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Structural and Stereochemical Studies on Reactive Iridium(III) Dihydride Complexes of the Triphosphine Ligand $C_6H_5P[CH_2CH_2CH_2P(C_6H_{11})_2]_2$

CHIHAE YANG, STEVEN M. SOCOL, DENNIS J. KOUNTZ, DEVON W. MEEK*
Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, U.S.A.

and ROBERT GLASER
Department of Chemistry, Ben Gurion University of the Negev, Beersheva, 84105, Israel

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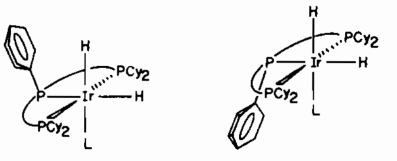
Abstract

The iridium(III) dihydride complexes $IrH_2X(Cyttp)$ (X = Cl, I) possess a *mer*-octahedral structure in which the hydrides are *cis* to each other and the Cyttp ligand is chelated around an edge of the octahedron. The phenyl group on the central phosphorus atom is oriented away from the chloride ligand in the crystal structure, and Nuclear Overhauser Effect (NOE) measurements show that this *anti* coordination geometry is maintained in solution. Treatment of $IrH_2Cl(Cyttp)$, **1a**, with $TlBF_4$ and CH_3CN results in a mixture of *anti* and *syn* diastereomers, whereas CO gives only the *syn* diastereomer of the type $[IrH_2(CH_3CN)(Cyttp)]^+$ and Tl^+.

Discussion

Transition metal hydride chemistry currently is attracting intense research interest [1]. Recent activity has resulted from discoveries that some phosphine–iridium–hydride compounds provide active homogeneous catalysts for hydrogenation of olefins [2], aromatization of cycloalkanes [3], and activation of C–H bonds [4]. Herein, we report the syntheses, structural characterizations, and stereochemical studies on some dihydride iridium(III) complexes of the chelating triphosphine ligand Cyttp ($Cyttp = C_6H_5P[CH_2CH_2CH_2P(C_6H_{11})_2]_2$).

The iridium(III) dihydride complex $IrH_2Cl(Cyttp)$, **1**, is prepared directly by treating $[IrCl(COD)]_2$ (COD = 1,5-cyclooctadiene) with the chelating triphosphine ligand Cyttp [5] in absolute ethanol**. On the basis of infrared, ^1H and $^{31}P\{^1H\}$ NMR spectra, the two hydrides are *cis* to each other and the Cyttp ligand is chelated around one edge of the octahedral iridium complex. Observation of one set of ^1H and ^{31}P NMR resonances indicated that only one of the two possible isomers of **1**, in which the phenyl group on the central phosphorus atom is oriented either *cis* or *trans* to the Cl, had been formed (Fig. 1) [6]. In order to determine the metrical details of the inner coordination geometry around



(mer, cis, anti) (mer, cis, syn)

Fig. 1. An illustration of the two projections of the phenyl group of an $IrH_2L(Cyttp)$ molecule relative to the IrP_3 plane. In the nomenclature of the complexes, *mer* designates the coordination geometry of the chelating triphosphine ligand, *cis* specifies that the two hydride ligands are adjacent to each other, *syn* designates the stereochemical position of the phenyl group on the central phosphorus atom as being on the same side of the IrP_3 plane as the ligand L, whereas *anti* specifies that the phenyl group is on the opposite side of the IrP_3 plane from L. In the text, **a** always corresponds to the *anti* diastereomer and **b** corresponds to the *syn* diastereomer.

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*Author to whom correspondence should be addressed.

