Competition between NH···HIr Intramolecular Proton−Hydride Interactions and NH···FBF_3^- or NH···O Intermolecular Hydrogen Bonds Involving [IrH(2-thiazolidinethione)$_4$(PCy_3)](BF_4)$_2$ and Related Complexes

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The reaction of $IrH_5(PCy_3)_2$ in acetone with 2 equiv of HBF_4 results in the formation of the air-stable complex $[Ir(H)_2(PCy_3)_2(acetone)_2]BF_4$, **1**. The reaction of **1** with an excess of 2-thiazolidinethione or 2-benzothiazolethione in the presence of 2 equiv of HBF_4 gives the complexes $[Ir(H)(PCy_3)(L)_4](BF_4)_2$ (**2a**, L = 2-thiazolidinethione; **2b**, L = 2-benzothiazolethione). Complex **2a** has an intramolecular NH···H(Ir)···HN interaction both in the crystalline solid as determined by X-ray diffraction and in a CD_2Cl_2 solution as determined by the T_1 method. The d_{HH} were determined to be 2.2 ± 0.1 Å in the solid state and 1.9 ± 0.1 Å in solution. The NH···H(Ir)···HN interactions and NH···F···HN hydrogen bonds which involve FBF_3^- form a four-member ring in a butterfly conformation. The nOe effect of the hydride on the NH proton is around 10%. A crystal of **2a** is in the triclinic space group $P\bar{1}$ with a = 11.426(3), b = 11.922(3), c = 19.734(4) Å, α = 87.05(1)°, β = 88.23(1)°, γ = 75.50(1)°, V = 2599(1) Å^3, and Z = 2 at T = 173 K; full-matrix least-squares refinement on F^2 was performed for 10 198 independent reflections; $R[F^2 > 2\sigma(F^2)] = 0.0480$, $R_w(F^2) = 0.099$. The formation of the NH···HIr proton−hydride interaction is as favorable as the formation of intermolecular hydrogen bonds NH···FBF_3^- or NH···O hydrogen bonds with $OPPh_3$ or H_2O in CD_2Cl_2. A similar NH···HIr interaction also has been observed in the complexes $[Ir(H)_2(PCy_3)_2(L)_2]BF_4$ (**3a**, L = 2-thiazolidinethione; **3b,** L = 2-benzothiazolethione) but not in the complexes with L = NH_2NH_2 (**3c**) and L = NH_3 (**3d**). Both the NH and IrH protons are deuterated when a solution of **2** or **3** in C_6D_6 is exposed to 1 atm of D_2 gas or D_2O.

Introduction

Recently intramolecular H···H interactions of the new types OH···H(Ir) and NH···H(Ir) have been reported.[1−3] Such hydride−proton interactions are thought to be important in the heterolytic splitting of dihydrogen and the formation of intermediate (dihydrogen)metal complexes.[4,5] We report here a study of the hydride−proton interactions NH···H(Ir)···HN and IrH···HN involving thiazolethione-type ligands and the crystal structure of [IrH(2-thiazolidinethione)$_4$(PCy_3)](BF_4)$_2$·CH_2Cl_2·Et_2O which contains three types of hydrogen-bonded units, namely NH···H(Ir)···HN, NH···F(B), and NH···F(B)···HN.

The strength of such proton−hydride interactions has been addressed in a variety of ways. Stevens et al.[1] noted that there appears to be a 2.40(1) Å proton−hydride interaction (IrH···HO) in the complex *cis*-[Ir(H)(HO)(PMe_3)$_4$]PF_6 in the crystal while there is no analogous IrH···HS interaction in the complex *cis*-[Ir(H)(HS)(PMe_3)$_4$]PF_6. Peris et al.[3a] have measured the barrier to C-NH_2 rotation when this group interacts with a hydride ligand as an IrH···HNH-C unit and compared it to intramolecular IrX···HN interactions. They found that IrH···HN interactions are favored over intramolecular IrCl···HN interactions in certain cases and that the ligand trans to the hydride can influence the strength of the proton−hydride interaction.[3] We have found that the strong hydrogen-bond acceptor $OPPh_3$ can disrupt the IrH···HN bonding in [Ir(H···HNC_5H_4S)$_2$(PCy_3)$_2$]$^+$ [2c] but not in [Ir(H···HNC_5H_4S)(NC_5H_4S)(PPh_3)$_2$]$^+$.[2a] In this paper we probe the strength of IrH···HN interactions by reaction with $OPPh_3$.

Experimental Section

All preparations were carried out under a dry argon atmosphere using Schlenk techniques. Benzene, diethyl ether, and hexanes were dried over and distilled from sodium. Acetone was dried over potassium carbonate. Dichloromethane was distilled from calcium hydride. Deuterated solvents were dried over Linde type 4Å molecular sieves and degassed prior to use. Tricyclohexylphosphine, triphenylphosphine, an 85% solution of HBF_4·Et_2O complex, 2-thiazolidinethione, and 2-benzothiazolethione were used as purchased from Aldrich Chemical Co. Inc. The complex $IrH_5(PCy_3)_2$ was prepared as described elsewhere.[6]

NMR spectra were recorded on Varian Unity-400 (400 MHz for ^{1}H, 61.4 MHz for ^{2}H) and Varian Gemini 300 (300 MHz for ^{1}H, 282.3 MHz for ^{19}F, 121.4 MHz for ^{31}P) spectrometers. All ^{31}P NMR spectra were recorded with proton decoupling. ^{31}P NMR chemical shifts were measured relative to 85% H_3PO_4 as an external reference, and ^{19}F NMR chemical shifts were measured relative to $CFCl_3$ as an external reference. ^{1}H chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. ^{2}H chemical shifts were referenced to natural-abundance deuterated solvent peaks. T_1 measurements were made at 400 or 300 MHz, as specified, using the inversion recovery method. The temperatures of the probes were calibrated with the temperature dependence of the chemical shifts of MeOH. Microanalyses were performed by Guelph Chemical Laboratories Ltd., Ontario, Canada.

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.

