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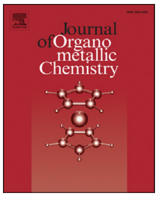

A convenient route to a norbornadiene adduct of iridium with chelating phosphines, $[Ir(R_2PCH_2CH_2PR_2)(NBD)][BAr^F_4]$ and a comparison of reactivity with H_2 in solution and the solid–state

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The straightforward synthesis of two cationic iridium norbornadiene species bearing simple bidentate phosphines is reported $[Ir(R_2PCH_2CH_2PR_2)(NBD)][BAr^F_4]$ [NBD = norbornadiene; R = ^tBu, Cy; Ar^F = 3,5–$C_6H_3(CF_3)_2$]. The hydrogenation of $[Ir(^tBu_2PCH_2CH_2P^tBu_2)(NBD)][BAr^F_4]$ in the solution phase and in the solid state is described in which saturated (solution) or unsaturated (solid–state) dimeric species with bridging hydrides are formed. The solid–state structures, as determined by single crystal X-ray diffraction, of these dimeric species are also discussed.

1. Introduction

We have recently reported that addition of H_2 to the norbornadiene precursors $[Rh(R_2PCH_2CH_2PR_2)(NBD)][BAr^F_4]$ [NBD = norbornadiene; R = e.g. ^iBu, Cy; Ar^F = 3,5–$C_6H_3(CF_3)_2$] [1,2] in a solid–gas, single–crystal to single–crystal transformation [3,4] forms the corresponding norbornane (NBA) sigma–alkane complexes $[Rh(R_2PCH_2CH_2PR_2)(\eta^2:\eta^2–C_7H_{12})][BAr^F_4]$ (Scheme 1). These complexes have pseudo square planar structures in which a Rh(I) cation is coordinated with a bidentate phosphine and two C–H sigma interactions. Extending this methodology to include iridium systems would be of significant interest in terms of the different oxidation state manifolds the two congeners generally occupy (Rh: +1/+3; Ir: +3/+5), as well as the role that Ir–complexes play in the catalytic dehydrogenation of alkanes, for which sigma alkane complexes are implicated as intermediates [5]. Remarkably, a survey of NBD complexes of iridium shows that the synthesis or characterisation of $[Ir(chelating–diphosphine)(NBD)]^+$ complexes has not been reported in the open literature; although $[Ir(dppe)(NBD)]^+$ has been described for use in alkene hydrogenation, its synthesis and spectroscopic characterisation were not described [6,7]. Simple complexes of the general formula $[IrL_2(NBD)]^+$ are also rare (L = 2 electron donor ligand) [8], although there is more extensive literature associated with NBD–like tetrafluorobenzobarrelene ligands complexed with iridium [9]. This is in contrast with Rh–NBD complexes that are widely used as precursors for many catalytic processes [10], such as hydrogenation [11] and hydroacylation [12], when activated by simple addition of H_2 in solution and loss of NBA.

In this communication we report the straightforward synthesis of $[Ir(R_2PCH_2CH_2PR_2)(NBD)][BAr^F_4]$ [R = ^tBu, Cy] and subsequent reactivity with H_2 in both solution and the solid–state [R = ^tBu] [13]. This does not result in the isolation of an alkane complex, but instead hydride bridged dimers are formed, the identity of which depends on the phase of hydrogenation: in solution a saturated mono–cationic $[Ir_2H_5]^+$ dimer is formed, but in the solid–state a novel unsaturated dicationic $[Ir_2H_4]^{2+}$ dimer results. Hydrogenation in the solid–state of $[Ir(L)(COD)]^+$ and $[Ir(L)(C_2H_4)]^+$ cations (L = mono or multidentate phosphine ligand) have previously been reported by Siedle [14,15] and Bianchini [16].

