Weak M—H···H—C interactions observed in ruthenium and iridium complexes containing hydride, amine, and bulky phosphine ligands

Wei Xu, Alan J. Lough, and Robert H. Morris

Abstract: New amineruthenium and amineiridium hydride derivatives have been synthesized and characterized with the objective of observing intramolecular MH···HN or MH···HO interactions. These include $RuHCl(CO)(L)(PPr^{i}_3)_2$ (**1***a*, L = NH_2NH_2; **1***b*, L = NH_3) and $IrCl_2(L)(H)(PCy_3)_2$ (**2***a*, L = $SC(NH_2)_2$; **2***b*, L = NH_3; **2***c*, L = NH_2NH_2; **2***d*, L = $NH_2(CH_2)_3NH_2$; **2***e*, L = NH_2OH). Instead, weak M—H···H—C van der Waals contacts have been detected in the solid state by X-ray analysis and in solution by NMR T_1 measurements and nOe techniques. Both X-ray crystal structure analysis and minimum T_1 measurements indicate that the H···H distances in the M—H···H—C interactions are ca. 2.0–2.2 Å. The weak interactions might influence the course of deuteration of these complexes under D_2 gas. The crystal and molecular structure of $IrCl_2(NH_3)(H)(PCy_3)_2$ **2***a* has been determined by X-ray diffraction at 173 K: monoclinic, space group $P2_1/n$, a = 14.859(2) Å, b = 18.579(3) Å, c = 18.548(3) Å, β = 97.29(1)°, V = 5079.1(13) Å^3, Z = 4, full-matrix least-squares refinement on F^2 for 10 953 independent reflections; $R[F^2 > 4\sigma(F^2)] = 0.0283$, $wR(F^2) = 0.0704$.

Key words: ruthenium, iridium, hydride, dihydrogen, complexes, hydrogen bond, NMR, X-ray.

Résumé : On a synthétisé et caractérisé de nouveaux hydrures dérivés de l'amineruthénium et de l'amineiridium pour observer des interactions intramoléculaires MH···HN ou MH···HO. Ils comprennent le $RuHCl(CO)(L)(PiPr_3)_2$ (**1***a*, L = NH_2NH_2; **1***b*, L = NH_3) et $IrCl_2(L)(H)(PCy_3)_2$ (**2***a*, L = $SC(NH_2)_2$; **2***b*, L = NH_3; **2***c*, L = NH_2NH_2; **2***d*, L = $NH_2(CH_2)_3NH_2$; **2***e*, L = NH_2OH). À la place des interactions recherchées, on a observé de faibles contacts de van der Waals MH···HC tant à l'état solide (par diffraction des rayons X) qu'en solution (par des mesures de T_1 et par les techniques d'eOn en RMN). L'analyse des structures cristallines et les minima dans les mesures de T_1 indique que les distances H···H dans les interactions M—H···H—C sont de l'ordre de 2,0–2,2 Å. Ces faibles interactions peuvent influencer le cours de la deutération de ces complexes par le D_2 à l'état gazeux. On a déterminé les structures cristalline et moléculaire du $IrCl_2(NH_3)(H)(PCy_3)_2$ (**2***a*) par diffraction des rayons X à 173 K; les cristaux sont monocliniques, groupe d'espace $P2_1/n$, avec a = 14,859(2), b = 18,579(3) et c = 18,548(3) Å, β = 97,29(1)°, V = 5079,1(13) Å^3, Z = 4, $R[F^2 > 4\sigma(F^2)] = 0{,}0283$ et $wR(F^2) = 0{,}0704$ pour un affinement par la méthode des moindres carrés sur F^2 pour 10 953 réflexions indépendantes.

Mots clés : ruthénium, iridium, hydrure, dihydrogène, complexes, liaison hydrogène, RMN, rayons X.

