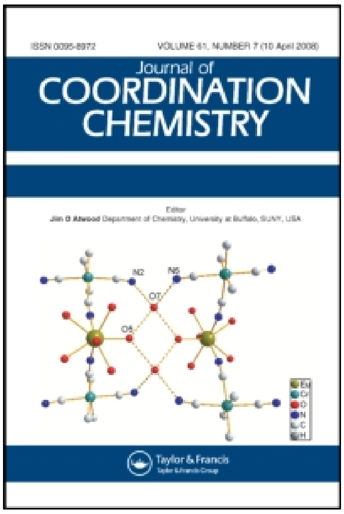

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ISOLATION AND X-RAY STRUCTURE OF $[Ir(CNBu^t)_5H](PF_6)_2$

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Reaction of *tert*-butyl isocyanide with $[Ir(COD)Cl]_2$ and NH_4PF_6 yields $[Ir(CNBu^t)_5H](PF_6)_2$ (**1**). The hydride ligand is observed by both proton NMR and infrared spectroscopy. Complex **1** is triclinic, P-1, $a = 11.307(3)$, $b = 14.619(3)$, $c = 15.486(3)$ Å, $\alpha = 98.204(3)$, $\beta = 106.851(3)$, $\gamma = 106.953(3)°$, $Z = 2$, 6746 reflections $[I \geq 2\sigma(I)]$, $R1 = 0.0397$, $wR2 = 0.0984$. The closest Ir–Ir interatomic distance within the crystal is 8.6 Å. EPR and cyclic voltammetry studies also support the identity of **1**.

Keywords: *tert*-Butyl isocyanide; DPPM; iridium hydride

INTRODUCTION

Rhodium and iridium isocyanide complexes have been shown to mediate important photoinduced electron-transfer reactions involving the transfer of hydrogen [1]. Several studies detailing the electrochemical and photophysical properties of these complexes have been reported [2–6]. Homolytic binuclear iridium isocyanide complexes have also been shown to encapsulate noble metal cations [7]. During our investigations to find mononuclear iridium isocyanide complexes that also form adducts with coinage metals, we have isolated the iridium oxidation-addition product $[Ir(CNBu^t)_5H](PF_6)_2$ that contains a hydride ligand.

EXPERIMENTAL

Preparation of $[Ir(CNC(CH_3)_3)_5H](PF_6)_2$ (**1**): Using Schlenkware, 0.785 g (1.17 mmol) of $[Ir(COD)Cl]_2$ was dissolved in 15 mL CH_2Cl_2 and degassed by repeated freeze-pump-thaw cycles. 1.5 mL (13.4 mmol) of *tert*-Butyl isocyanide (Aldrich) in 15 mL of similarly degassed CH_2Cl_2 was added rapidly *via* cannula. The solvent was removed under vacuum and replaced with ~10 mL of degassed methanol. To this solution 0.560 g (3.4 mmol) of NH_4PF_6, dissolved in degassed methanol, was added producing

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a white precipitate. The product was filtered in air, washed with cold methanol and hexane, and dried. Yield = 1.21 g (57%).

Characterization of $[Ir(CNC(CH_3)_3)_5H](PF_6)_2$: ^{1}H NMR (300 MHz, CD_3CN, 25°C), δ: 1.63 (s, 9 H, axial $CN(CH_3)_3$ protons), 1.58 (s, 36 H, equatorial $CN(CH_3)_3$ protons), −12.51 (s, 1 H, hydride); $^{13}C\{^1H\}$ NMR (75.7 MHz, CD_3CN, 25°C), δ: 95.80 (t, isocyanide carbons, $J_{N^{14}-C^{13}} = 22$ Hz), 62.27 (s, equatorial quaternary carbons), 61.26 (s, axial quaternary carbon), 29.98 (s, axial methyl carbons), 29.81 (s, equatorial methyl carbons); IR (thin film, ATR) ν(CN) 2239 cm^{-1}; ν(IrH) 2120 cm^{-1}; Anal. Calcd. for $IrC_{25}H_{46}F_{12}N_5P_2$(%): C, 33.41; H, 5.16; N, 7.79. Found: C, 33.77; H, 5.22; N, 7.54. Elemental analysis was conducted by MHW Laboratories of Pheonix, AZ.

