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Formation of a $\sigma$-alkane Complex and a Molecular Rearrangement in the Solid-State: [Rh(Cyp$_2$PCH$_2$CH$_2$PCyp$_2$)(η$^2$-η$^2$-C$_7$H$_{12}$)][BAr$_4$]

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3 Supporting Information

**ABSTRACT:** Addition of H$_2$ to the precursor [Rh(Cyp$_2$PCH$_2$CH$_2$PCyp$_2$)(η$^2$-η$^2$-C$_7$H$_{12}$)][BAr$_4$]$^*$ gives the $\sigma$-alkane complex [Rh(Cyp$_2$PCH$_2$CH$_2$PCyp$_2$)(η$^2$-η$^2$-C$_7$H$_{12}$)][BAr$_4$] by a single-crystal to single-crystal reaction, as characterized by X-ray crystallography, SSNMR spectroscopy, and periodic DFT. An unexpected rearrangement of the {Rh(L$_2$)}$^+$ fragment is revealed.

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C omplexes in which an alkane acts as a ligand to a metal center using its C–H bonding electrons, so-called $\sigma$-alkane complexes, are of considerable interest due to their role as intermediates in C–H activation processes and the challenges involved with their synthesis and characterization. As C–H bonds are strong and non-nucleophilic, alkanes are very poor ligands, and direct observation of $\sigma$-alkane complexes has generally been limited to very low temperature in situ solution spectroscopic techniques. We have recently reported that they may be prepared by solid/gas single-crystal to single-crystal transformations (Scheme 1), enabling structural characterization by single crystal X-ray crystallography. Addition of H$_2$ to the diene precursor [Rh(R$_3$PCH$_2$CH$_2$PPh$_2$)$(\eta^2$-NBD)][BAr$_4$]$^-$ (NBD = norbornadiene, Ar$^f$ = 3,5-(CF$_3$)$_2$C$_6$H$_4$) leads to the generation of [Rh(R$_3$PCH$_2$CH$_2$PPh$_2$)$(\eta^2$-NBD)][BAr$_4$]$^-$ (NBD = norbornane; R = Bu, [1-NBA][BAr$_4$]$^-$; R = Cy, [2-NBA][BAr$_4$]$^-$). When R = Bu, rapid loss of NBA in the solid-state at 298 K gives the [BAr$_4$]$^-$ coordinated zwitterion [1-BAr$_4$]$^+$. In contrast, when R = Cy, the $\sigma$-alkane complex is stable in the solid state for months at 298 K. The precise factors that are responsible for these differences are currently not fully resolved. Both species feature encapsulation of the cation by an octahedral arrangement of [BAr$_4$]$^-$ anions, which provides a well-defined lattice environment, while the butressing Cy groups in [2-NBA]-[BAr$_4$]$^-$ may install a kinetic penalty toward rearrangement in the solid state.‡§ We now report the synthesis of [Rh(Cyp$_2$PCH$_2$CH$_2$PCyp$_2$)(η$^2$-η$^2$-NBA)][BAr$_4$]$^-$ using a cyclopentyl (Cyp)-substituted chelating phosphine which was designed to sit between the steric profiles of flexible Bu and rigid/tall Cy. This leads to not only a relatively stable $\sigma$-alkane complex but also an unexpected metal-fragment reorientation within the [BAr$_4$]$^-$ anion cavity while retaining the integrity of the single crystal.

The precursor complex [Rh(Cyp$_2$PCH$_2$CH$_2$PCyp$_2$)(η$^2$-η$^2$-NBD)][BAr$_4$]$^-$ ([2-NBD][BAr$_4$]$^-$) was prepared as for [2-NBD][BAr$_4$]$^-$.$^5$ A single-crystal X-ray diffraction study at 150 K (Figure 1A) demonstrated crystallographically imposed C$_2$ rotational symmetry with Rh1 and NBD bridge methylene (C7) occupying special positions. The Cyp groups are disordered, while the long-range structure was found to be modulated (Supporting Information),$^6$ which was modeled with a $q$ vector of (0.03433,0).$^7$ The [BAr$_4$]$^-$ anions are organized so that each cation is contained within a pseudo-octahedral cage of anions, and the overall motif and structural

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metrics are very similar to those reported for [2-NBD][BF4]−. In particular, the NBD ligand sits in a cleft between two [BF4]− aryl groups so that the C7-methylene protons point toward the centers of two of the aromatic rings. In the 298 K 31P[1H] solid-state NMR (SSNMR) spectrum two distinct, but very close, phosphine environments are observed (δ 66.2, JBF 149 Hz; δ 65.7, JBF 151 Hz), consistent with P(CyP, disorder and/or the modulated structure. In the 13C[1H] SSNMR spectrum four signals observed between δ 90 and 55 are assigned to the NBD fragment under C3 symmetry. The disorder/modulation was not resolved in this spectrum.