[Traduit par la rédaction]

Introduction

Weak hydrogen bonds involving carbon–hydrogen bonds, C—H···X (X = O, N, or Cl), have been found to play a significant role in molecular conformation, molecular assemblies, and crystal engineering (1–3). They sometimes are crucial in structural stabilization of biological systems (4). Such weak interactions are difficult to observe in solution. In our study on intramolecular interactions between iridium hydrides and protons on nitrogen (see Fig. 1(a)), we found that, in addition to the NH proton at about 1.8 Å, some hydrogens of cyclohexyl groups on phosphine ligands contribute to the rate of dipole–dipole relaxation of hydride ligands in iridium complexes containing pyridiniumthiolato and tricyclohexylphosphine ligands (5–7). Desrosiers et al. (8) have already discussed the importance of ligand-hydrogen to metal-hydride dipole–dipole interactions in the analysis of T_1 values of metal hydride and dihydrogen complexes. We find that intramolecular CH···HM interactions also appear to influence the chemistry of the complexes described here.

These observations were made while trying to observe new intramolecular interactions between a metal hydride and an HN or HO hydrogen bond donor as shown in Fig. 1. Amino groups and iminol groups acting as H-bond donors to hydrides have been reported by Crabtree and co-workers (9–12). In all cases but one, a six-membered ring similar to that of (a) in Fig. 1 is involved; the exception is the first intermolecular Re—H···HN interaction (12). Strong evidence for the existence of intermolecular W—H···HO (13) and B—H···HN (14)

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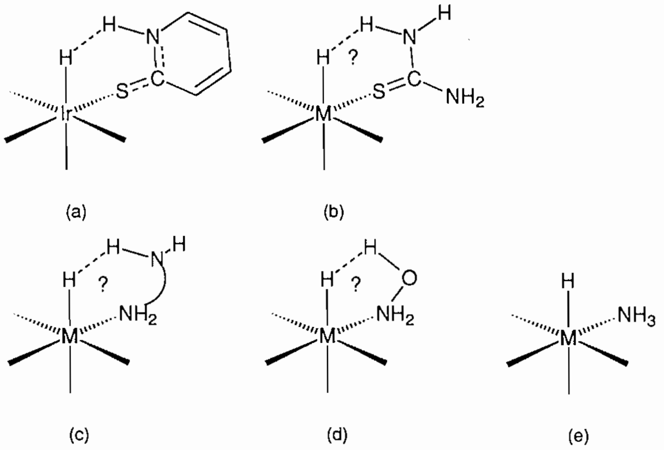
Fig. 1. Observed (a) and hypothetical ((b)–(d)) intramolecular proton–hydride interactions between hydrogen bond donors and a metal hydride. The hydrogens in (e) are probably too far apart to interact.



(a) (b) (c) (d) (e)

interactions has also been provided recently. We wondered whether five-membered rings (Fig. 1 (c) with NH_2NH_2 ligand or (d) with NH_2OH ligand) would form. The corresponding ammine complexes (e) were prepared for comparison since they were not expected to show such an interaction in a four-membered ring; however, Milstein et al. postulated that there might be a weak attractive interaction between a *cis* hydride and hydroxide hydrogen in such a ring at an H—H distance of 2.4(1) Å in $[Ir(H)(OH)(PMe_3)_4]^+$ (15, 16).

Experimental

General procedures and materials

All operations were conducted in an argon atmosphere by use of Schlenk line techniques, or in a purified nitrogen atmosphere using a Vacuum Atmospheres glove box. Deuterated solvents were dried over Linde type 4 Å molecular sieves and degassed with argon using several evacuate–refill cycles. Reagent-grade chemicals were used as purchased from Aldrich Chemical Company, Inc. unless otherwise stated. Tricyclohexylphosphine (PCy_3) and triisopropylphosphine (PPr^i_3) were purchased from Strem Chemical Co. $IrCl_3{\cdot}3H_2O$ and $RuCl_3{\cdot}3H_2O$ were received as a loan from Johnson–Matthey Co. $IrHCl_2(PCy_3)_2$ was prepared from $IrCl_3{\cdot}3H_2O$–HCl–EtOH and PCy_3 as described elsewhere (17). Methods of preparation starting from other iridium complexes have been described (18). $RuHCl(CO)(PPr^i_3)_2$ was prepared by previously reported methods (19).

NMR spectra were recorded on Varian Unity-400 and Varian Gemini-300 spectrometers. Reported chemical shifts refer to room temperature conditions (20°C) unless specified otherwise. ^{31}P chemical shifts were measured in the proton decoupled mode and referenced externally to 85% H_3PO_4. ^1H chemical shifts were measured relative to partially deuterated solvent peaks, but are reported relative to tetramethylsilane. Fast atom bombardment mass spectrometry (FAB MS) spectra were obtained with a VG 70-250S mass spectrometer using a nitrobenzyl alcohol (NBA) or nitrophenyl octyl ether (NPOE) matrix. Microanalyses were performed by Guelph Chemical Laboratories Ltd.