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Preparation of $[Ir(H)_2(PCy_3)_2(acetone)_2]BF_4$, 1. $IrH_5(PCy_3)_2$ (1 g, 1.32 mmol) was suspended in acetone (20 mL) in a Schlenk flask under argon. An Et_2O solution of ca. 2 equiv of HBF_4 (85% ethyl ether complex, 0.4 mL, 2.6 mmol) was added slowly (ca. 5 min) to the solution at room temperature. After completion of the addition, the solution was stirred for a further 10 min. The solvent was then partially removed under vacuum. Hexane (30 mL) was added to the mixture to produce a white powder. The white powder was filtered off, washed with *n*-hexane several times, and dried under vacuum. The yield was 90% (1.1 g). NMR (CD_2Cl_2, δ). $^{31}P\{^1H\}$ 38.2 (s); $^{19}F\{^1H\}$ −148.8 (s, br); ^1H −31.3 (t, 2H, $^2J_{PH}$ = 16.1 Hz, Ir−H), 1.2−2.1 (m, 66H, $P(C_6H_{11})_3$), 2.1 (s, 12H, C_3H_6O). Anal. Calc for $C_{42}H_{80}BF_4IrO_2P_2\cdot 0.1HBF_4$, **1**: C, 52.2; H, 8.3. Found: C, 51.9; H, 8.3.

Preparation of $[Ir(H)(PCy_3)(L)_4](BF_4)_2$ (2a, L = 2-Thiazolidinethione; 2b, L = 2-Benzothiazolethione). A mixture of $[Ir(H)_2(PCy_3)_2(acetone)_2]BF_4$, **1** (0.2 g, 0.21 mmol), L (excess, ≈1 mmol) and Et_2O solution of ca. 2 equiv of HBF_4 (85% diethylether complex, 0.65 mL, 0.42 mmol) in toluene (10 mL) were stirred under Ar for 2 h. Small amounts of insoluble impurities were filtered off. Then Et_2O (20 mL) was layered on the top of the solution. This was cooled in a refrigerator overnight. The next day, the resulting yellow crystalline **2** was filtered and washed with n-hexane several times and dried under vacuum. NMR (CD_2Cl_2, δ) for $[Ir(H)(PCy_3)(2\text{-thiazolidinethione})_4](BF_4)_2$, **2a** (yellow solid, yield 70%): $^{31}P\{^1H\}$ 29.4 (s); $^{19}F\{^1H\}$ −149.6 (s, 6F), −149.5 (s, 2F); ^1H −18.7 (d, H, $^2J_{HH}$ = 16.8 Hz, Ir−H), 1.1−2.5 (m, 33H, $P(C_6H_{11})_3$), 3.7 (m, 8H, $-SCH_2CH_2N-$), 4.33 (t, 4H, $^3J_{HH}$ = 8 Hz, $-SCH_2CH_2N-$), 4.22 (t, 2H, $^3J_{HH}$ = 8 Hz, $-SCH_2CH_2N-$), 4.20 (t, 2H, $^3J_{HH}$ = 8 Hz, $-SCH_2CH_2N-$), 8.95, 8.94 (br, 2s, 2H, N*H*), 9.23 (br, s, 2H, N*H*···H−Ir). Anal. Calc for $C_{30}H_{54}B_2F_8IrN_4PS_8\cdot 2C_7H_8\cdot C_4H_{10}O$, **2a**: C, 41.7; H, 5.8; N 4.1. Found: C, 41.5; H, 6.2, N, 4.2. NMR (CD_2Cl_2, δ) for $[Ir(H)(PCy_3)(2\text{-benzothiazolethione})_4](BF_4)_2$, **2b** (yellow solid, yield 66%): $^{31}P\{^1H\}$ 28.7 (s); ^1H −19.8 (d, H, $^2J_{HH}$ = 17 Hz, Ir−H), 1.1−2.5 (m, 33H, $P(C_6H_{11})_3$), 7−8 (m, 16H, Ar *H*), 8.55, 8.45 (br, 2s, 2H, N*H*), 8.6 (br, s, 2H, N*H*···H−Ir). Anal. Calc for $C_{46}H_{54}B_2F_8IrN_4PS_8$, **2b**: C, 42.0; H, 4.1; N 4.26. Found: C, 41.6; H, 5.1; N, 3.3.

Preparation of $[Ir(H)_2(PCy_3)_2(L)_2]BF_4$ (3a, L = 2-Thiazolidinethione; 3b, L = 2-Benzothiazolethione; 3c, L = NH_2NH_2; 3d, L = NH_3). A mixture of $[Ir(H)_2(PCy_3)_2(acetone)_2]BF_4$, **1** (0.2 g, 0.21 mmol), and L (0.42 mmol) in CH_2Cl_2 (10 mL) was stirred in a Schlenk flask under argon for 2 h. By an isolation procedure similar to that for **2**, yellow crystalline **3** was obtained. NMR (CD_2Cl_2, δ) for $[Ir(H)_2(PCy_3)_2(2\text{-thiazolidinethione})_2]BF_4$, **3a** (yellow solid, yield 75%): $^{31}P\{^1H\}$ 22.0 (s); ^1H −19.04 (t, 2H, $^2J_{PH}$ = 15 Hz, Ir−H), 1.0−2.1 (m, 66H, $P(C_6H_{11})_3$), 3.6 (t, 4H, $-SCH_2CH_2N-$), 4.2 (t, 4H, $-SCH_2CH_2N-$), 11.0 (br, s, 2H, NH). Anal. Calc for $C_{42}H_{78}BF_4IrN_2P_2S_4\cdot 0.5CH_2Cl_2$, **3a**: C, 45.5; H, 7.2; N, 2.6. Found: C, 45.2; H, 5.6; N, 2.6. NMR (CD_2Cl_2, δ) for $[Ir(H)_2(PCy_3)_2(2\text{-benzothiazolethione})_2]BF_4$, **3b** (yellow solid, yield 71%): $^{31}P\{^1H\}$ 16.2 (s); ^1H −19.2 (t, 2H, $^2J_{PH}$ = 15 Hz, Ir−H), 1.0−2.1 (m, 66H, $P(C_6H_{11})_3$), 7.2−8.0 (m, 8H, Ar), 12.0 (br, s, 2H, NH). Anal. Calc for $C_{50}H_{78}BF_4IrN_2P_2S_4$, **3b**: C, 51.1; H, 6.7; N, 2.4. Found: C, 51.2; H, 7.0; N 1.7. NMR (CD_2Cl_2, δ) for $[Ir(H)_2(PCy_3)_2(NH_2NH_2)_2]BF_4$, **3c** (yellow solid, yield 79%): $^{31}P\{^1H\}$ 16.5 (s); ^1H −24.2 (t, 2H, $^2J_{PH}$ = 15 Hz, Ir−H), 1.0−2.1 (m, 66H, $P(C_6H_{11})_3$), 3.6 (br, s, 4H, Ir−NH_2NH$_2$), 4.9 (br, s, 4H, Ir−NH$_2$NH_2). Anal. Calc for $C_{36}H_{76}BF_4IrN_4P_2$, **3c**: C, 49.4; H, 8.5; N, 6.18. Found: C, 49.3; H, 8.0; N, 5.6. NMR (CD_2Cl_2, δ) for $[Ir(H)_2(PCy_3)_2(NH_3)_2]BF_4$, **3d** (yellow solid, yield 77%): $^{31}P\{^1H\}$ 17.5 (s); ^1H −21.9 (t, 2H, $^2J_{PH}$ = 16 Hz, Ir−H), 1.0−2.1 (m, 66H, $P(C_6H_{11})_3$), 3.0 (br, s, 6H, NH_3).