Addition of H2 to a single-crystal sample of [3-NBD][BF4]− (2 bar, 10 min, 298 K) led to the quantitative formation of the σ-alkane complex [Rh(CyP,PCH2CH2PCyP)(η3-η2-NBA)][BF4]− ([3-NBA][BF4]−) ([Scheme 1]). Crystallinity is retained in this process, and the resulting structure determined by single-crystal X-ray diffraction (100 K, R(2θ) = 7.0%) clearly shows a saturated NBD fragment interacting with the Rh center through two 3c-2e Rh···H-C interactions, in which the relevant hydrogen atoms were located but refined using a riding model (Figure 2). Although there are no significant changes to the arrangement of the [BF4]− anions, this transformation proceeds with loss of the crystallographically imposed C3 rotational symmetry: [3-NBD][BF4]−, C3/c, Z = 4; [3-NBA][BF4]−, P21/c, Z = 4.21 Space group changes have been noted in other single-crystal transformations.21 The alkane ligand binds to the (Rh(L0))4+ fragment through two C–H σ-interactions, resulting in a Rh(I) square-planar, d8 metal center coordination motif. The Rh–C1/C2 distances (2.388(5) and 2.392(5) Å, respectively) are the same, within error, as for [2-NBA][BF4]− (2.389(3) and 2.400(3) Å). The C1–C2 and C4–C5 distances (1.550(7) and 1.541(9) Å) signal the hydrogenation of the diene to form C=C bonds. The Rh–P distances (2.207(1) and 2.206(1) Å) are shorter than those in [3-NBD][BF4]− (2.2712(12) Å), reflecting the weaker trans influence C–H σ interactions. The CyP groups showed some disorder.

The changes upon hydrogenation were also probed by the optimization of the extended solid-state structure with periodic DFT calculations at the PBE-D3 level. These provided excellent agreement both for the molecular geometries of the Rh cations (see the caption of Figure 2 for [3-NBA][BF4]− and the Supporting Information for [3-NBD][BF4]−) and for the extended structure (see Figure S15 in the Supporting Information). Moreover, the calculations provide further insight into the Rh···alkane interaction, with short average computed Rh···H11/H21 distances (1.89 Å) and elongated C1–H11 and C2–H21 distances (1.15 Å). In contrast, the C1–H12 and C2–H22 bonds exhibit standard distances of 1.10 Å, consistent with an absence of any interaction with Rh in that case. The Rh···H-C σ-interaction is confirmed by a quantum theory of atoms in molecules (QTAIM) study that identifies Rh···H11 and Rh···H21 bond paths with reduced electron densities for the C1–H11 and C2–H21 bond critical points in comparison to the C1–H12 and C2–H22 bonds.9

Consideration of the relationship between the cation and the proximal capping [BF4]− anion (Figure 1) shows that the NBD ligand in [3-NBA][BF4]− adopts an orientation very similar to that of the NBD ligand in [3-NBD][BF4]−, in particular the orientation of the C7-methylene protons that are still directed toward the aryl rings. In contrast the (Rh(L0))4+ fragment has undergone a ca. 90° twist with respect to the precursor as defined by, for example, the interplane angle C38,C54,Rh1/Rh1,P1,P2 = 88.12(12)° (Figure 1). We have previously noted that the octahedral cavity described by the anions accommodates a variety of structural changes associated at the metal cation. Clearly it can also accommodate significant movement of the (Rh(L0))4+ fragment. Whether this occurs in concert with hydrogenation, or immediately afterward, is opaque to experiment. This situation is different from that observed in the transformations that afforded [2-NBA][BF4]−, in which it is the organic fragment that responds by moving rather than (Rh(L0))4+ cation. For [3-NBA][BF4]− the parallel structure is ca. 14 kcal/mol above the optimized “orthogonal” form. The parallel structure is therefore not viable thermodynamically, but it may be kinetically accessible, 14 kcal/mol representing a lower limit to the

Figure 1. Solid-state structures (ball and stick) relative to a local [BF4]− anion: (A) [3-NBA][BF4]−, average structure; (B) [3-NBD][BF4]−. Selected interplane angles: C38,C38,Rh1/Rh1,P1,P1′ = 6.39(17)°; C38,C54,Rh1/Rh1,P1,P2 = 88.12(12)°.

Figure 2. (A) Solid-state structure of [3-NBA][BF4]−, with the cation and selected H atoms shown (100 K, 50% displacement ellipsoids). (B) Alternate view of [3-NBA][BF4]−, with P-alkyl groups removed. Selected bond lengths (Å): Rh1–C1 2.388(5), Rh1–C2 2.392(5), Rh1–P1 2.207(1), Rh1–P2 2.206(1), C1–C2 1.550(7), C4–C5 1.541(9). Computed bond lengths (Å) periodic DFT, PBE-D3): Rh1–C1 2.425, Rh1–C2 2.420, Rh1–P1 2.219, Rh1–P2 2.215, C1–C2 1.561, C4–C5 1.565, Rh1–H11 1.895, Rh1–H21 1.886, C1–H11 1.154, C2–H21 1.154.
parallel structure lies 22 kcal/mol below the alternative orthogonal form.

