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A Structurally Characterized Cobalt(I) σ -Alkane Complex

Timothy M. Boyd,^[a,b] Bengt E. Tegner,^[c] Graham J. Tizzard,^[d] Antonio Martínez-Martínez,^[a] Samuel E. Neale,^[b] Michael A. Hayward,^[a] Simon J. Coles,^[d] Stuart A. Macgregor,^{*[b]} Andrew S. Weller.^{*[a,b]}

Abstract: The synthesis, and x-ray structure, of a cobalt σ -alkane complex, $[\text{Co}(\text{Cy}_2\text{P}(\text{CH}_2)_4\text{PCy}_2)(\text{norbornane})][\text{BAR}^{\text{F}}_4]$, is achieved by a single-crystal to single-crystal solid/gas hydrogenation from a norbornadiene precursor. Magnetic data show this complex to be a triplet. Periodic DFT and electronic structure analyses identify weak C–H \rightarrow Co σ -interactions, augmented by dispersive stabilization between the alkane ligand and the anion-microenvironment. The calculations are most consistent with a $\eta^1:\eta^1$ -alkane binding mode.

σ -Alkane complexes, where a C–H group interacts with a metal, in a 3-center 2-electron bond (3c–2e), are key intermediates in stoichiometric and catalytic hydrocarbon C–H activation processes.^[1,2] The directional, non-nucleophilic and strong C–H bond means that alkanes are poor ligands (40–60 kJ mol⁻¹), making σ -alkane complexes challenging to observe, due to displacement by solvent or other ligands.^[3] Elegant methods have thus been developed to generate and characterize σ -alkane complexes in the solution-phase (Fig. 1A). Low temperature NMR spectroscopy, using in situ photolysis or protonolysis, reveals σ -alkane complexes such as **1**^[4] and **2**,^[5] respectively, while fast time-resolved spectroscopic studies (TRIR)^[6] probe the formation and onward reactivity of transient σ -alkane complexes (e.g. **3**).^[7,8]

We have recently developed molecular solid-state routes to σ -alkane complexes that circumvent the need for solvent. By using single-crystal to single-crystal (SC-SC) gas/solid reactivity^[9,10] synthetically significant amounts (up to ~1 g) of σ -alkane complexes such as $[\text{Rh}(\text{L}1)\text{-NBA}][\text{BAR}^{\text{F}}_4]$ (Fig. 1B, NBA = norbornane, Ar^F = 3,5-(CF₃)₂C₆H₃, L1 = Cy₂PCH₂CH₂PCy₂) can be formed by simple hydrogenation of a cationic diene precursor (norbornadiene, NBD). These complexes can show remarkable stabilities (months, 25 °C),^[11] allowing for their full characterization (single-crystal x-ray diffraction, solid-state NMR) and studies into alkane mobility and reactivity.^[10,12,13] Their isolation comes, in large part, from the stabilizing $[\text{BAR}^{\text{F}}_4]$ -anion microenvironment which often forms an $\sim\text{O}_h$ cage surrounding the metal cation. We have termed this methodology Solid-state Molecular Organometallic (SMOM) chemistry.^[12]