A Typical NH···HIr Interception Experiment. A CD_2Cl_2 (1 mL) solution of complex **2a** (0.05 g) and $OPPh_3$ (0.05 g) or H_2O (0.005 g) was placed in an NMR tube under Ar and was shaken and left for 0.5 h to reach equilibrium. (a) NMR (δ) of the solution with the $OPPh_3$: ^1H −18.7 (d, HIr, J_{PH} = 16.8 Hz), −20.6 (d, HIr, J_{PH} = 19.2 Hz); ^{31}P 30.0 (s, br), 28.4 (s, $OPPh_3$). (b) NMR (δ) of the solution with H_2O: ^1H −18.7 (d, HIr, J_{PH} = 16.5 Hz), −20.7 (d, HIr, J_{PH} = 18.8 Hz); ^{31}P 30.0 (s, br).

X-ray Crystal Structure Analysis of 2a. Crystals of **2a** were prepared by slow diffusion of diethyl ether into a CH_2Cl_2 (1.5 mL) solution of complex **2a** (200 mg) under 1 atm of Ar.

A pale yellow crystal was mounted on a glass fiber. Intensity data were collected on a Siemens P4 diffractometer at 173 K, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The ω-scan technique was applied using variable scan speeds (6−60°/min in ω). The intensities of 3 standard reflections measured every 97 reflections showed no decay. Data were corrected for Lorentz, and polarization effects. A semiempirical absorption correction (minimum and maximum corrections were 0.5998 and 0.8042) was carried out using SHELXA-90 (in SHELXL-93).[7a]

The position of the Ir atom was determined from a Patterson map, and the other non-hydrogen atoms were located from successive difference Fourier maps. Non-hydrogen atoms were refined with anisotropic thermal parameters by least-squares calculations to minimize $\sum w(F_o^2 - F_c^2)$ where $w = 1/(\sigma^2(F_o) + (0.0236P)^2 + 3.877P)$ and $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms were included in calculated positions (C−H = 0.96 Å) with U_{iso} of 0.042(3) Å^2 for ring hydrogens, 0.092(27) A^2 for dichloromethane hydrogens, and 0.158(20) Å^2 for the hydrogens of the diethyl ether solvate. Hydrogen atoms bonded to Ir and N were refined with isotropic thermal parameters. Crystal data, data collection details, and least squares parameters are listed in Table 1. All calculations were performed, and diagrams were created on a 486-66 personal computer using SHELXL-93 and SHELXTL-PC V4.2.[7] Atomic coordinates and other data concerning the crystal structures are given in the Supporting Information. The structure of **2a**, including the crystallographic labeling scheme, is shown in Figure 1, and selected bond distances and angles are listed in Table 2.

Table 1. Crystal Data for **2a**

empirical formula: $C_{30}H_{54}IrN_4PS_8B_2F_8\cdot CH_2Cl_2\cdot C_4H_{10}O$

fw	1283.09	crystal system	triclinic
space group	$P\bar{1}$	λ, Å	0.71073
a, Å	11.426(3)	α, deg	87.05(1)
b, Å	11.922(3)	β, deg	88.23(1)
c, Å	19.734(4)	γ, deg	75.50(1)
V, Å^3	2599(1)	Z	2
D_{calcd}, mg m^{-3}	1.640	T, K	173(2)
μ(Mo Kα), mm^{-1}	3.086	2θ, deg	5.32−52.00
R^a	0.0480	$R_{2w}{}^b$	0.099

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $R_{2w} = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2a**

Ir−H(Ir)	1.44(6)	Ir−P	2.326(2)
H(Ir)···H(N1)	2.10(10)	H(Ir)···H(N2)	2.27(9)
N(1)−H(1A)	0.79(8)	N(2)−H(2A)	0.83(7)
N(3)−H(3A)	0.92(9)	N(4)−H(4A)	0.75(7)
F(2)···H(N1)	2.27(8)	F(2)···H(N2)	2.15(8)
F(8)···H(N4)	2.16(8)	Ir−S(1)	2.343(2)
Ir−S(2)	2.351(2)	Ir−S(4)	2.434(2)
Ir−S(3)	2.499(2)		
H(N1)···H(Ir)···H(N2)	105(4)	H(N1)···F(2)···H(N2)	103(4)
Ir−H(Ir)···H(N1)	116(4)	Ir−H(Ir)···H(N2)	114(4)
H(Ir)−Ir−P	83(3)	H(Ir)−Ir−S(1)	93(3)
P−Ir−S(1)	91.80(6)	H(Ir)−Ir−S(2)	97(3)
P−Ir−S(2)	90.91(6)	S(1)−Ir−S(2)	170.35(6)
H(Ir)−Ir−S(4)	79(3)	P−Ir−S(4)	61.70(5)
S(1)−Ir−S(4)	91.51(6)	S(2)−Ir−S(4)	88.82(6)
H(Ir)−Ir−S(3)	175(3)	P−Ir−S(3)	101.42(6)
S(1)−Ir−S(3)	86.16(6)	S(2)−Ir−S(3)	84.22(6)
S(4)−Ir−S(3)	96.76(6)	Ir−H(Ir)−P	63(2)