Preparation of $RuHCl(CO)(L)(PPr^i_3)_2$ (1*a*, L = NH_2NH_2; 1*b*, L = NH_3)

$RuHCl(CO)(PPr^i_3)_2$ (0.5 g, 1 mmol) in toluene (20 mL) and L (L = 90% NH_2NH_2 aq. for **1***a*; L = 30% NH_3 aq. for **1***b*) were vigorously stirred for 20 min. The red toluene suspension of $RuHCl(CO)(PPr^i_3)_2$ turned to a light yellow solution very quickly. When methanol (50 mL) was added to the mixture, a light yellow crystalline compound $RuHCl(CO)(L)(PPr^i_3)_2$ **1** was formed. It was obtained in almost quantitative yield after washing the solid with methanol (2 × 5 mL) and drying under vacuum. $RuHCl(CO)(NH_2NH_2)(PPr^i_3)_2$ **1***a* (light yellow solid, yield 90%): ^1H NMR (CD_2Cl_2, 20°C) δ: −14.5 (br), −15.7 (t, J_{P-H} = 21 Hz). ^1H NMR (CD_2Cl_2, −60°C) δ: −13.6 (t, J_{P-H} = 21 Hz), −13.9 (t, J_{P-H} = 21 Hz), −15.9 (t, J_{P-H} = 21 Hz), 0.9–1.4 (m, 36H, CH_3), 2.56 (m, 6H, $CHMe_2$), 2.09 (br, $RuNH_2NH_2$), 2.36 (br, $RuNH_2NH_2$), 3.46 (br, $RuNH_2NH_2$), 3.60 (br, $RuNH_2NH_2$), 4.8 (s, CH_3OH, 3H). ^{31}P NMR δ: 45.6 (s), 43.0 (s). FAB MS: calcd. for $C_{19}H_{47}{}^{35}ClN_2OP_2{}^{101}Ru$: 517; observed: 517 ($M^+$). Anal. calcd. for $C_{19}H_{47}ClN_2OP_2Ru{\cdot}CH_3OH$: C 43.7, H 9.3, N 5.1; found: C 43.5, H 8.9, N 5.1. $RuHCl(CO)(NH_3)(PPr^i_3)_2$ **1***b* (light yellow solid, yield 88%): ^1H NMR (CD_2Cl_2, 20°C) δ: −14.1 (t, J_{P-H} = 21 Hz, relative int. 10), −14.4 (t, J_{P-H} = 20.5 Hz, relative int. 1), −15.9 (t, J_{P-H} = 20.6 Hz, relative int. 1), 0.9–1.4 (m, 36H, CH_3), 2.56 (m, 6H, $CHMe_2$), 2.3 (br, $RuNH_3$). ^{31}P NMR δ: 49.3 (s, relative int. 1), 49.1 (s, relative int. 10), 48.3 (d, J_{HP} = 20 Hz, relative int. 1). FAB MS: calcd. for $C_{19}H_{46}{}^{35}ClNOP_2{}^{101}Ru$: 502; observed: 502 ($M^+$). Anal. calcd. for $C_{19}H_{46}ClNOP_2Ru$: C 45.4, H 9.2, N 2.8; found: C 45.1, H 9.2, N 2.6.

Preparation of $IrCl_2(L)(H)(PCy_3)_2$ (2*a*, L = $SC(NH_2)_2$; 2*b*, L = NH_3; 2*c*, L = NH_2NH_2; 2*d*, L = $NH_2(CH_2)_3NH_2$; 2*e*, L = NH_2OH)