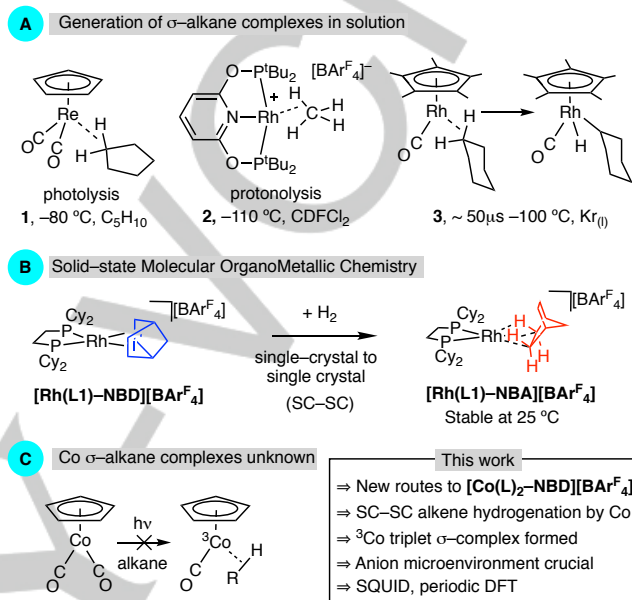


Figure 1. (A) Examples of σ -alkane complexes, generated using in situ photolysis (**1**) or protonation (**2**), and as intermediates in C–H activation (**3**). (B) Single-crystal to single-crystal generation of a Rh σ -alkane complex by hydrogenation of a diene. (C) Instability of Co σ -alkane complexes.

Despite these advances in both solution and solid-state chemistries there remain significant challenges. One of these is that while the heavier congeners of group 9 (Rh and Ir) have offered a rich hunting ground for the generation of σ -alkane complexes and subsequent catalytic C–H activation,^[2,3,7,14] no cobalt examples are known. Indeed the only σ -alkane complex of cobalt so far reported in the literature is $\text{Co}(\text{CH}_4)$, generated using isolated Co atoms in an Ar matrix at -261 °C.^[15] While the 3d-metal cobalt is expected to form weak 3c–2e bonds with alkanes, an additional problem is the accessibility of the triplet ³Co-spin state, that further discourages the formation of strong bonds. For example, while the photogenerated $\{^1\text{Rh}(\text{CO})\text{Cp}^*\}$ singlet fragment forms a transient σ -alkane complex (**3**),^[7] no such complexes are observed for equivalent $\{\text{Co}(\text{CO})\text{Cp}\}$ (Fig. 1C).^[16] Calculations show that a ³Co(CO)Cp \cdots HCH₃ interaction would be repulsive, and while ¹Co(CO)Cp \cdots HCH₃ is accessible, its formation is endergonic with respect to the reactants.^[17] In contrast, ³Mn(CO)₂Cp(heptane) has been implicated as a transient intermediate on the pathway to C–H activation based on TRIR, DFT calculations and kinetic modeling.^[18] σ -H₂ complexes of cobalt are known.^[19]

We now report that, by harnessing the stabilizing microenvironment of the $[\text{BAR}^{\text{F}}_4]$ anions with a cationic $[\text{Co}(\text{diphosphine})\text{-NBD}]^+$ precursor, we have been able to structurally characterize a very weakly-bound Co σ -alkane complex using SMOM-techniques. This also has a ³Co triplet

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spin state – as probed by magnetic measurements and computation.

$[\text{Rh}(\text{L})\text{-NBD}][\text{BAr}^{\text{F}}_4]$ is a versatile motif for the generation of σ -alkane complexes by SC-SC transformations ($\text{L} = \text{Cy}_2\text{P}(\text{CH}_2)_n\text{PCy}_2$).^[9, 11] We have thus developed a route to the equivalent cobalt(I) complexes of these Schrock-Osborn^[20] systems (Fig. 2; $n = 2$, **L1**; $n = 4$, **L2**). This starts from CoCl_2 , involves a KC_8 reduction, a CH_2Cl_2 extraction, and delivers, respectively, lilac and green crystalline products in moderate yield.^[21] Our method complements that recently reported by Chirik using DuPhos-based ligands.^[22] $[\text{Co}(\text{L1})(\text{arene})][\text{BF}_4]$ complexes are also known.^[23] The solid-state structure of $[\text{Co}(\text{L2})\text{-NBD}][\text{BAr}^{\text{F}}_4]$ is shown in Fig. 2, with that for $[\text{Co}(\text{L1})\text{-NBD}][\text{BAr}^{\text{F}}_4]$ given in the supporting materials. Both show the cobalt coordination sphere is twisted from square planar towards tetrahedral. This distortion is greater with the wider bite angle ligand in $[\text{Co}(\text{L2})\text{-NBD}][\text{BAr}^{\text{F}}_4]$ ($28.0(3)^\circ$ versus $22.5(2)^\circ$).^[24] The $[\text{BAr}^{\text{F}}_4]^-$ anions adopt the $\sim\text{O}_h$ motif in the solid-state, being very similar to the direct analogs $[\text{Rh}(\text{L})\text{-NBD}][\text{BAr}^{\text{F}}_4]$.^[9, 11]