Results and Discussion

Preparation of the Complexes. Treatment of $IrH_5(PCy_3)_2$ with 2 equiv of HBF_4 in acetone gives a clear solution (see eq 1).[8] The analytically pure, air-stable complex $[Ir(H)_2(PCy_3)_2$-

(7) (a) Sheldrick, G. M. *SHELXL-93: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1994. (b) Sheldrick, G. M. *SHELXTL PC*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

(8) The method of protonation of $IrH_5(PPh_3)_2$ to give $[Ir(H)_2(acetone)_2(PPh_3)_2]^+$ has been reported: Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1 and references cited therein.

$$Ir(H)_5(PCy_3)_2 + HBF_4 \xrightarrow{\text{acetone}} [Ir(H)_2(\text{acetone})_2(PCy_3)_2]BF_4 \quad (1)$$

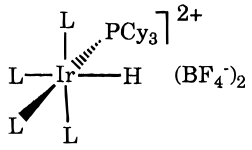
1

$(\text{acetone})_2]BF_4$ (**1**) crystallizes from the acetone solution in 2 h. A nearly quantitative yield can be achieved when **1** is separated from a concentrated acetone solution by addition of *n*-hexane. Other complexes of the type $[Ir(H)_2(PR_3)_2(L)_2]BF_4$ (R = Ph, Cy) are well known.[9]

When complex **1** was treated with an excess of 2-thiazolidinethione or 2-benzothiazolethione in CH_2Cl_2 in the presence of 2 equiv of HBF_4 for 2 h, a clear yellow solution was obtained (see eq 2). The yellow complexes $[Ir(H)(PCy_3)(L)_4](BF_4)_2$ (**2a**,

$$[Ir(H)_2(\text{acetone})_2(PCy_3)_2]BF_4 + L\ (\text{excess}) \xrightarrow{2\ HBF_4}$$

1



(2)

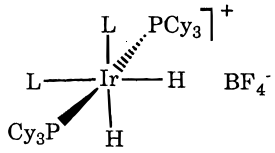
2a: L = 2-thiazolidinethione
2b: L = 2-benzothiazolethione

L = 2-thiazolidinethione; **2b**, L = 2-benzothiazolethione) can be obtained by slowly diffusing diethyl ether into the solution followed by washing with hexanes and drying under vacuum. The analytical and spectroscopic data are consistent with the proposed structure **2**.

The addition of 2 equiv of L to a C_6H_6 solution of **1** at room temperature under Ar atmosphere produces the complexes $[Ir(H)_2(PCy_3)_2(L)_2]BF_4$ (**3a**, L = 2-thiazolidinethione; **3b**, L = 2-benzothiazolethione; **3c**, L = NH_2NH_2; **3d**, L = NH_3) as yellow solids after precipitation of the product from the solution by addition of ethyl ether (see eq 3). The analytical and spectroscopic data are consistent with the proposed structure **3**.

$$[Ir(H)_2(\text{acetone})_2(PCy_3)_2]BF_4 + 2L \longrightarrow$$

1



(3)

3a: L = 2-mercaptothiazoline
3b: L = 2-mercaptobenzothiazole
3c: L = NH_2NH_2
3d: L = NH_3

X-ray Diffraction Study of 2a at 173 K. The molecular structure of **2a** contains an iridium atom in a distorted octahedral environment (Figure 1). The iridium atom is surrounded by one PCy_3 ligand, four 2-thiazolidinethione ligands bonded *via* sulfur atoms in a monodentate fashion, and a hydride ligand *cis* to the PCy_3 ligand. The phosphorus atom of the tricyclohexylphosphine and the sulfur atom *trans* to it are slightly bent toward the hydride. The H−N−C−S− units of two 2-thiazolidinethione ligands coordinated to the iridium atom at *cis* positions to the hydride are planar and embrace the Ir−H hydride with close NH···HIr contacts at an H···H distance of 2.2 ± 0.1 Å. The hydride on iridium and the hydrogen on the protonated nitrogens N1, N2 (Figure 2) and N4 are well-defined in electron difference maps. Selected bond lengths and bond angles are listed in Table 2.

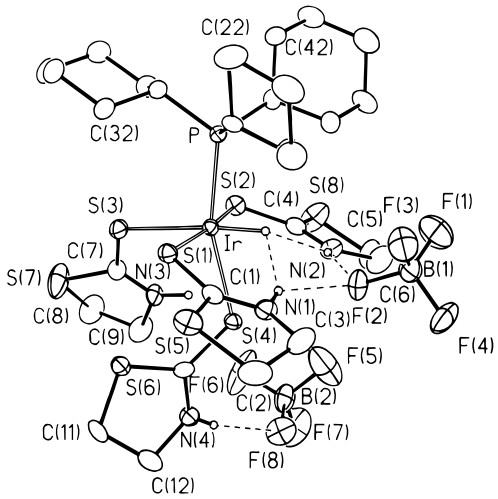


Figure 1. View of **2a** showing the atomic labeling scheme. Thermal ellipsoids are at the 50% probability level. For clarity, hydrogen atoms are shown as small spheres.

