\text{-}H_2)$ species are most commonly observed with d^6 4*d* and 5*d* metal centers, which form stronger M−L bonds and are better at π-backbonding than 3*d* metals.[2] Hence, well characterized H_2 adducts of first-row transition metals remain rare.[2a,3] The study of such interactions represents a fundamental step towards improving the catalytic activity of base metals in H_2 transfer reactions.[4]

Examples of nonclassical dihydrogen adducts of cobalt are limited (Figure 1a). Following the detection of transient $Co(\eta^2\text{-}H_2)$ species in inert-gas matrices,[5] the characterization of $[(\text{tetraphos})Co(H)_2]^+$ and $[Cp^*Co(\eta^2\text{-}H_2)H(PR_3)]^+$ was complicated by facile H_2 activation and H_2/hydride exchange, respectively.[6] A bonafide $Co(\eta^2\text{-}H_2)$ phosphinite pincer system was investigated by low-temperature NMR methods.[7] The tris(phosphino) silyl or borane ligand platforms allowed for the isolation of thermally stable $Co(\eta^2\text{-}H_2)$ complexes and elucidation of their solid-state structures.[8] More recently, a $Co(\eta^2\text{-}H_2)$ bis(carbene) pincer complex was shown to catalyze olefin hydrogenation and *E*-selective alkyne semihydrogenation.[9]

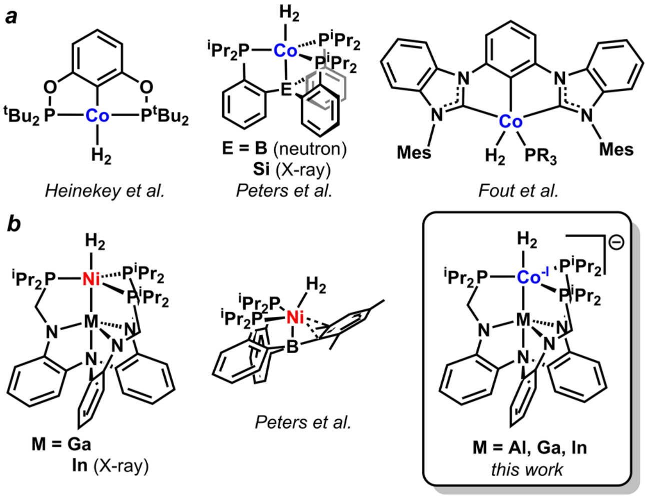

Figure 1. (a) Selected cobalt H_2 complexes[7−9] and (b) rare H_2 adducts of d^{10} transition metals.[3,12a] Three structures were elucidated by single-crystal X-ray or neutron diffraction studies, as indicated.

Currently well-defined H_2 adducts of d^{10} centers[10] are isolated to three Ni(0) complexes that feature a Z-type[11] group 13 metalloligand (Figure 1b). The $Ni^0(\eta^2\text{-}H_2)$ bis(phosphino)-borane complex was observed as a transient intermediate prior to H_2 addition across the Ni → B bond.[3c,d] Using Z-type ligands of heavier group 13 congeners, two additional $Ni^0(\eta^2\text{-}H_2)$ adducts were characterized, including an X-ray structure of $Ni^0(\eta^2\text{-}H_2)InL$, where L is $[N((o\text{-}C_6H_4)NCH_2P^iPr_2)_3]^{3-}$.[12] The rarity of d^{10} $M(\eta^2\text{-}H_2)$ complexes can be understood by considering a simple bonding rationale: d^{10} metals lack an empty d-orbital that is needed to accept electron density from the H_2 σ-bond.[13] Inspired by the Ni precedents, we targeted the isoelectronic d^{10} $Co^{-I}(\eta^2\text{-}H_2)$ species using the group 13 metalloligands, ML, where M = Al, Ga, and In.[14] The triad of $Co^{-I}(\eta^2\text{-}H_2)$ complexes was investigated by NMR methods, single-crystal X-ray diffraction, and density functional theory (DFT). The data are consistent with the formulation of these species as H_2 adducts of subvalent cobalt(−I). Moreover, the choice of the group 13 ion fine-tunes H_2 activation at Co. We further propose an inverse *trans*-influence exerted by the group 13 supporting ions to explain the stability of the $Co^{-I}(\eta^2\text{-}H_2)$ complexes.