**For footnote see right hand column.

**In a typical preparation $[IrCl(COD)]_2$ (500 mg, 0.745 mmol) in absolute ethanol (50 ml) was treated with 6.0 ml of a 0.25 M stock solution of Cyttp in benzene. The solution changed color, from red to yellow, as it was refluxed for 2 h. The solvent was removed at reduced pressure and the resultant residue was dissolved in CH_2Cl_2. Ethanol (30 ml) was added to the CH_2Cl_2 solution; subsequently, most of the CH_2Cl_2 was removed under reduced pressure and a solid precipitated. The solid was collected on a filter and washed with Et_2O; it was isolated in yields ranging from 30 to 50%. Infrared (KBr): 2235 (Ir–H2), 1995 (Ir–H1) cm^{-1}. $^{31}P\{^1H\}$ NMR (C_6H_6): $\delta = -0.7$ (d, P2, $^2J_{PP} = 27$ Hz); $\delta = -25.6$ (t, P_1); ^1H NMR (C_6D_6): $\delta = -9.1$ (H1, $^2J_{P1-H1} = 131$ Hz), $\delta = -22.3$ (H2). *Anal.* Calc. for $C_{36}H_{63}ClIrP_3$: C, 52.97, H, 7.72; Cl, 4.34. Found: C, 53.13; H, 7.67; Cl, 4.07%.

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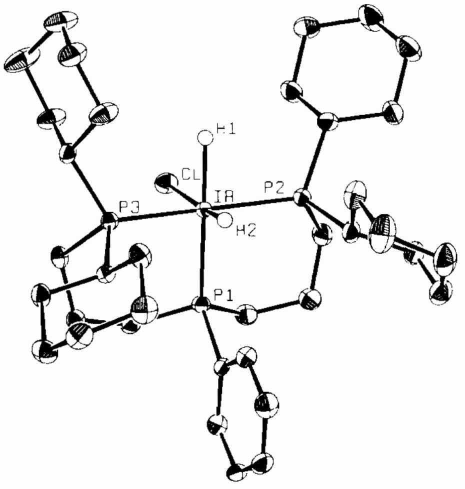

Fig. 2. ORTEP view of *mer, cis, anti*-IrH_2Cl(Cyttp). Selected bond distances (Å) are: Ir–P1 2.309(1), Ir–P2 2.305(1), Ir–P3 2.298(1), Ir–Cl 2.528(1), Ir–H(2) 1.70(5), Ir–H1 1.63, selected bond angles (deg) are: H2–Ir–Cl 173, P2–Ir–P3 170.67(4), H(1)–Ir–H(2) 80.1, H1–Ir–Cl 94(2), P1–Ir–P2 92.97(4), P1–Ir–Cl 84.66(4), P3–Ir–Cl 94.44(4), P1–Ir–P3 90.52(4), P2–Ir–Cl 94.50(4).

iridium and the relative orientation of the phenyl ring on the central phosphorus atom, an X-ray crystal structure analysis was performed.*

The structure of IrH_2Cl(Cyttp) is a six-coordinate, pseudo-octahedron (Fig. 2) in which three phosphorus atoms define a meridonal plane and the phenyl group on the central phosphorus atom is oriented away from the chloride ligand. The Ir–P distances (2.30–2.31 Å) are comparable to the Ir–P distances (2.28–2.43 Å) found in other Ir(III) phosphine complexes [8]. The Ir–Cl distance (2.528(1) Å) is similar to the Ir–Cl distance found in $IrH_2Cl[(C_6H_5)_2P(CH_2)_2CH{=}CH(CH_2)_2P(C_6H_5)_2]$ (2.510(5) Å [9] and $IrCl(H)(SH)(CO)(PPh_3)_2$ (2.492(3) Å) [10] but is significantly longer than the Ir–Cl distances (2.36–2.45 Å) found in other Ir(III) complexes, where Cl is not *trans* to a hydride ligand [11].

Nuclear Overhauser Effect (NOE) measurements provide direct evidence that the coordination geometry depicted in Fig. 2 is maintained in solution. On irradiation of the phenyl protons, the signal of the hydride ligand *trans* to Cl shows an NOE of ~5% in a nondegassed CD_2Cl_2 solution. The observation of a NOE is a consequence of the proximate orientation of the phenyl group toward H2 in space [12].