Crystallography: Crystals were grown by vapor diffusion of diethyl ether into a solution of **1** in acetone. Structures were solved using SHELXS-97 [8] and refined using SHELXL-97 [8]. No higher symmetry than triclinic could be found and the choice of P-1 as the space group was made on the basis of intensity statistics. Hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Highest residual peak and hole difference peaks are located next to the iridium metal atom. The hydride was not found in the final difference map and was placed in an idealized position [9]. Table I lists additional crystal and refinement information.

Two hexafluorophosphate (PF_6) anions were found in the asymmetric unit. One PF_6 anion is not disordered; however the second PF_6 was found disordered over two positions (1 : 1 ratio) around a common linear F–P–F axis. The disordered fluorine atoms were refined isotropically, and all other nonhydrogen atoms were refined with

TABLE I Crystal data and structure refinement for **1** · 2 acetone

Empirical formula	$C_{31}H_{58}F_{12}Ir\,N_5O_2P_2$
Formula weight	1014.96
Crystal system	Triclinic
Space group	P-1
a, Å	11.307(3)
b, Å	14.619(3) Å
c, Å	15.486(3) Å
α, °	98.204(3)
β, °	106.851(3)
γ, °	106.953(3)
Volume, Å^3	2270.1(9)
Z	2
Density (calculated) g.cm^{-3}	1.49
Absorption coef. mm^{-1}	3.090
F(000)	1020
θ range	1.42–25.06°
Index ranges	$-13 \leq h \leq 13$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$
Independent reflections	7883 [*R*(int) = 0.0368]
Observed reflections	6746
Max–Min trans.	1.000–0.461
Data/restraints/parameters	7883/52/405
Goodness-of-fit	1.004
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0397$, $wR2 = 0.0984$
R indices (all data)	$R1 = 0.0481$, $wR2 = 0.101$
Peak and hole e Å^{-3}	2.864 and −1.645

anisotropic displacement parameters. The structure of **1** also contains disordered solvent molecules that could not be satisfactorily modeled, so electron density associated with these molecules was removed using the SQUEEZE function of the program PLATON [10]. A void volume of ~526 Å^3 was produced and 118 electrons per unit cell removed. This is approximately equal to four acetone molecules (128 electrons), which are included in the calculation of density, μ and $F(000)$.

RESULTS AND DISCUSSION

Addition of more than a five-fold excess of *tert*-butyl isocyanide (per iridium metal center) to $[Ir(COD)Cl]_2$ produces white $[Ir(CNBu^t)_5H](PF_6)_2$ (**1**) after precipitation with ammonium hexafluorophosphate in methanol. Elemental analyses are in good agreement with this composition, and the source of the hydride is either the protic solvent or ammonium ion as has been previously observed in the formation of $[Ir(DPPM)(CNBu^t)_3H]^{2+}$ (DPPM = bis(diphenylphosphino)methane) [11]. Recrystallization by vapor diffusion of diethyl ether into an acetone solution of **1** gave colorless crystals that were the subject of an X-ray structural characterization. The ORTEP diagram of **1** is shown in Fig. 1. Five *t*-butyl isocyanides are bound to iridium in a square pyramidal arrangement. Selected interatomic distances and angles are also listed in Fig. 1. The isocyanide ligands are bonded in an idealized square pyramidal geometry, C(1)–Ir–C angles average ~90°, and only a slight bending, C(11)–Ir–C(31) = 176.4 and C(21)–Ir–C(41) = 173.6°, of the isocyanide ligands out of the equatorial plane is observed. The axial isocyanide ligand–iridium bond is also noticeably bent (Ir–C(1)–N(1) = 168.61°, *vs* ~175° average all other Ir–C–N angles).