The triad of cobaltate complexes, $[Co(\eta^2\text{-}H_2)ML]^-$ (M = Al (**1**), Ga (**2**), and In(**3**)), was synthesized by adding 3.1 equiv of Li or $K[HBEt_3]$ to a cooled mixture of the corresponding group 13 metalloligand, ML, and $CoBr_2$ in THF under argon (Scheme 1). Effervescence, presumably due to H_2 release, was observed, and the diamagnetic products **1**−**3** were cleanly generated (*vide infra*). The diamagnetism of **1**−**3** are consistent with a d^{10} count of the subvalent Co(−I) oxidation state, and **1**−**3** add to a growing number of well-defined Co(−I) coordination complexes.[15] Complexes **1**−**3** are exceedingly air sensitive, as is typically observed for Co(−I) compounds supported by phosphine donors.[15c]

Complexes **1**−**3** each exhibit a single ^{31}P resonance that indicates trigonal symmetry in solution. The ^{31}P NMR shifts of

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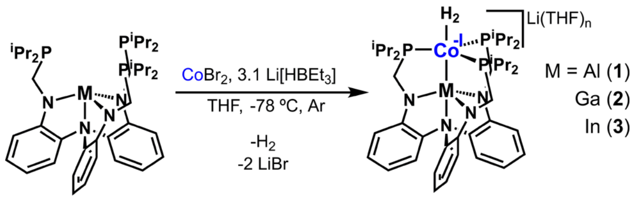
Scheme 1. Synthesis of Anionic Co(η^2-H_2)ML Complexes 1−3



73.2, 84.5, and 91.9 ppm for **1−3**, respectively, move downfield as the supporting ion is varied down group 13. A similar trend was reported for the NiML series, where increasing Lewis acidity moving down group 13 for the Ni(0) Lewis base was proposed to account for the depleting electron density at the Ni center and decreasing Ni → P π-backbonding.[12]

Notably, the ^1H NMR spectra of **1−3** each contain a broad resonance with an integration of 2H in the upfield region at −7.0, −7.7, and −7.7 ppm, respectively, which could correspond to either an intact H_2 ligand or two discrete hydrides. To discern between these bonding extremes, we conducted $T_{1\,\mathrm{min}}$ and J_{HD} measurements on **1−3**. Complexes **1−3** exhibit $T_{1\,\mathrm{min}}$ relaxation times of 26, 27, and 29 ms, respectively (d_8-THF, 400 MHz, Figure S5). Furthermore, the addition of HD (or 1:1 H_2/D_2) leads to the observation of both the H_2 and HD isotopologues by ^1H NMR spectroscopy due to fast scrambling at ambient temperature. The presence of the HD isotopologues is evidenced by a 1:1:1 triplet in the upfield region with corresponding J_{HD} values of 28.5(3), 27.6(16), and 26.3(8) Hz for **1−3**, respectively (Figures S1−S3). Both the short $T_{1\,\mathrm{min}}$ and large J_{HD} values for **1−3** compare well to the reported values for other Co(η^2-H_2) complexes and are closest to the Co(η^2-H_2) phosphinite pincer complex (Figure S6).[7,8]