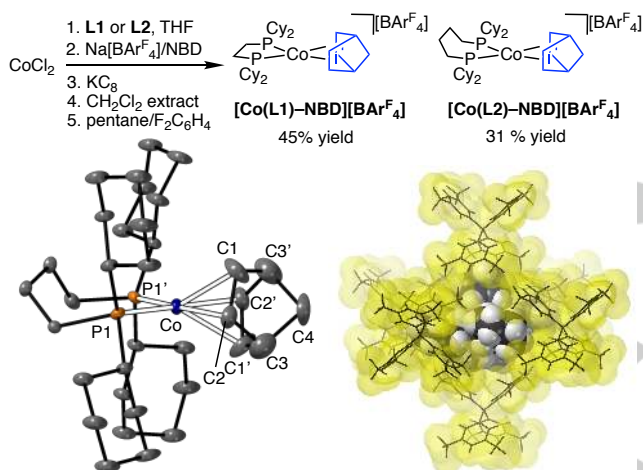


Figure 2. Synthesis of cationic Co-NBD precursors. **L1** = $\text{Cy}_2\text{P}(\text{CH}_2)_2\text{PCy}_2$, **L2** = $\text{Cy}_2\text{P}(\text{CH}_2)_4\text{PCy}_2$. Solid-state structure of the cationic portion of $[\text{Co}(\text{L2})\text{-NBD}][\text{BAr}^{\text{F}}_4]$, 15% displacement ellipsoids, anion and H-atoms not shown, -173°C data collection. $\sim\text{O}_h$ packing of $[\text{BAr}^{\text{F}}_4]^-$ anions around a single cation. Surfaces shown at van der Waals radii. Selected bond lengths (Å) and angles ($^\circ$): Co-C1, 2.212(6) Co-C2, 2.110(4); C1-C2, 1.394(6); Co-P1, 2.2717(8); P-Co-P1, 103.09(4); $\angle \text{CoP1P1}'/\text{Co}(\text{centC1C2})(\text{centC1}'\text{C2}') = 28.0(3)^\circ$.

In FC_6H_5 solution $[\text{Co}(\text{L1})\text{-NBD}][\text{BAr}^{\text{F}}_4]$ reacts quantitatively with H_2 to form (in 90% isolated yield) the brown, crystallographically characterized,^[21] arene adduct $[\text{Co}(\text{L1})(\eta\text{-FC}_6\text{H}_5)][\text{BAr}^{\text{F}}_4]$, with the concomitant formation of norbornane. This result shows that these cationic Co(I)-systems will promote the hydrogenation of alkenes,^[25] similar to the DuPhos variants.^[22] For $[\text{Co}(\text{L2})\text{-NBD}][\text{BAr}^{\text{F}}_4]$ hydrogenation in FC_6H_5 solution results in decomposition to a mixture of products. However, as we,^[12, 26] and others,^[27] have previously reported, organometallic synthesis in the solid-state can promote desirable changes in selectivity when compared to solution routes. This is the case for $[\text{Co}(\text{L2})\text{-NBD}][\text{BAr}^{\text{F}}_4]$.