Considering the relatively long Ir–Cl bond, it was somewhat surprising that treatment of IrH_2Cl(Cyttp), **1a**, with $TlBF_4$ in THF or EtOH solution did not yield an immediate precipitate of TlCl. However, by use of CH_3CN (which has previously been shown to be a better ligand than EtOH or THF in complexes of the type $[IrH_2(PPh_3)_2(solv.)_2]^+$) [13] as a solvent, TlCl precipitated and $[IrH_2(CH_3CN)(Cyttp)]^+$ was isolated in 70% yield as a ~35/65 ratio of isomers **2a**/**2b**.** Isomers **2a** and **2b** were assigned on the basis of an NOE experiment [12]. On irradiation of the phenyl protons, an NOE was observed on only one of the hydride resonances (*i.e.*, the hydride ligand *trans* to CH_3CN of only one of the diastereomers (Fig. 3)). This diastereomer is assigned structure **2a**. In contrast, if one stirs a 40:1 ratio of NaI: **1a** in a THF solution, exclusive formation of *mer, cis, anti*-IrH_2I(Cyttp), **3a**, occurs; this iodide complex can be isolated in 85% yield on extraction with benzene†.

Introduction of CO bubbles (at atmospheric pressure) into a THF solution containing equivalent amounts of **1a** and $TlBF_4$ for a period of 4 h resulted in 40% conversion of IrH_2Cl(Cyttp) to the carbonyldihydride cation $[IrH_2(CO)(Cyttp)]^+$, **4**†† as determined by ^{31}P NMR spectroscopy. Compound **4**

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*Crystallographic data for *mer, cis, anti*-IrH_2Cl(Cyttp): triclinic space group $P\bar{1}$; $a = 12.636(2)$, $b = 13.110(2)$, $c = 11.120(1)$ Å, $\alpha = 97.65(1)°$, $\beta = 92.02(1)°$, $\gamma = 78.58(1)°$, $V = 1789.5(4)$ Å^3. Intensity data were collected on a Syntex P1 four-circle diffractometer at 159 K. The iridium atom was located by the Patterson method. All other nonhydrogen atoms were located by standard Fourier techniques (SHELX-76) [7]. The metal-hydride hydrogen atoms were located in a difference electron density map. Isotropic thermal parameters of both hydride ligands and the position of atom H2 were refined satisfactorily. Atom H1 was fixed at the position found on the difference electron density map. The remaining organic hydrogen atoms were assigned calculated positions ($d_{C-H} = 0.95$ Å, $B(H) = B_{iso}(C) + 1.0$ Å^2). Full matrix least squares refinement with all nonhydrogen atoms anisotropic (7945 reflections with $F_o^2 \geqslant 0$ ($\sin\theta/\lambda \geqslant 0.650$ Å^{-1} using Mo Kα radiation) converged at $R = 0.040$ and $R_w = 0.032$.

2: Infrared (KBr): 2285 (C≡N), 2245 (Ir–H2), 1995 (Ir–H1) cm^{-1}. *Anal.* Calc. for $C_{38}H_{66}BF_4IrNP_3$: C, 50.20; H, 7.33; N, 1.54. Found: C, 50.07; H, 7.41; N, 1.76%. **2a: ^{31}P NMR (CH_3CN): $\delta = -4.4$ (d, P2, $^2J_{PP} = 26$ Hz); $\delta = -30.5$ (t, P1); ^1H NMR (CD_3CN): δ – 10.3 (H1, $^2J_{P1-H1} = 121$ Hz), –21.0 (H2). **2b**: ^{31}P NMR (CH_3CN) $\delta = -0.5$ (d, P2, $^2J_{PP} = 24$ Hz), –37.9 (t, P1); ^1H NMR (CD_3CN) $\delta = -11.2$ (H1, $^2J_{P1-H1} = 121$ Hz), –21.8 (H2).