Using previously established correlations, the J_{HD} values of **1−3** correspond to d_{HH} distances of 0.96(1), 0.98(3), and 1.00(1) Å, respectively.[2a,16] In addition, there is excellent agreement between d_{HH} distances obtained from J_{HD} and those from corrected $T_{1\,\mathrm{min}}$ values, or $T_{1\,\mathrm{min\_calc}}$ (Table 1), which considers relaxation effects from dipolar interactions with the Co nucleus and the ligand protons, in the regime of fast H_2 rotation (Supporting Information (SI) Tables S3−S4).[17] The calculated d_{HH} distances lie on the periphery of values for Kubas-type complexes (0.77−1.0 Å) and stretched dihydrogen complexes (1.0−1.2 Å).[2a,18] The H_2 ligand in complexes **1−3** is substantially more activated than the isoelectronic Ni(η^2-H_2)GaL and Ni(η^2-H_2)InL counterparts (0.87 and 0.91 Å, respectively), which do not scramble H_2/D_2. Additionally, the H_2 ligand in **1−3** is not labile under vacuum. Though Ni(η^2-H_2)InL shows similar stability, Ni(η^2-H_2)GaL is formed only under an H_2 atmosphere. These collective observations are consistent with the greater π-basicity of Co relative to Ni,[19] and/or the negative charge of the Co fragment relative to the neutral Ni analogues.

Table 1. Geometrical Parameters, Including Bond Lengths (Å) and Angles (deg), and NMR Data for 1−3

parameter	1[a]	2[a]	3
Co−M	2.471(2)	2.383(5)	2.465(1)
r[b]	1.00	0.96	0.92
Co−P	2.144(2)	2.158(9)	2.201(9)
M−N_{ax}	2.331(4)	2.454(2)	2.472(2)
M−N_{eq}	1.908(4)	1.965(2)	2.131(2)
∑P−Co−P	356.03(6)	354.43(3)	354.30(4)
∑N_{eq}−M−N_{eq}	344.84(2)	337.03(1)	337.23(9)
M−N_3 plane	0.436	0.555	0.599
Co−P_3 plane	0.249	0.294	0.306
J_{HD} (Hz)	28.5(3)	27.6(16)	26.3(8)
$T_{1\,\mathrm{min}}$ (ms)[c]	26	27	29
$T_{1\,\mathrm{min\_calc}}$ (ms)[d]	44	45	52
d_{HH} (Å)	0.96(1)[e] 0.97(1)[f]	0.98(3)[e] 0.98(1)[f]	1.00(1)[e] 1.00(1)[f]

[a] Values are the averages of 2 independent molecules. [b] Ratio of the Co−M bond length to the sum of Co and M covalent radii.[20c] See Table S2. [c] Measured at 400 MHz. [d] Corrected for 500 MHz and dipolar interactions.[17a] See SI for details. [e] Based on J_{HD}. [f] Based on $T_{1\,\mathrm{min\_calc}}$ with fast H_2 rotation.[17b,c]

Single yellow crystals of **1−3** were obtained by recrystallization from DME/hexane (**1**) or THF/pentane solutions (**2** and **3**). The molecular structures of the Li(solvent)$_n$ salts of **1−3** are shown in Figure 2, and relevant geometrical parameters are provided in Table 1. All three structures are close to ideal trigonal symmetry (SI, Table S2). The average Co−P bond lengths elongate modestly moving down group 13, from 2.14 to 2.20 Å for **1−3**, respectively. Notably, the Co−P bond lengths in **1** (avg. 2.144(2) Å) compare well to those for the cobaltate end-on N_2 species, [Li(crypt-222)][Co(N_2)AlL] (avg. 2.177(1) Å), which also contains a subvalent Co(−I) center bonded to AlL.[14b] By contrast, the neutral Co(N_2)AlL complex with a formal Co(0) center has a substantially longer Co−P bond length of 2.2408(8) Å.[14a] Additionally, the Co−Al bond distances in **1** and [Co(N_2)AlL]$^-$ are similar at 2.471(2) and 2.507(2) Å, respectively. Lastly, to compare Co−M interactions in **1−3**, a particularly useful parameter is the covalent ratio (r) of the Co−M bond distance to the sum of the metals' tabulated covalent radii.[20] The r values of **1−3** decrease significantly from 1.00 to 0.92, suggesting a strengthening Co → M interaction for M = Al < Ga < In. A similar trend was observed in the NiML series.[12]