Addition of H_2 to single-crystals of $[\text{Co}(\text{L2})\text{-NBD}][\text{BAr}^{\text{F}}_4]$ results in the formation of the highly reactive σ -alkane complex $[\text{Co}(\text{L2})\text{-NBA}][\text{BAr}^{\text{F}}_4]$ in a SC-SC transformation. By optimizing H_2 addition time (2 bar, 1 hr, 298 K), data collection parameters (2 hrs, -173°C , frozen oil-drop), and rapid transfer to the diffractometer, an acceptable refinement ($R1 = 8\%$) and unambiguous structural solution was achieved. $[\text{Co}(\text{L2})\text{-NBA}][\text{BAr}^{\text{F}}_4]$ is so reactive that even at -173°C longer data acquisition times than 2 hrs resulted in steady decomposition, loss of diffraction and a color change of the crystal from brown to blue [i.e. Co(II)], which we suggest is due to reaction with adventitious oxygen in the mounting oil.

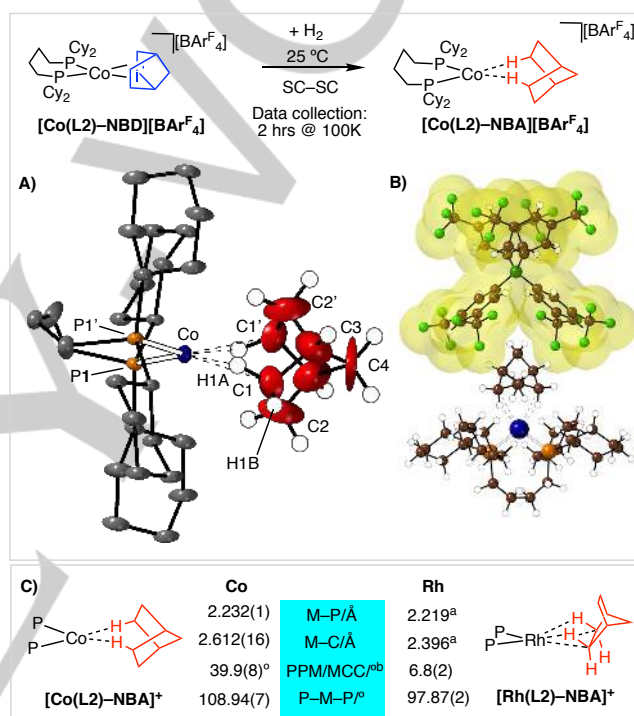


Figure 3. Synthesis of $[\text{Co}(\text{L2})\text{-NBA}][\text{BAr}^{\text{F}}_4]$ (A) Solid-state structure of the cation, 15% displacement ellipsoids, anion and most H-atoms not shown. Hydrogen atoms were placed in calculated positions. -173°C data collection. Selected bond lengths (Å) and angles ($^\circ$): Co-P, 2.232(1); Co-C1, 2.612(16); C1-C2, 1.470(12), P1-Co-P1', 108.94(7); $\angle \text{CoP1P1}'/\text{CoC1C1}' = 39.9(8)^\circ$. (B) Relationship between the cation and the proximate anion, van der Waals surface shown. (C) Comparison of selected structural metrics between $[\text{Co}(\text{L2})\text{-NBA}][\text{BAr}^{\text{F}}_4]$ and $[\text{Rh}(\text{L4})\text{-NBA}][\text{BAr}^{\text{F}}_4]$.^(a) average distances, ^(b) angle between planes.

The solid-state structure of $[\text{Co}(\text{L2})\text{-NBA}]^+$ is presented in Fig. 3A. This shows a $\{\text{Co}(\text{Cy}_2\text{P}(\text{CH}_2)_4\text{PCy}_2)\}^+$ fragment, with crystallographically-imposed C_2 symmetry, in which the NBA ligand sits in a cleft formed between two $[\text{BAr}^{\text{F}}_4]^-$ aryl rings in the $\sim\text{O}_h$ anion microenvironment, as noted for Rh-analogs.^[9, 11] The phosphine backbone is disordered over two conformations, and only one is shown. Hydrogen atoms were placed in calculated positions. The metal center is weakly bound with a saturated NBA fragment through two, mutually opposing, *endo*- $\text{Co}\cdots\text{H}-\text{C}$ interactions: $\text{Co}\cdots\text{H}(1)$, 1.766 Å; $\text{Co}\cdots\text{C1}$, 2.612(16) Å. The other