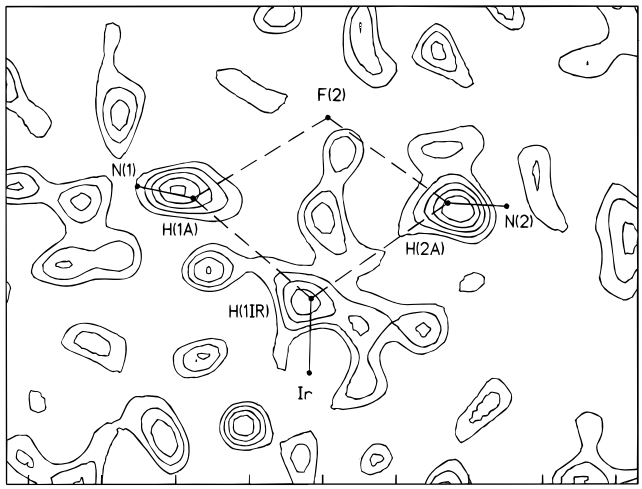
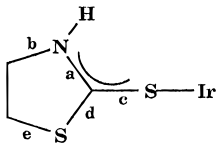


Figure 2. Difference electron density map around the Ir and N centers showing the positions of hydrogen atoms (calculated in the plane of H(1Ir), H(1A), and H(2Aa) with contours every 0.1 e $Å^{-3}$).

One of the fluorine atoms (F2) of a BF_4 anion forms two weak hydrogen bonds (H···F···H) at distances of 2.15(8) and 2.27(8) Å with the two NH units which are interacting with hydride. The NH···H(Ir)···HN interactions and NH···F···HN hydrogen bonds form a four-membered ring in a butterfly conformation (see Figure 1). A weaker interaction of this type with H···F distances of 2.4 Å is present in the structure of $[IrH(\cdots HNC_5H_4S)_2(NC_5H_4S)(PCy_3)]BF_4$.[2b] The observation of a bifurcated hydrogen bond IrH···H(N)···F(B) involving one NH group has also been reported.[2a] The other BF_4^- anion in the lattice forms a strong hydrogen bond with another free NH group (F···H distance of 2.16(8) Å). No close NH···S contact is observed in the structure, and hence there is no indication of an NH···S hydrogen bond. In the S-bonded 2-thiazolidinethione ligand, the proton is located only on nitrogen and not on a sulfur. The double-bond character is delocalized on both (S)C−N and S−C(S) bonds, although a S=C(S) double bond is drawn in the molecular structures of **2** and **3**. Both bond

(9) (a) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032. (b) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Sen, A.; Chebolu, V. *Inorg. Synth.* **1989**, *26*, 122−126. (c) Luo, X.-L.; Schulte, G. K.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 682.

Table 3. N−C and S−C Bond Distances of Complex **2a**



a:[a] N−C(S)		b:[a] N−C(C)		c:[a] S−C(S)		d:[a] S−C(S)		e:[a] S−C(C)	
N1−C1	1.304(9)	N1−C3	1.470(9)	S1−C1	1.690(7)	S5−C1	1.741(6)	S5−C2	1.828(7)
N2−C4	1.293(9)	N2−C6	1.449(9)	S2−C4	1.701(7)	S6−C10	1.740(7)	S6−C11	1.829(7)
N3−C7	1.317(9)	N3−C9	1.448(8)	S3−C7	1.688(7)	S7−C7	1.730(7)	S7−C8	1.826(7)
N4−C10	1.294(8)	N4−C12	1.466(9)	S4−C10	1.702(7)	S8−C4	1.727(7)	S8−C5	1.797(7)

[a] The bond types refer to the structure above.

Table 4. Proton Minimum T_1 Values (at 400 MHz) of Complexes **2** and **3** in CD_2Cl_2, Calculated NH···HIr Distances, and nOe Enhancements

complex	T_1(min)(IrH), s	T, K	$d_{NH\cdots HIr}$, Å	T_1(min)(NH···H), s	T, K	nOe(NH···H−Ir), %
2a	0.18 ± 0.01	233	1.9 ± 0.1	0.23 ± 0.01	233	14.3
2b	0.19 ± 0.01	243	2.0 ± 0.1	0.24 ± 0.01	243	13.2
3a	0.22 ± 0.01	213	2.0 ± 0.1[a]	0.24 ± 0.01	213	10
3b	0.23 ± 0.01	213	2.1 ± 0.1[a]			8.5
3c	0.24 ± 0.01	213				0

[a] The relaxation contributions of the four cyclohexyl protons at about 2.4 Å have been subtracted.

distances of N−C(S) and S−C(S) are considerably shorter than the corresponding bond distances of N−C(C) and S−C(C) (see Table 3). The Ir−S bond distances are also influenced by the NH···H(Ir)···HN interactions. Sulfur atom S(3) which is *trans* to the hydride and sulfur atom S(4) which is *cis* to the hydride have significantly longer Ir−S bonds (2.499(2) and 2.434(2) Å, respectively) than the sulfur atoms of 2-thiazolidinethione which have NH···HIr interactions (2.343(2) and 2.351(2) Å, respectively). The *trans* influence of the hydride causes Ir−S(3) to be the longest distance.

NMR Studies of Complexes 2. The ^{1}H NMR study of complexes **2** provides additional evidence for the existence of the $NH_a\cdots H(Ir)\cdots H_aN$ interaction in solution (refer to Scheme 1 for labeling of H_a, H_b, and H_c). The hydride of **2a** has a very short minimum T_1 value of 0.18 s (at 400 MHz, 243 K), and this implies a strong H···H interaction. When the relaxation contributions of the two cyclohexyl protons at about 2.3 Å are subtracted from the hydride relaxation rate, the calculated hydride to H_a distance is 1.9 ± 0.1 Å.[10,11] Interestingly, the protons bonded to nitrogen atoms have quite different minimum T_1 values. The two NH_a protons with a resonance at 9.23 ppm have a shorter minimum T_1 value (0.23 s, at 400 MHz, 243 K) than that of the other two NH protons (H_b, H_c) with resonances at 8.94 and 8.95 ppm with the same T_1(min) value (0.35 s, at 400 MHz, 243 K). The NH_a protons are considered to have an interaction with the hydride which leads to efficient dipole−dipole relaxation. The NH_a protons are close to three types of dipolar nuclei: ^{14}N, ^{19}F, and ^{1}H (hydride). When the contributions of the one ^{14}N nucleus at 0.95 Å and one ^{19}F nucleus at 2.2 Å to the rate of dipolar relaxation are subtracted, the calculated (Ir)H to HN distance is 1.9 ± 0.1 Å, in agreement with the distance calculated on the basis of the hydride T_1(min) value. This NH···HIr distance estimated by the T_1 method is close to the H···H distance revealed by the X-ray structural analysis of 2.2 Å. The presence of the NH···H(Ir)···HN interaction in solution was also confirmed by the nOe difference experiments. By selective irradiation of the hydride resonance, a 14% nOe enhancement of the NH_a peak at 9.23 ppm was observed while there was less than a 3% nOe enhancement for the NH_b and NH_c protons which have no close contact with the hydride (see Table 4). Very similar results were obtained for complex **2b** (see Table 4).