Because X-ray crystallography cannot accurately resolve positions of hydrogen atoms, the H_2 ligand was not modeled. However, the presence of the H_2 ligand is suggested by the difference Fourier maps shown in Figure 2. The difference maps for **1−3** show a relatively concentrated volume of excess electron density in the apical binding site of Co on the axis defined by the Co−M interaction. Moreover, the nearly ideal trigonal structure of **1−3** is inconsistent with a H−Co(μ-H)M structure.[3b]

To further probe the nature of the Co−H_2 bonding, density functional theory (DFT) calculations were performed (M06−L,[21] full ligand; see SI for details). Three structural isomers were investigated: the dihydrogen adduct [Co(η^2-H_2)ML]$^-$, the terminal dihydride [Co(H)$_2$ML]$^-$, and the bridging/terminal dihydride [H−Co(μ-H)ML]$^-$. Of note, all three isomers were optimized for M = Al and Ga. For M = In, attempts to optimize the [H−Co(μ-H)InL]$^-$ isomer converged to the corresponding terminal dihydride. Across the Co−M series, the dihydrogen adduct (d_{HH} ≈ 0.87 to 0.88 Å) was energetically lower than both the terminal dihydride (Δ = 0.4 to 1.0 kcal/mol, d_{HH} ≈ 1.8 Å), and the bridging/terminal dihydride isomers (Δ = 3.5 to 4.6 kcal/mol, d_{HH} > 2.6 Å). We note that the small energy difference between the H_2 adduct and terminal dihydride species is within the error of the calculation. The small energy difference may suggest facile H_2

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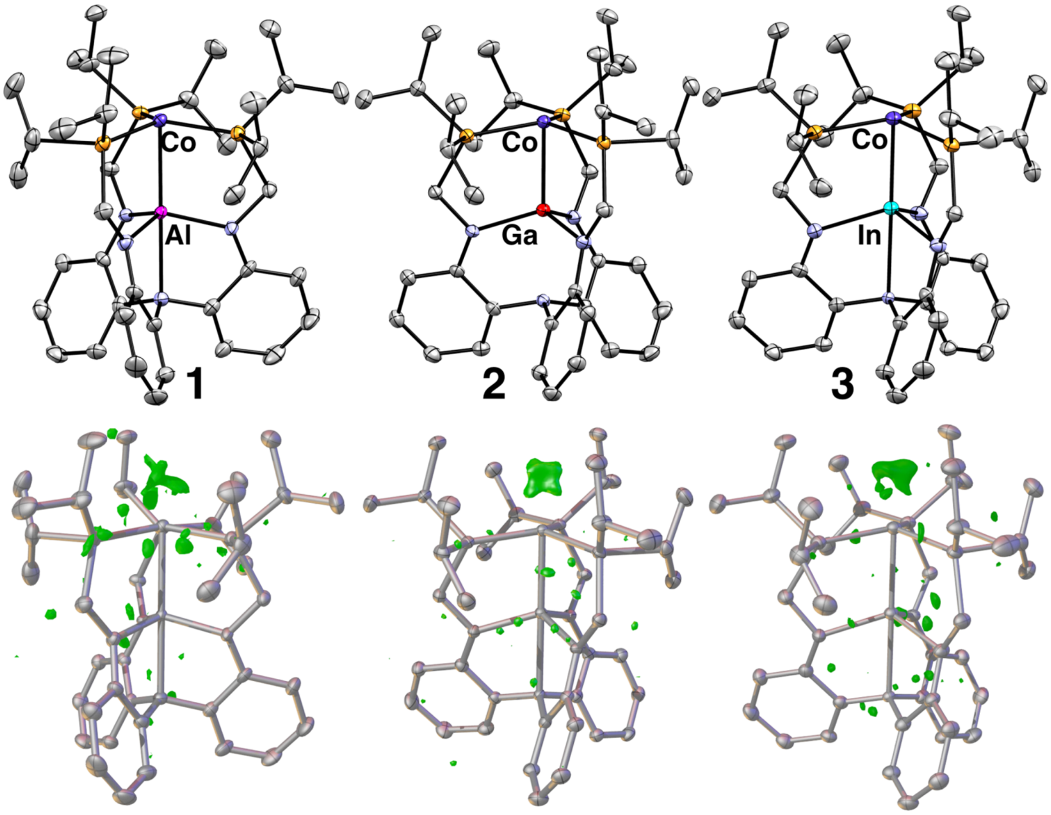