carbon atoms in the NBA ligand are significantly further away [Co...C2, 2.92(2) Å]. The Co–P distances become slightly shorter on hydrogenation [2.232(1) Å cf. 2.2747(9)], suggesting a weaker *trans*-ligand. As for the precursor, the NBA fragment is twisted away from square planar [\angle CoP1P1'/CoC1C1' \sim 40°], see Fig. S13.^[21] Overall this is different from the orientation found in [Rh(L2)–NBA][BARF₄] (Fig. 3C), in which the alkane interacts through two adjacent η^2 -*endo*-Rh...H–C bonds at a pseudo square planar Rh(I) center. The M...C distances are also \sim 0.22 Å longer than in [Rh(L2)–NBA][BARF₄], which is a significant observation given the small difference in covalent radii between Rh(I) and high-spin Co(I) [1.42 and 1.50 Å respectively].^[28] While the atomic displacement parameters associated with the Co, phosphine and anion are unremarkable, those of the NBA fragment are both significantly larger and show pronounced ellipticity. This signals that the alkane is, relatively, less constrained in the \sim O_h [BARF₄][–] microenvironment. As a consequence of this the C1–C2 distance in the NBA fragment was restrained to be in the range of a C–C bond, 1.470(12) Å. All these data point to a very weakly bound σ -alkane ligand at a Co(I)-center that is electronically very different from its Rh-analog. That this is a weak intermolecular interaction is signaled by the Co...C distances being much longer than found for the small number of structurally characterized Co...H–C intramolecular agostic complexes [\sim 2.2 Å],^[29] being more comparable to weak agostic M...H–C interactions [M = Rh, Ir, \sim 2.8 Å].^[30] While rare, σ -alkane complexes of 3d metals have been characterized at low temperature by in situ NMR spectroscopy.^[31]

The SC–SC hydrogenation on addition of H₂ to [Co(L2)–NBD][BARF₄] is confirmed by adding CD₂Cl₂ to [Co(L2)–NBA][BARF₄] and vacuum transfer of the volatiles. This shows NBA has been formed (¹H NMR), with no residual NBD observed. Addition of H₂ to [Co(L1)–NBD][BARF₄] resulted in complete loss of crystallinity, although NBA is – again – formed.

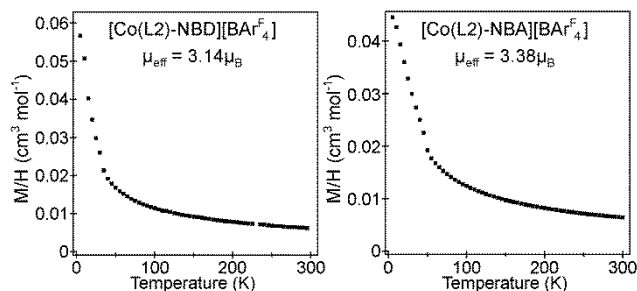


Figure 4. Magnetisation data for [Co(L2)–NBD][BARF₄] and [Co(L2)–NBA][BARF₄]. See supporting materials for more details.

The magnetisation data for both [Co(L2)–NBD][BARF₄] and [Co(L2)–NBA][BARF₄] can be fit by the Curie-Weiss law ($\chi = C/(T-\theta) + K$) over the temperature range 50 \leq T/K \leq 300 to yield values consistent with a ³Co spin state, Figs. 4 and S14. Low-temperature deviations from Curie-Weiss behavior below 50 K are attributed to intermolecular magnetic couplings. The observation of a temperature independent component to the

susceptibility of both compounds is indicative of a small unquenched orbital contribution to the magnetisation, and is consistent with the slightly elevated moments for both compounds, compared to expected spin-only values: [Co(L2)–NBD][BARF₄] $\mu_{\text{eff}} = 3.14 \mu_{\text{B}}$; [Co(L2)–NBA][BARF₄] $\mu_{\text{eff}} = 3.38 \mu_{\text{B}}$; $S = 1$, spin-only $\mu_{\text{eff}} = 2.82 \mu_{\text{B}}$. The slightly larger moment for the alkane complex is in line with NBA being a weaker field ligand than NBD. Consistent with the ³Co spin state for both complexes ³¹P{¹H} SSNMR spectra are featureless, as are the EPR spectra.