2. Results and discussion

2.1. Synthesis of NBD–adducts

Addition of H_2 to a CH_2Cl_2 solution of $[Ir(^tBu_2PCH_2CH_2P^tBu_2)(COD)][BAr^F_4]$ [17], also recently prepared as the $[O_3SCF_3]^-$ salt [18], in the presence of excess NBD resulted in the formation of $[Ir(^tBu_2PCH_2CH_2P^tBu_2)(NBD)][BAr^F_4]$ (**1**) as a brown solid in good isolated yield (78%) after recrystallization from CH_2Cl_2/pentane.

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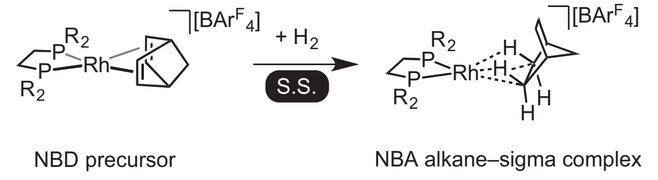


Scheme 1. Synthesis of a Rh(I) sigma–alkane complex by addition of H_2 to a NBD precursor. [R = Cy, ^{i}Bu].

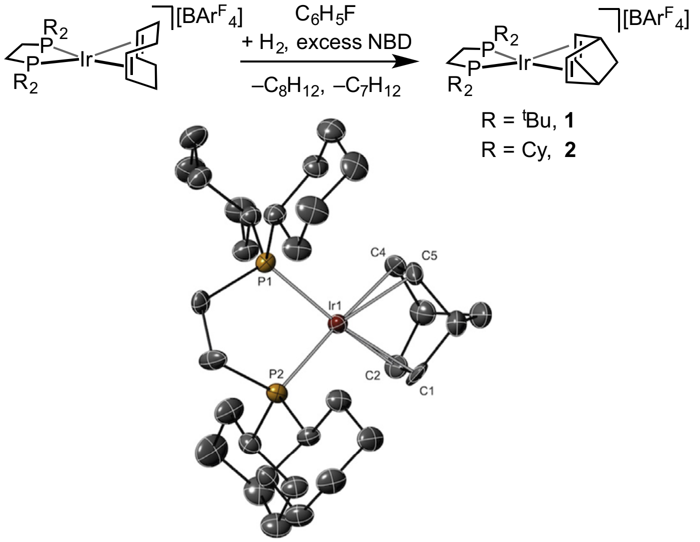
Although we have not studied this reaction in detail we assume that it operates via Ir(3+) hydride intermediates, which when H_2 is the limiting reagent are consumed by excess NBD to from **1** [8]. For this reason the reaction required significant optimisation and monitoring using $^{31}P\{^1H\}$ NMR spectroscopy to maximise the compositional purity and yield of **1**. Although large, high quality, crystals of **1** could be grown, structural refinement was severely hampered by the very large unit cell ($Z = 32$). NMR, ESI–MS and micro analytical data are, however, in full accord with the formulation. The analogous cyclohexyl–phosphine complex $[Ir(Cy_2PCH_2CH_2PCy_2)(NBD)][BAr^F_4]$, **2**, was prepared in a similar way (69%, 0.11 g) [17] for which a single crystal X-ray diffraction study confirmed the structure (Scheme 2). There is no crystallographically imposed symmetry and bond–lengths and angles are unremarkable.

Both complexes **1** and **2** display a single environment in the solution $^{31}P\{^1H\}$ NMR spectrum (e.g. δ 77.5, **1**), and signals in the ^1H NMR spectrum fully consistent with time–averaged C_{2v} symmetry. The $^{31}P\{^1H\}$ Solid–State Magic Angle Spinning NMR (SSNMR) spectrum of **1** also shows a single signal at δ 77.5, although this is likely a 1 + 1 coincidence as the phosphorus atoms are not crystallographically equivalent. In the $^{13}C\{^1H\}$ SSNMR spectrum only 4 signals assigned to the NBD ligand are observed at δ 72.8, 70.3, 58.7 and δ 52.9, again presumably due to coincidence as 7 would be expected. These are similar in chemical shift to those reported in the solid–state for $[Rh(Cy_2PCH_2CH_2PCy_2)(NBD)][BAr^F_4]$ [2], and in solution for $[Ir(PPh_3)_2(NBD)][PF_6]$ [8].