$Ir(H)Cl_2(PCy_3)_2$ (0.5 g, 0.6 mmol) in toluene (20 mL) and L (L = $SC(NH_2)_2$, 0.1 g, 0.6 mmol for **2***a*; L = NH_3, 5 mL of 30% aq., for **2***b*; L = NH_2NH_2, 5 mL of 90% aq. for **2***c*; L = $NH_2(CH_2)_3NH_2$, 5 mL for **2***d*, L = NH_2OH, 0.1 g of $NH_2OH{\cdot}HCl$ and 1 g KOH dissolved in 1 mL water for **2***e*) were vigorously stirred for 24 h. The red toluene solutions turned slowly into light yellow solutions and then pale yellow solids precipitated from the solutions. The products were filtered off, washed with methanol several times, and dried under vacuum. **2***a* (light yellow solid, 88% yield): ^1H NMR (CD_2Cl_2, 20°C) δ: −24.04 (t, $^2J_{HP}$ = 15.9 Hz, Ir-H), −24.07 (t, $^2J_{HP}$ = 18 Hz, Ir-H), 1.0–3.0 (m, C_6H_{11}), 4.8 (s, CH_3OH, 3H). ^{31}P NMR δ: −4.0 (s), −6.0 (s). FAB MS: calcd. for $C_{37}H_{71}{}^{35}Cl_2{}^{193}IrN_2SP_2$: 900; observed: 863 ($M^+$ − HCl− H), 823 (M^+ − $SC(NH_2)_2$ − H). Anal. calcd. for $C_{37}H_{71}Cl_2IrN_2SP_2{\cdot}CH_3OH$: C 48.9, H 8.1, N 3.0; found: C 48.6, H 8.2, N 3.1. **2***b* (light yellow solid, 100% yield): ^1H NMR (CD_2Cl_2, 20°C) δ: −24.4 (br, 1H), 1.0–3.0 (m, C_6H_{11}). ^1H NMR (CD_2Cl_2, −40°C) δ: −24.4 (t, $^2J_{HP}$ = 25.9 Hz, 1H). ^{31}P NMR δ: −6.2 (s). Anal. calcd. for $C_{36}H_{70}Cl_2IrNP_2$: C 51.4, H 8.4, N 1.7; found: C 51.2, H 8.6, N 1.6. **2***c* (light yellow solid, 100% yield): ^1H NMR (CD_2Cl_2, 20°C) δ: 3.83 (br, $IrNH_2NH_2$, 2H), 5.01 (br, $IrNH_2NH_2$, 2H), −24.1 (br, Ir-H, 1H). ^1H NMR (CD_2Cl_2, −40°C) δ: −24.1 (t, $^2J_{HP}$ = 25.9 Hz, 1H). ^{31}P NMR δ: −6.5 (s). FAB MS: calcd. for $C_{36}H_{71}{}^{35}Cl_2{}^{193}IrN_2P_2$: 856; observed: 819 ($M^+$ − HCl − H). Anal. calcd. for $C_{36}H_{71}Cl_2IrN_2P_2$: C 50.5, H 8.4, N 3.3; found:

Table 1. Summary of crystal data, details of intensity collection, and least-squares refinement parameters for **2***b*.

Empirical formula	$[C_{36}H_{70}Cl_2IrNP_2]\cdot3(C_4H_8O)$
M_r	1058.28
Crystal size, mm	0.23 × 0.24 × 0.18
Crystal class	Monoclinic
Space group	$P2_1/n$
Temperature, K	173(2)
a, Å	14.859(2)
b, Å	18.579(2)
c, Å	18.548(3)
β, °	97.29(1)
V, A^3	5079.1(13)
Z	4
D_{calc}, g cm^{-3}	1.385
μ(MoKα), cm^{-1}	28.35
F(000)	2216
ω scan width, °	0.53
Range θ collected, °	3.05–27.01
Absorption correction	Empirical (ref. 20)
Min. and max. transmission	0.3790, 0.8114
No. reflections collected	11365
Independent reflections	10953
R_{int}	0.0209
No. observed data ($I > 2\sigma(I)$)	7559
R_1 ($I > 2\sigma(I)$)	0.0283
wR_2 (all data)	0.0704
Weighting a,b	0.0382, 0.00
Goodness of fit	0.927
Parameters refined	530
Max density in ΔF map, e/A^3	0.937

Definition of R indices: $R_1 = \Sigma(F_o - F_c)/\Sigma(F_o)$, $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