Spin-state energetics for [Co(L2)–NBA][BARF₄] and [Co(L2)–NBD][BARF₄] were also probed with periodic DFT, with geometries based on the crystal structures with H and F positions optimised in the triplet state with the PBE-D3 functional and energies recomputed with the hybrid PBE0-D3 approach.^[32] For [Co(L2)–NBA][BARF₄] the ³Co spin-state is favored by 32.3 kcal/mol (at each Co center), consistent with the experimental magnetisation data. In contrast for [Co(L2)–NBD][BARF₄] the ³Co spin-state is only lower by 4.1 kcal/mol and further tests showed the computed preferred spin-state is highly sensitive to both methodology and NBD ligand orientation.^[21]

The computed structure of the [Co(L2)–NBA]⁺ cation (Fig. 5A) reveals a short Co...H11 distance of 1.82 Å, with an elongation of the C1–H11 bond to 1.12 Å, that together suggest a degree of C1–H11→Co σ -interaction. In contrast, the Co...H21 distance is 2.58 Å and no elongation of the C2–H21 bond is seen. The QTAIM molecular graph (Fig. 5B) is consistent with these features and confirms a Co...H11 bond path. Fig. 5C and D show the NCI plot of the [Co(L2)–NBA][BARF₄] ion-pair, with weak interactions color-coded from blue (most stabilizing), through green (weakly stabilizing) to red (destabilizing). Viewed from the Co centre (Fig. 5C), the localised blue regions between Co...H11 and Co...H11' suggest two η^1 -C–H→Co σ -interactions, with turquoise regions between Co...H21/H21' reflecting weaker, dispersive stabilizations. The side-on view of the ion-pair (Fig. 5D) highlights broad regions of

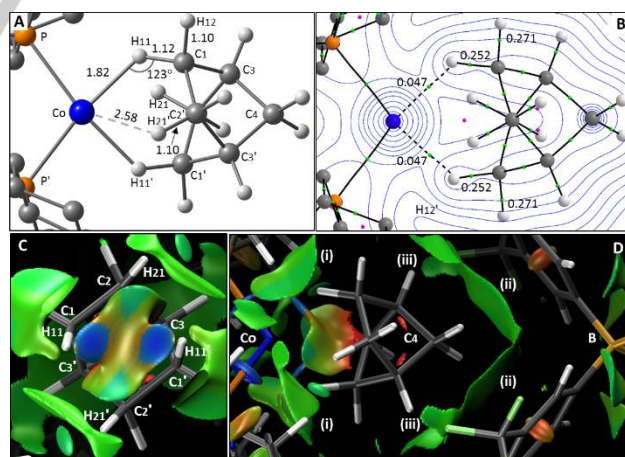


Figure 5. (A) Computed structure of the [Co(L2)–NBA]⁺ cation viewed down the C2...C2' axis highlighting key distances (Å) and angles to H atoms. (B) Quantum Theory of Atoms in Molecules (QTAIM) molecular graph with bond critical bonds (BCPs) in green, ring critical points (RCPs) in pink and selected BCP electron densities, $\rho(r)$, in ebohr^{–3}. (C) Non-Covalent Interaction (NCI) plot of the proximate [Co(L2)–NBA][BARF₄] ion-pair viewed from the Co center. (D) NCI plot perpendicular to the Co...C4...B axis highlighting the (i) the PCy₂ substituents, (ii) [BARF₄][–] aryl groups, (iii) C–F...H–C H-bonding.

dispersive stabilization between the NBA ligand and (i) the PCy₂ substituents, (ii) the aryl groups of the [BAR^F₄]⁻ anion and (iii) non-classical C-F...H-C H-bonding. These features, combined with the C-H→Co σ-interactions, indicate how both inter- and intra-molecular interactions contribute to stabilize the alkane complex within the binding pocket.