2.2. Hydrogenation of *$[Ir(^tBu_2PCH_2CH_2P^tBu_2)(NBD)][BAr^F_4]$ in the solid–state*

Addition of H_2 (1 atm) to crystalline **1** resulted in a rapid reaction, so that after 5 min of exposure to H_2, and placing the sample back under an Ar–atmosphere [19] the $^{31}P\{^1H\}$ SSNMR spectrum showed the complete consumption of **1** and the formation of a new product by a single broad environment at δ 99.4. The $^{13}C\{^1H\}$ SSNMR shows the absence of signals in the region 100–40 ppm, consistent with hydrogenation of the diene. The sample looses its single–crystallinity on addition of H_2 as determined by X-ray diffraction. Recrystallisation from CH_2Cl_2/pentane resulted in the isolation of pale yellow crystals in 70% isolated yield, for which a single crystal X-ray diffraction study showed to be dimeric, unsaturated, $[Ir(^tBu_2PCH_2CH_2P^tBu_2)(H)(\mu\text{–}H)]_2[BAr^F_4]_2$ (**3**, Scheme 3); presumably formed alongside NBA which is removed by recrystallisation [1,2]. The solid–state structure shows a dimeric Ir–core, sitting on a crystallographically imposed inversion centre, with an Ir…Ir distance of 2.7134(8) Å. The hydride ligands were located (but not freely refined): two sit bridging to the metals, and two sit opposite to a vacant site on Ir in a mutually anti–configuration. There is no evidence for an agostic C–H…Ir interaction, with the closest Ir…C distance measured as 3.319 Å. Although the Ir–Ir bond distance might point to a M–M bond (and thus a formal 18–electron count at each metal), using electron counting schemes recently highlighted [20] each metal centre can be considered as Ir(3+) and 16–electron, leading to no M–M bond. This unsaturated model is consistent with: (i) the high field chemical shift of the hydride that indicates being *trans* to a vacant site; (ii) and there is no significant structural change to the dimer on addition of MeCN, *vide infra*. Unsaturated late–transition metal hydrido clusters are well known [21], and **3** is also related to unsaturated dimers such as $[Ru(P^iPr_3)_2(H)(\mu\text{–}F)]_2$ [22] and $[Ru(^tBu_2PCH_2P^tBu_2)(H)(\mu\text{–}Cl)]_2$ [23].

The solution (CD_2Cl_2) $^{31}P\{^1H\}$ NMR spectrum of isolated **3** is very similar to that observed in the solid–state (δ 99.2 versus δ 99.4 respectively). The room temperature ^1H NMR spectrum shows two ^{t}Bu environments at δ 1.37 and δ 1.29 that also show coupling to ^{31}P, and a broad signal at δ 2.15 assigned to the methylene groups. A very high–field signal is observed at δ −43.3 characteristic of a hydride *trans* to the vacant site [24]. The other hydride signal was not apparent in the ^1H NMR spectrum, even on cooling to −80 °C. Repeating the synthesis of **3** in the solid–state using D_2 gas revealed a broad signal in the ^2H NMR spectrum (fwhm = 42 Hz) at δ 1.19 which we assign to the bridging hydride, as well as a high–field signal at δ −42.7. This signal at δ 1.19 would be obscured



Scheme 2. Synthesis of NBD complexes **1** and **2**, and the solid–state structure of the cation in **2**. Selected bond distances(Å): Ir1–P1, 2.299(2); Ir1–P2, 2.290(2); Ir1–C1, 2.185(8); Ir1–C2, 2.227(7); Ir1–C4,2.208(8); Ir1–C5, 2.226(7); C1–C2, 1.389(12); C4–C5, 1.379(14).