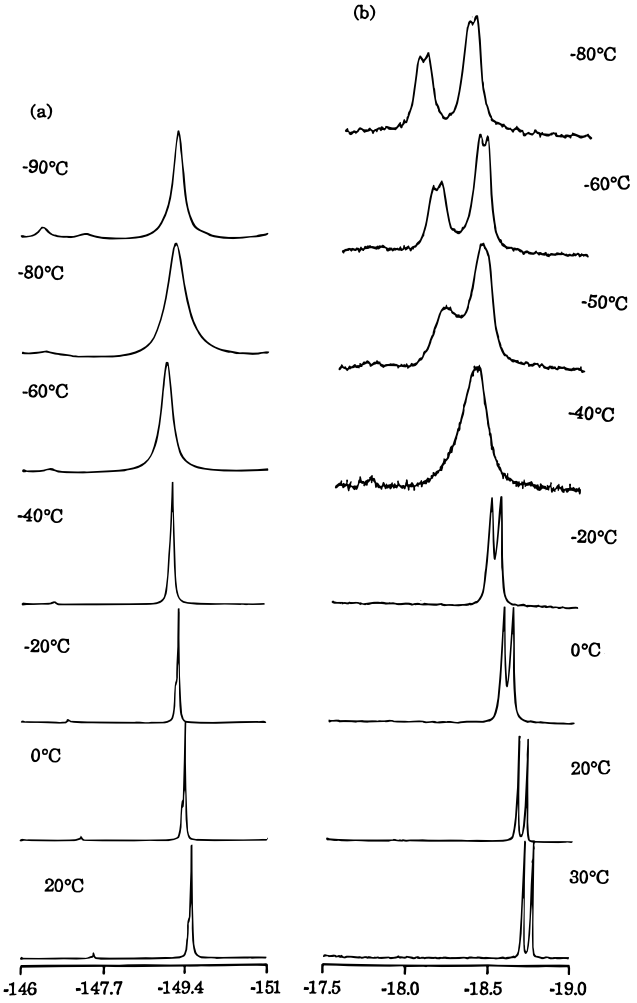
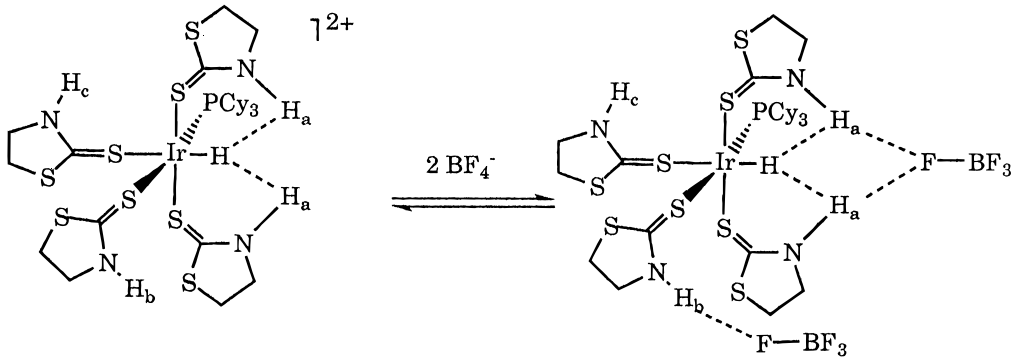


Figure 3. Variable-temperature NMR study of **2a** in CD_2Cl_2: (a) ^{19}F NMR (282 MHz); (b) ^{1}H NMR (300 MHz) in the hydride region (−17.5 to −19.0 ppm).

(10) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173−4184.
(11) Sudmeier, J. L.; Anderson, S. E.; Frye, J. S. *Concepts Magn. Reson.* **1990**, *2*, 197−212.

Scheme 1



Although the NH_b and NH_c protons have longer minimum T_1 values than the NH_a protons, the minimum T_1 values of the NH_b and NH_c protons are still shorter than would be expected for an NH proton which is only relaxed by the one ^{14}N nucleus at 0.95 Å (minimum T_1 value of ca. 0.6 s). The (B)F···HN hydrogen bond should have an important contribution to the dipole−dipole relaxation of HN. After subtracting the contributions of the one ^{14}N nucleus at 0.95 Å to the dipole−dipole relaxation, the calculated NH···F(B) distance is 2.2 ± 0.1 Å which is the same as the distance revealed by the X-ray analysis (2.16(8) Å). Therefore, the BF_4^- anions are associated with these NH groups in solution.