A spin-unrestricted NBO 2nd order perturbation analysis delineates interactions in the α- and β-spins at the ³Co center (see Fig. 6, which also gives the Lewis structure used). For α-spin, occupation of all five 3d orbitals means donation from σ_{C-H} can only occur into a Co low-valent (4s) NBO (3.5 kcal/mol). A similar interaction is seen in the β-spin (4.7 kcal/mol), but donation can now also occur into a vacant Co d orbital (5.9 kcal/mol). Back-donation from P lone pairs into the σ*_{C-H} NBOs is seen for both spins, with additional back donation from an occupied Co 3d NBO in the α-spin (1.7 kcal/mol).^[21]

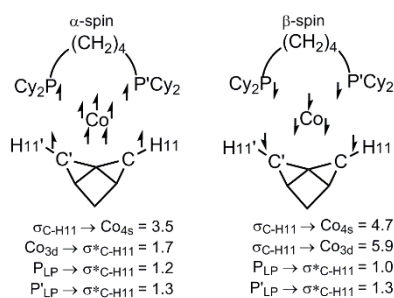


Figure 6. Spin unrestricted NBO 2nd order perturbation analysis highlighting key donor-acceptor interactions (kcal/mol) in [Co(L2)-NBA]⁺. The resultant NLMOs are provided in the Supporting Materials.

These NBO data indicate NBA is less strongly bound in [Co(L2)-NBA]⁺ than in the [Rh(L2)-NBA]⁺ cation (where total σ_{C-H} donation ≈ 19.7 kcal/mol and back-donation to σ*_{C-H} ≈ 8.5 kcal/mol^{[10][33]}). This also aligns with the reduced C-H11 bond elongation and BCP ρ(r) of the ³Co system. The Co-H11-C angle of 123° along with the localised, stabilizing, features along the C-H11/C'-H11...Co vectors in the NCI plot suggest an η¹:η¹-NBA binding mode in [Co(L2)-NBA]⁺, again in contrast with the η²:η²-NBA ligand in [Rh(L2)-NBA]⁺.^[10] The NCI plot also reveals intermolecular dispersive interactions in this ³Co system and these are likely to contribute relatively more to overall stability than in the related, more strongly covalently bound, ¹Rh system.

The synthesis of [Co(L2)-NBA][BAR^F₄]⁺ thus rests upon the stabilizing microenvironment provided by the [BAR^F₄]⁻ anions, underscoring the importance of such weak interactions in isolating σ-alkane complexes in the solid-state.^[3, 9] That this now also allows for the isolation of complexes that sit on a triplet-surface opens up new opportunities for exploring the synthesis, reactivity and catalysis of such species that have, at best, only a fleeting existence when generated in solution.^[1, 18]

Conflict of interest

The authors declare no conflict of interest.

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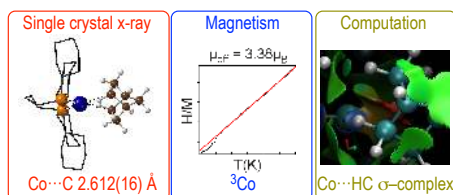
Keywords: Cobalt • Single-Crystal to Single-Crystal • Alkane Complex • Squid • Periodic DFT

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COMMUNICATION



The synthesis, and single-crystal x-ray structure, of a ³Co σ-alkane complex is achieved by a single-crystal to single-crystal solid/gas hydrogenation from a corresponding ³Co-diene precursor.

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Alkane Complex.

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