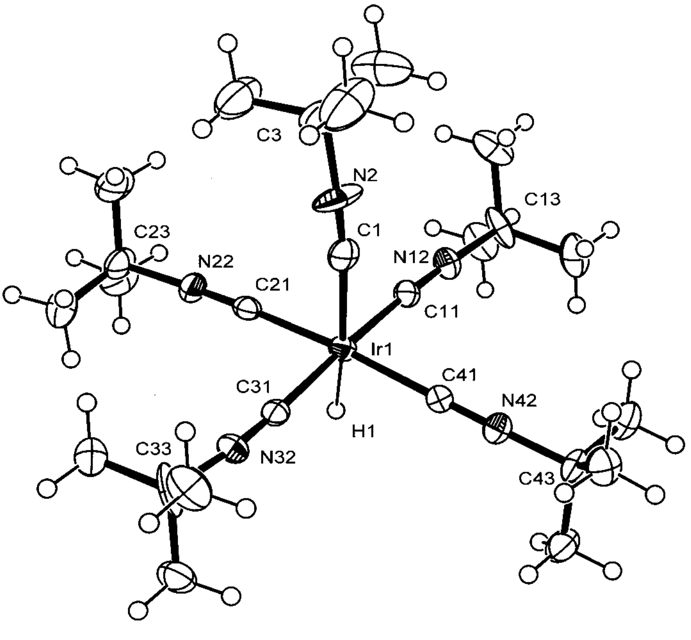

FIGURE 1 ORTEP (50%) diagram of the $[Ir(CNBu^t)_5H](PF_6)_2\cdot 2(CH_3COH_3)$ cation. Selected bond distances and bond angles: Ir–C(1) = 2.117(6), Ir–C(11) = 2.000(5), Ir–C(21) = 2.019(5), Ir–C(31) = 2.016(5), Ir–C(41) = 2.019(6) Å, C(11)–Ir–C(31) = 176.4(2), C(21)–Ir–C(41) = 173.6(2)°.

Additional physical studies, *vida infra*, suggest that a hydride atom is present in the molecule; however residual electron density in the difference map did not locate a hydride atom in the apparent open coordination site on the iridium, and for this reason, a hydride atom was placed in an idealized position (Ir–H = 1.6 Å) in accordance with reference 9. The axial carbon–iridium bond (C(1)–Ir = 2.117(6) Å) is ~0.1 Å longer than the other equatorial C–Ir bond distances, and the axial isocyanide carbon–nitrogen triple bond is also shorter (C(1)–N(1) = 1.108 Å). This is consistent with the *trans*-influence of an opposing hydride ligand. Ir–C bond distances compare well with other Ir–isocyanide complexes and are provided in the caption of Fig. 1 [11,12]. Figure 2 also shows the packing of the cations within the unit cell. Although equatorial planes do face each other, complexes are offset from each other and metal–metal bonds do not exist. The closest Ir–Ir contact is greater than 8.6 Å. Compound **1** is the structural analogue of $[Ir(DPPM)(CNBu^t)_3H]^{2+}$ generated by the addition of DPPM and NH_4PF_6 to $[Ir(CNBu^t)_4]Cl$ in ethanol [11]. This compound is also colorless and the hydride also exhibits a small *trans*-influence on the axial isocyanide Ir–C bond. $[Ir(CNR)_3(PPh_3)_2H]^{2+}$ complexes have also been isolated, but were not characterized by X-ray crystallography [13].