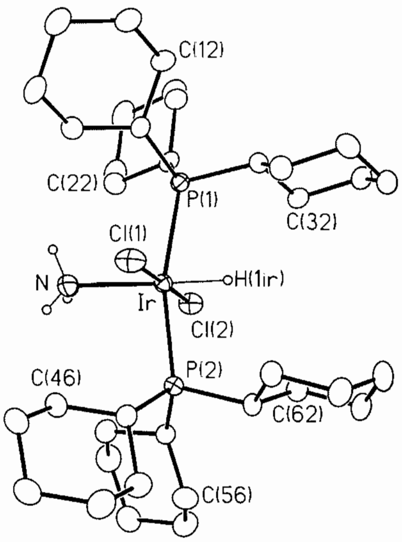
C 50.0, H 8.4, N 2.4. **2***d* (light yellow solid, yield 95%): ^{1}H NMR (CD_2Cl_2, 20°C) δ: −24.8 (br, 1H). ^{31}P NMR δ: −6.2 (s). Anal. calcd. for $C_{39}H_{77}Cl_2IrN_2P_2$: C 52.1, H 8.6, N 3.1; found: C 51.9, H 8.3, N 3.1. **2***e* (light yellow solid, yield 100%): ^{1}H NMR (CD_2Cl_2, −40°C) δ: 7.4 (s, OH, 1H), 6.7 (s, 2H, NH_2), −24.8 (t, $^2J_{HP}$ = 14 Hz, Ir-H, 1H). ^{31}P NMR δ: −5.2 ppm (s). Anal. calcd. for $C_{36}H_{70}Cl_2IrNOP_2\cdot CH_3OH$: C 49.9, H 8.4, N 1.6; found: C 49.7, H 8.2, N 1.2.

X-ray crystal structure determination of 2*b*

A summary of selected crystallographic data for **2***b* is given in Table 1. Crystals were prepared by slow diffusion of methanol into a THF (2 mL) solution of complex **2***b* (50 mg) under 1 atm (101.3 kPa) Ar. A suitable pale yellow crystal was mounted on a glass fiber. Data were collected on an Siemens P4 diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The intensities of three standard reflections measured every 97 reflections showed no decay. The data were corrected for Lorentz and polarization effects and for absorption (20).

The structure was solved using the SHELXTL PC V5.0 (21) package and refined by full-matrix least squares on F^2 using all data (negative intensities included). The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms were included in calculated positions and treated as riding atoms. The hydride atom was refined with an isotropic thermal parameter. The hydrogen atoms of the -NH_3 group were visible from a difference Fourier map as a torus of electron density and these atoms were included in the refinement as six half-occupancy H atoms riding on N. The structure contains three THF molecules of solvation and in one of these molecules the oxygen is disordered over two sites (0.76/0.24). The structure of **2***b*, including the crystallographic labelling scheme, is shown in Fig. 2. Selected bond lengths and angles are listed in Table 2. A complete set of crystallographic tables have been deposited as supplementary material.[3]

Fig. 2. The molecular structure of **2***b* as determined by single crystal X-ray diffraction at 173 K.



Results and discussion

Synthesis

The yellow, air-sensitive complexes $RuCl(CO)H(L)(PPr^i_3)_2$ (**1***a*, L = NH_2NH_2; **1***b*, L = NH_3) can be obtained by reaction of $RuH(Cl)(CO)(PPr^i_3)_2$ with an excess of hydrazine (90% aq.) or amine (30% aq.) in toluene. There are a total of three possible isomers of the complexes **1** when the two bulky phosphine ligands stay in *trans* positions (Fig. 3). The ^{1}H and ^{31}P NMR spectra of $RuH(Cl)(CO)(NH_3)(PPr^i3)_2$ **1***b* show three different hydride and ^{31}P resonances in a 10:1:1 ratio by integration corresponding to three isomers. The exact assignments are not certain. The ^{1}H and ^{31}P NMR spectra of the complex **1***a* have only two hydride resonances at −14.5 and −15.7 ppm and ^{31}P