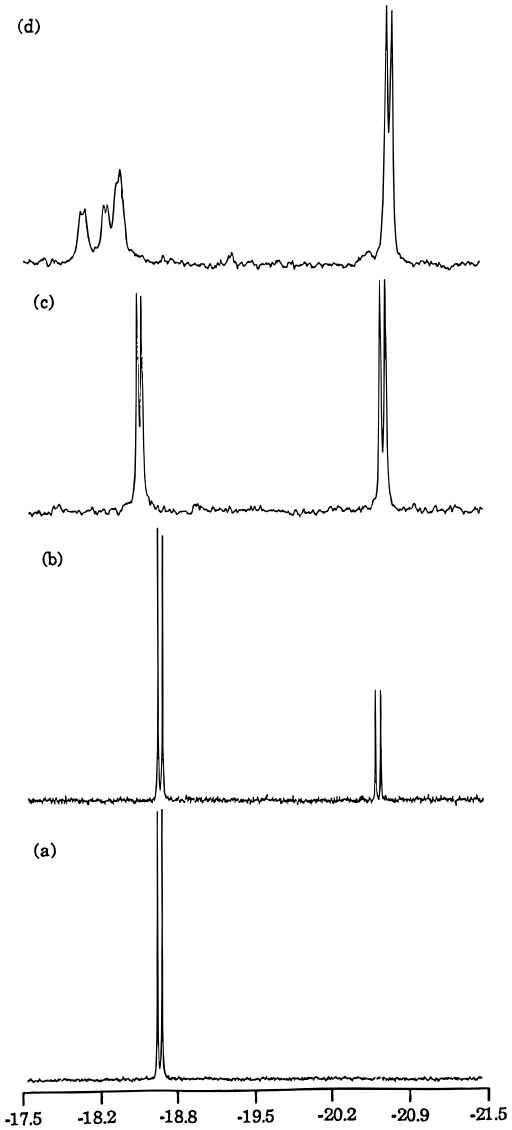
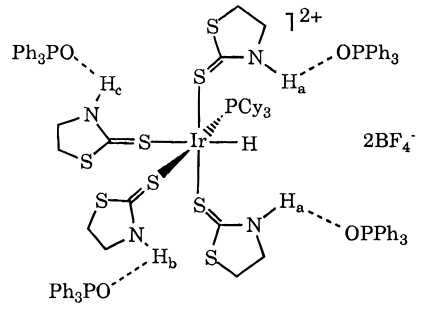


Figure 4. ^1H NMR spectra (400 MHz) of **2a** in the hydride region (−17.5 to −21.5 ppm) in CD_2Cl_2: (a) without $OPPh_3$ at 0 °C; (b) with $OPPh_3$ at 0 °C; (c) with $OPPh_3$ at −20 °C; (d) with $OPPh_3$ at −80 °C.

The X-ray structure analysis of **2a** reveals that the BF_4 anions form hydrogen bonds at two different sites. However the variable-temperature ^{19}F NMR study of **2a** in CD_2Cl_2 solution indicates that the BF_4^- anions which produce a sharp peak at −149.6 ppm are apparently rapidly moving among all of the possible hydrogen-bonding sites in solution at room temperature (see Figure 3a). Even at −90 °C, the fluxional process of the BF_4^- cannot be frozen out although some new small resonances at −146.5 and −147.4 ppm begin to grow in. With decreasing temperature, the ^{19}F resonances become very broad. The variable-temperature ^1H NMR study of complex **2a** in CD_2Cl_2 confirms that at least one exchange process is occurring. At lower temperature (< −40 °C), the doublet at −18.7 ppm splits into two doublets (see Figure 3b) probably due to the BF_4^- anion forming hydrogen bonds at different NH sites (see Scheme 1). The NH proton resonances at 9.23, 8.95, and 8.94 ppm also shift with decreasing temperature and become broad multiplets at −80°C. It is believed that the hydrogen bonds between the BF_4^- anion and the NH protons of the 2-thiazolidinethione ligands are more fully formed at low temperature as shown in Scheme 1 to generate two or even more different hydride NMR resonances and two or more sets of NH proton resonances.

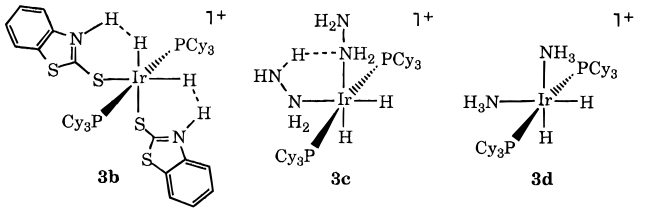
The NH···H(Ir)···HN interaction in **2** is comparable in strength to that of NH···O hydrogen bonds. In the presence of a better hydrogen-bond acceptor such as $OPPh_3$, H_2O, or THF, the NH···HIr interaction is partly intercepted (see Figure 4). A new species with a hydride resonance at −20.6 ppm (d, J_{PH} = 19.2 Hz) appears, and its intensity increases with an increasing ratio of $OPPh_3$ to **2a**. However, the NH···(Ir)···HN interaction cannot be completely disrupted even in the presence of excess $OPPh_3$. That the pattern of the new hydride resonance at −20.6 ppm does not change with decreasing temperature (see Figure 4d) implies that all the NH interactions with the iridium hydride and the fluorine of the BF_4^- anions have been replaced by hydrogen bonds with $OPPh_3$ (see structure **A**). The competition



A

between the two types of hydrogen bonds, NH···H(Ir)···HN and O···HN reaches equilibrium at room temperature in a slow exchange mode. At low temperature (−20 °C), the equilibrium favors the formation of the O···HN hydrogen bond (see Figure 4b,c). The pattern of the hydride resonance at −18.7 ppm still changes with decreasing temperature to give several doublet resonances of hydrides, apparently due to the formation of complex hydrogen-bonded structures. The disappearance of the nOe enhancement of the NH resonances when the new hydride resonance at −20.6 ppm was irradiated and the longer minimum T_1 value (0.34 s, at 400 MHz, 273 K) of this hydride resonance are strong evidence for the breaking of the NH···HIr interactions. Therefore, the intramolecular NH···(Ir)···HN interaction has a stability similar to that of an intermolecular NH···O hydrogen bond which should be favored on the basis of enthalpy of formation but disfavored on the basis of entropy. These H···H interactions are more stable than the interionic NH···FBF_3 hydrogen bonds. They are also favored over NH···S intramolecular hydrogen bonds which might have formed between the thiazolidinethione moieties.