NMR and infrared studies provide strong evidence that this complex contains a hydride. A hydride resonance is observed at −12.5 ppm (singlet) in CD_3CN. This compares to hydride resonances of −10.6, −10.1, −10.9 and −16.2 ppm found in $[Ir_2(TM4)_4H_2]^{2+}$ (TM4 = 2,5-diisocyano-2,5-dimethylhexane), [12] $[Ir(DPPM)(CNR)_3H]^{2+}$ [11], $Ir(PPh_3(CNR)_3H]^{2+}$ [13], and $[Ir_2(\mu\text{-}CO)(\mu\text{-}H)(C(O)NHR)_2(CNR)_2(Me_2PCH_2PMe_2)_2]Cl$, [14] respectively. At room temperature, hydrogen and carbon resonances of the axial and equatorial ligands are also distinguishable in the correct 1 : 4 ratios, indicating **1** is nonfluxional. A weak hydride stretch at ~2120 cm^{-1} is

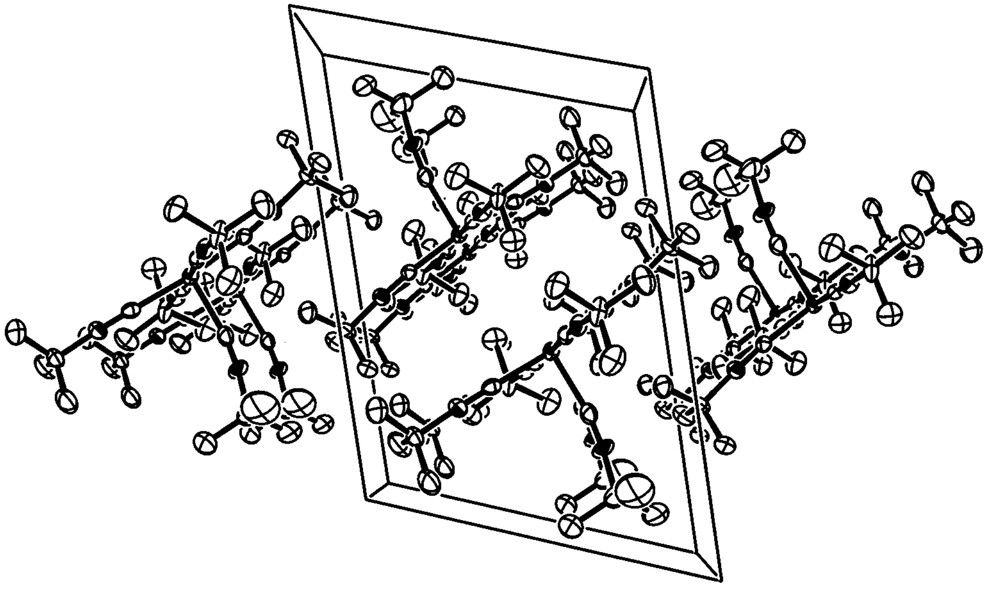

FIGURE 2 Packing diagram of the $[Ir(CNBu^t)_5H](PF_6)_2 \cdot 2(CH_3COCH_3)$ cation as viewed down the *b*-axis. PF_6 anions and all hydrogen atoms have been omitted for clarity.

observed in the infrared for films of **1** evaporated onto the surface of an ATR cell. This feature is completely lost after 24 h exchange in CH_3OD, and a new broad Ir–D stretch is observed at 1510–40 cm^{-1}. The position of the Ir–D band was dependent on whether deuterium exchange occurred before or after the growth of the ATR film, and the new peaks are quite broad and weak compounding the difficulty of an exact assignment.

The presence of the hydride and two PF_6 anions requires an oxidation state of +3 for iridium, which for an octahedral iridium complex would be d^6, low-spin, and diamagnetic. NMR spectra of **1** are normal for a diamagnetic complex and EPR measurements show that the complex is also diamagnetic, suggesting the complex is not an unusual paramagnetic, Ir(II) monomer. Lastly, cyclic voltammetry of **1** in acetone or acetonitrile/TBAH shows an irreversible reduction at ~ -1.60 V *vs* Ag/AgCl that is consistent with reduction of Ir(III) to either Ir(II) or Ir(I) species. No oxidative processes were observed as far positive as +2.0 V *vs* Ag/AgCl.

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