The hydrogenation of microcrystalline [3-NBD][BAr$_F$$_4$] was studied by SSNMR. A $^{31}$P($^1$H) SSNMR spectrum (298 K) taken immediately after H$_2$ addition (10 min) shows complete consumption of [3-NBD][BAr$_F$$_4$], with two overlapping doublet signals observed ($\delta$ 109.2, $J_{HF}$ = 189 Hz; $\delta$ 108.1, $J_{HF}$ = 188 Hz), consistent with at least two crystallographically independent $^{31}$P environments. Such a downfield shift and increase in the $J_{HF}$ value are consistent with the formation of a $\sigma$-alkane complex. The $^{13}$C($^1$H) SSNMR spectrum lacks signals between $\delta$ 100 and 50 due to NBD. We and others, have previously used HETCOR SSNMR experiments to indirectly detect $^1$H NMR signals in $\sigma$ complexes, which in combination with computed chemical shifts has led to assignment of signals arising from $\sigma$-Rh...H=−C interactions in $\sigma$-alkane complexes. The projected $^1$H NMR spectrum from the $^{13}$C/$^1$H FSLG-HETCOR SSNMR experiment conducted on freshly prepared [3-NBA][BAr$_F$$_4$] showed a broad high-field signal centered at $\delta$ 1.46 which correlates to a partially obscured $^{13}$C signal at $\delta$ 25. These chemical shifts are comparable to those reported for the $\sigma$-Rh...H=−C interactions in [2-NBA][BAr$_F$$_4$]. An additional high-field signal at $\delta$$^{11}$H = 0.16 (cross peak $\delta$$^{13}$C 40.5) is assigned to the ring-current-affected methylene bridge (C7) protons. A similar cross peak is observed for [3-NBD][BAr$_F$$_4$] ($\delta$$^{11}$H = 1.74/$\delta$$^{13}$C 69.3) in line with a similar orientation of the NBD ligand in the precursor.

Assignment of these NMR data on the basis of the computed $^{13}$C and $^1$H chemical shifts for [3-NBA][BAr$_F$$_4$] derived from the full extended solid-state structure (GIPAW method, PBE functional) is shown in Figure 3. Those for C1 and C2 ($\delta$calc ca. 27) are in good agreement with experiment, while the associated H11 and H21 exhibit appreciable shielding (coincident at $\delta$calc −4.65) but are shifted more upfield than those in experiment ($\delta$ −1.46). The C7 position ($\delta$calc 40.4) matches experiment, and the ring current effect that shields the C7 hydrogens is also captured. The different values for H71 and H72 ($\delta$calc −1.35 and 0.04) reflect the asymmetry of the environment in the static structure. The observation experimentally of single resonances for H71/72 ($\delta$ −0.16) and H11/21 may therefore reflect a fluxional process occurring on the NMR time scale at 298 K that renders these sets of protons equivalent. Cooling to 158 K resulted in a broadened $^{31}$P($^1$H) SSNMR spectrum and a HETCOR in which signals due to the NBD ligand were too broad to be observed, consistent with a low-energy (~7 kcal/mol) fluxional process occurring in the solid-state. SSNMR calculations also reproduce well the change in $J_{HF}$ upon hydrogenation.

Powdered crystalline [3-NBA][BAr$_F$$_4$] displayed stability intermediate between those of [1-NBA][BAr$_F$$_4$] (minutes) and [2-NBA][BAr$_F$$_4$] (months), as measured by $^{31}$P($^1$H) SSNMR spectroscopy. Signals for [3-NBA][BAr$_F$$_4$] were slowly (96 h) replaced by a broad signal centered at $\delta$ 84, assigned to zwiterionic [3-BAr$_F$$_4$], as confirmed by an independent synthesis. Decomposition is effectively halted at 273 K.

Although we currently do not have a definitive explanation for the factors that control relative stabilities and the movements of NBA versus the metal fragment in the solid state, it may be noteworthy that the PCyp$_2$ groups offer a more curved exterior surface in comparison with the rigid/tall PCy$_2$ that could encourage [Rh(L$_2$)$_2$] movement for the former in the relatively high symmetry cavity of [BAr$_F$$_4$]$^-$ anions (Figure 4). The delineation of such electronic and steric influences will be important in the continued development of the coordination chemistry and reactivity of $\sigma$-alkane complexes in the solid-state.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00645.

Experimental and characterization details, including NMR spectroscopic data, X-ray crystallographic data, and computational details (PDF)

X-ray crystallographic data (CIF)

Cartesian coordinates for calculated structures (XYZ)

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Notes
The authors declare no competing financial interest.

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