†**3a**: Infrared (KBr): 2225 (Ir–H2), 2000 (Ir–H1) cm^{-1}. $^{31}P1$ (C_6H_6): δ –8.6 (d, P2, $^2J_{PP} = 25$ Hz), –34.8 (t, P1); ^1H NMR (C_6D_6): δ –12.3 (H1, $^2J_{P1-H1} = 124$ Hz), –20.1 (H2). *Anal.* Calc. for $C_{36}H_{63}IIrP_3$: C, 47.62; H, 6.99; I, 13.98. Found: C, 47.55; H, 7.08; I, 13.76%.

††**4b**: Infrared (Nujol): 2103 (Ir–H2) *ca.* 2000 (Ir–H1) 1980 (CO) cm^{-1}. ^{31}P NMR ($(CH_3)_2CO$): $\delta = -1.7$ (d, P2, $^2J_{PP} = 22$ Hz), $\delta = -38.8$ (t, P1); ^1H NMR ($(CD_3)_2CO$): $\delta = -12.1$ (H1, $^2J_{P1-H1} = 105$ Hz), $\delta = -11.8$ (H2). *Anal.* Calc. for $C_{37}H_{63}BF_4IrOP_3$: C, 49.61; H, 7.09; P, 10.37. Found: C, 49.78; H, 7.29; P, 10.10%.

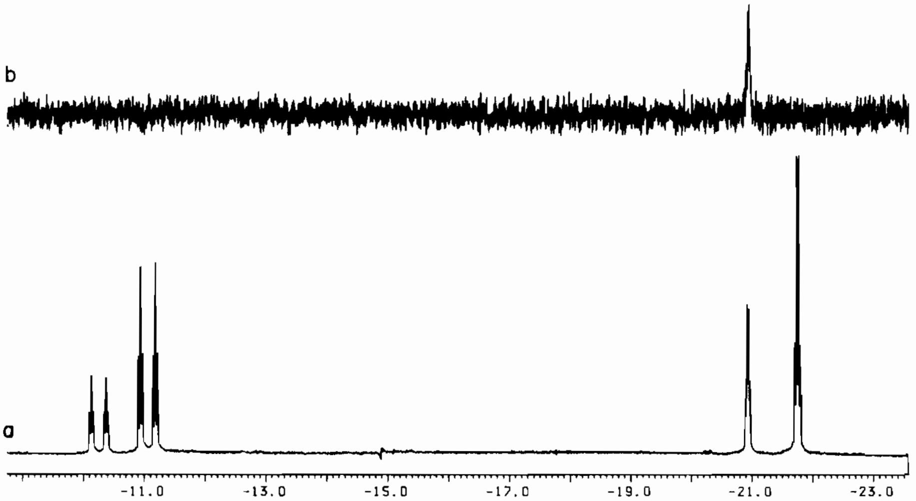

Fig. 3. (a) Proton NMR spectrum (500 MHz) of the hydride region of **2a**/**2b**; (b) NOE difference spectrum of the hydride region of **2a**/**2b** on irradiating the phenyl region (500 MHz).

can be separated from **1a** by extracting the mixture with acetone. Only one diastereomer of **4** was observed in its ^1H NMR spectrum. This isomer was later determined to be **4b** by an NOE experiment*. Introduction of CO bubbles into a THF solution containing a 35/65 ratio of **2a**/**2b** for 4 h converted that mixture into **4b** quantitatively.

The mechanistic details of formation of two diastereomers of **2** from the reaction of **1a** with Tl^+ in CH_3CN, the formation of only **3a** upon methathesis of the Ir–Cl bond in **1a** with excess I^- and the inversion of configuration at P1 on treating **1a** with CO in the presence of Tl^+ are presently unclear. Investigations of the stereochemical details of these reactions are continuing.

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*Preliminary X-ray diffraction studies confirm that the phenyl ring on P1 is orientated towards the CO moiety in **4b** (C.-H. Yang, S. M. Socol, R. Glaser, D. J. Kountz, J. C. Gallucci and D. W. Meek, to be published).

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