Figure 2. (Top) Molecular structures of the anionic fragment of $[Li(DME)_3]$**1**, $[Li(THF)_4]$**2**, and $[Li(THF)_4]$**3**, shown with thermal ellipsoids at 50% probability. The cationic fragment, residual solvents, and hydrogen atoms were omitted for clarity. Co, dark blue; P, orange; N, light blue; C, gray; Al, pink; Ga, red; In, aquamarine. (Bottom) Residual electron density (shown in green) from the difference Fourier map, rendered at 0.1 Å resolution and at 0.2, 0.6, and 0.6 e/Å^3 for **1**−**3**, respectively.

cleavage at Co(−I), which is consistent with the fast H/D scrambling observed for **1**−**3**.

Complexes **1**−**3** are rare examples of d^{10} dihydrogen adducts. Previously, the only well-defined examples were the Ni^0(η^2-H_2)M species. In common, all the d^{10}-H_2 adducts feature a d^{10} center that is directly appended to a Lewis acidic group 13 (B, Al, Ga, or In) metalloligand. We propose that their stability is due to an inverse *trans*-influence of the group 13 metalloligand, which is a σ-acceptor. To our knowledge, the inverse *trans*-influence has been invoked primarily for actinide[22] (e.g., uranium) and lanthanide[23] complexes.[24] Moreover, the d^{10}-H_2 complexes are distinct from typical Kubas dihydrogen complexes, where the H_2 ligand is *trans* to a strong σ-donor such as CO.[2a] This bonding has been rationalized using an antisymbiotic effect, where the strong metal−CO bond is favorably poised opposite to the weak metal−H_2 interaction.[25] In **1**−**3**, the H_2 ligand is *trans* to a strong σ-acceptor, allowing for symbiotic (H_2) → Co and Co → M bonding interactions that reinforce each other. The relationship between H_2 binding strength and the σ-acceptor strength is well demonstrated by the isoelectronic Ni^{0}ML series. Under 1 atm of H_2, NiAlL does not bind H_2 appreciably, whereas Ni(η^2-H_2)GaL binds H_2 reversibly. On the other hand, Ni(η^2-H_2)InL is stable to vacuum and isolable in the solid state.

In summary, the Lewis acidic group 13 metalloligands lead to exceptionally reduced cobaltate species **1**−**3** that bind H_2 with moderate activation. These complexes are unique examples of isolable H_2 complexes in which the metal center is formally subvalent. Additionally, these complexes are rare examples of d^{10} H_2 adducts, which had been previously limited to three Ni^0 complexes. Lastly, and more significantly, we showcase that electronic tuning via a metal−group 13 inverse dative bond can effectively induce H_2 binding and modulate its activation. Efforts are currently underway to examine if these unique complexes are capable of H_2 transfer reactivity, and what ramifications bimetallic cooperativity may have in such processes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b02870.

X-ray crystallographic data for **1**−**3** (CIF)

Experimental procedures, characterization data, computational methods, and calculated structures (PDF)

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Notes

The authors declare no competing financial interest.

X-ray crystallographic data have also been deposited in the CCDC database (1538725 to 1538727).

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