NMR Studies of Complexes 3. The same NH···HIr interactions have been detected for complexes **3a** and **3b** in solution (see diagram **B** for structure of **3b**). The T_1 and nOe studies



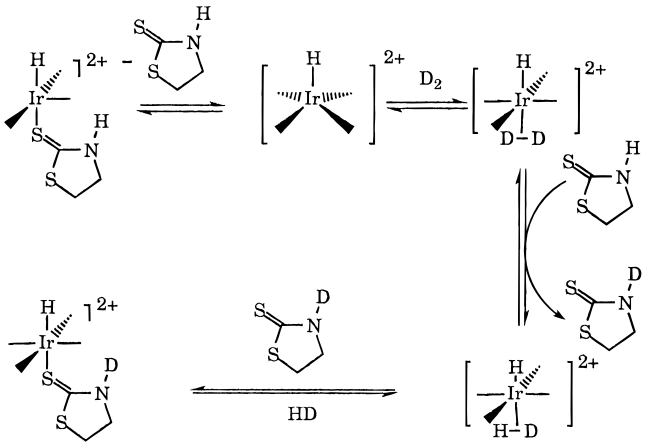
B

(see Table 4 for details) of **3a** and **3b** verify the existence of the NH···HIr interactions. The calculated NH···HIr distances by the minimum T_1 method are listed in Table 4. Crystals of these complexes lose solvent easily, making them unsuitable for X-ray analysis. The observation of a partially resolved splitting of 4 Hz in the hydride resonance of **3b** may be due to a coupling to H on nitrogen and indicates a close contact between NH and hydride. A similar $^1J_{NH\cdots HIr}$ coupling constant has been observed by Crabtree and co-workers.[3] The NH···HIr interaction in **3a** or **3b** is weaker than NH···O hydrogen bonds. In the presence of a better hydrogen-bond acceptor such as $OPPh_3$ or H_2O, the NH···HIr interaction is intercepted completely. As in the case of complex **2a**, the disappearance of the nOe enhancement of the NH resonances when the hydride of complex **3a** was irradiated, the disappearance of the possible coupling between the NH proton and the Ir−H resonance, and the longer minimum T_1 value (0.35 s at 400 MHz, 263 K) of the hydride resonance are strong evidence for the interception.

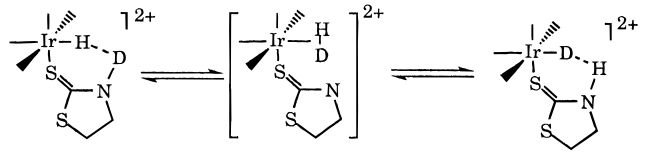
When the hydride resonance of complex **3c** is irradiated in CD_2Cl_2 at room temperature, no nOe enhancement of the NH proton resonances is observed. Instead, CH proton resonances of the PCy_3 ligand are enhanced. When the terminal amine of the hydrazine ligand is irradiated, a strong nOe enhancement is observed on the NH_2 coordinated to Ir. Therefore, there is no intramolecular NH···HIr interaction (see **B**) in **3c**. Apparently, the intramolecular NH···N hydrogen bonds are stronger than the intramolecular NH···HIr interactions.

Hydrogen/Deuterium Exchange Reactions. When a solution of either complex **2a** or **2b** in CD_2Cl_2 is exposed to D_2 (1 atm) or is mixed with D_2O (excess) for 5 min, the intensities of both the NH and IrH resonances in the ^{1}H NMR decrease by

Scheme 2



Scheme 3



about 5%. After 12 h, about 100% of NH and 30% of (Ir)H have been deuterated. ^{2}H NMR experiments confirm that there is deuteration of these two sites. The deuteration processes of **3a** and **3b** under D_2 gas are much faster than that of **2**. The deuteration of **3a** or **3b** is finished in less than 10 min at the NH sites and about 6 h at the (Ir)H sites. The NH proton is deuterated much faster than the iridium hydride. In contrast, the deuteration of **3c** or **3d** is much slower, although a partial deuteration (∼20%) has been observed after a 24 h exposure to D_2 gas. Therefore, it is quite possible that the H/D exchange of **2**, **3a**, and **3b** with D_2 results from the formation of an intermediate dihydrogen complex by dissociation of one thione ligand, probably the one *trans* to the hydride. The exchange between acidic dideuterium and the active protons of amides results in the deuteration of NH protons as shown in Scheme 2. Since the deuteration of the NH is much faster than that of the hydride, the dideuterium is thought to coordinate *trans* to the hydride. Otherwise the dideuterium and hydride exchange would be expected to be very fast if the deuterium and hydride were in *cis* positions.[5]

The NH···H(Ir)···HN interaction may be responsible for the deuteration of the iridium hydride. Initially, the NH···H(Ir)···HN interaction generates a dihydrogen intermediate via intramolecular proton transfer from NH to IrH. Then the exchange between the two tautomers (see Scheme 3) leads to deuteration of the hydride. This mechanism has been proposed previously to explain the H/D exchange reactions of [Ir(H···$HNC_5H_4S)_2(PCy_3)_2$]BF_4.[2c]

Conclusions

The intramolecular NH···H(Ir)···HN interaction with $d_{HH} \approx$ 1.9 is established to exist in complexes **2a** ([IrH(2-thiazolidinethione)$_4$(PCy_3)](BF_4)$_2$) and **2b**. These NH···HIr interactions are as stable as intermolecular NH···O hydrogen bonds in solution and more stable than intermolecular NH···F(B) hydrogen bonds to the BF_4^- anions. The deuteration of the NH protons by reaction of **2a** with D_2 may result from the formation of an acidic dideuterium intermediate formed after a thione ligand dissociates whereas the deuteration of the iridium hydride may proceed *via* an exchange process between the ND groups

and hydride in the intramolecular ND···H(Ir)···DN interaction. The crystalline structure of **2a** contains a novel four-membered ring defined by the NH···H(Ir)···HN and NH···F(B)···NH interactions.

Complexes **3a** and **3b** with these thione ligands also have NH···HIr contacts as indicated by T_1(min) and nOe experiments. Here again, the NH groups are deuterated upon reaction with D_2 at a greater rate than the hydride on iridium. The hydrazine ligands in complex **3c** preferentially form intramolecular NH···N hydrogen bonds over NH···HIr interactions. As expected, complex **3d** with ammine ligands does not have an NH···HIr contact.

Acknowledgment. This work was supported by grants to R.H.M. from the NSERC of Canada and the Petroleum Research Fund, administered by the American Chemical Society, by a loan of iridium salts from Johnson Matthey Ltd., and by an NSERC postdoctoral fellowship to W.X.

Supporting Information Available: Tables giving a structure determination summary, atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates (9 pages). Ordering information is given on any current masthead page.

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