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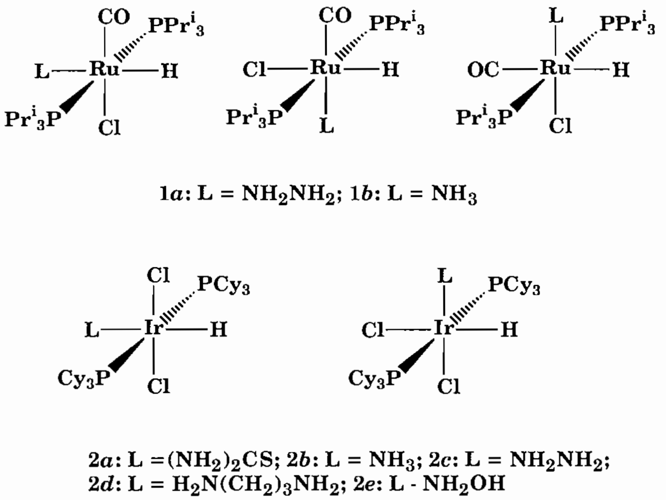
[3] Copies of material on deposit may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. With the exception of thermal parameters, these data have also been deposited with the Cambridge Crystallographic Data Centre, and can be obtained on request from the Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K. Structure factor amplitudes are no longer being deposited and may be obtained directly from the author.

Table 2. Selected bond lengths (Å) and angles (°) for **2***b*.

Ir—N	2.259(3)	Ir—H(1IR)	1.49(4)
H(Ir)···H(C32)	2.235(10)	H(Ir)···H(C36)	2.208(10)
H(Ir)···H(C62)	2.223(10)	H(Ir)···H(C66)	2.351(10)
Ir—P(2)	2.3473(10)	Ir—P(1)	2.3486(10)
Ir—Cl(1)	2.3676(9)	Ir—Cl(2)	2.3761(9)
N-Ir-P(2)	98.03(8)	N-Ir-P(1)	97.68(8)
P(2)-Ir-P(1)	164.28(3)	N-Ir-Cl(1)	88.81(8)
P(2)-Ir-Cl(1)	89.52(3)	P(1)-Ir-Cl(1)	90.54(3)
N-Ir-Cl(2)	90.22(8)	P(2)-Ir-Cl(2)	90.50(3)
P(1)-Ir-Cl(2)	89.70(3)	Cl(1)-Ir-Cl(2)	179.02(3)
N-Ir-H(1IR)	178(2)	P(2)-Ir-H(1IR)	83.7(13)
P(1)-Ir-H(1IR)	80.6(13)	Cl(1)-Ir-H(1IR)	93(2)
Cl(2)-Ir-H(1IR)	88(2)		

Fig. 3. Possible isomers of complexes **1** and **2**.



1*a*: L = NH_2NH_2; **1***b*: L = NH_3

2*a*: L =$(NH_2)_2CS$; **2***b*: L = NH_3; **2***c*: L = NH_2NH_2; **2***d*: L = $H_2N(CH_2)_3NH_2$; **2***e*: L - NH_2OH

resonances at 45.6 and 43.0 ppm in a 2:1 ratio at room temperature. The broad peak at −14.5 ppm in the ^{1}H NMR spectrum splits into two triplets at −80°C (see Fig. 4(*a*)). Therefore there appear to be three isomers of this complex as well. However, we do not have a definitive explanation for the spectral changes that occur with the change in temperature.

The air-stable iridium derivatives $IrH(Cl)_2(L)(PCy_3)_2$ (**2***a*, L = $(NH_2)_2CS$; **2***b*, L = NH_3; **2***c*, L = NH_2NH_2; **2***d*, L = $NH_2(CH_2)_3NH_2$; **2***e*, L = NH_2OH) were prepared by the addition of excess L to a toluene suspension of $IrH(Cl)_2(PCy_3)_2$. There are two possible isomers for the complexes **2** (see Fig. 3). The ^{1}H and ^{31}P NMR spectra of complex **2***a* do show two different hydride and ^{31}P resonances in approximately equal amounts at room temperature. Complexes **2***b*–*d* have one broad hydride resonance in the ^{1}H NMR spectrum and one singlet in the ^{31}P NMR spectrum. The broad hydride resonance becomes a sharp triplet at temperatures of less than 0°C. The broadening is apparently caused by the dissociation and reassociation of the ligand L, which is labilized by a high *trans*-influence ligand, probably the hydride. The structure determination of crystalline **2***b* (see below) confirms that the ammine is *trans* to hydride. A broad triplet is observed for the hydride resonance of **2***e* at 20°C.

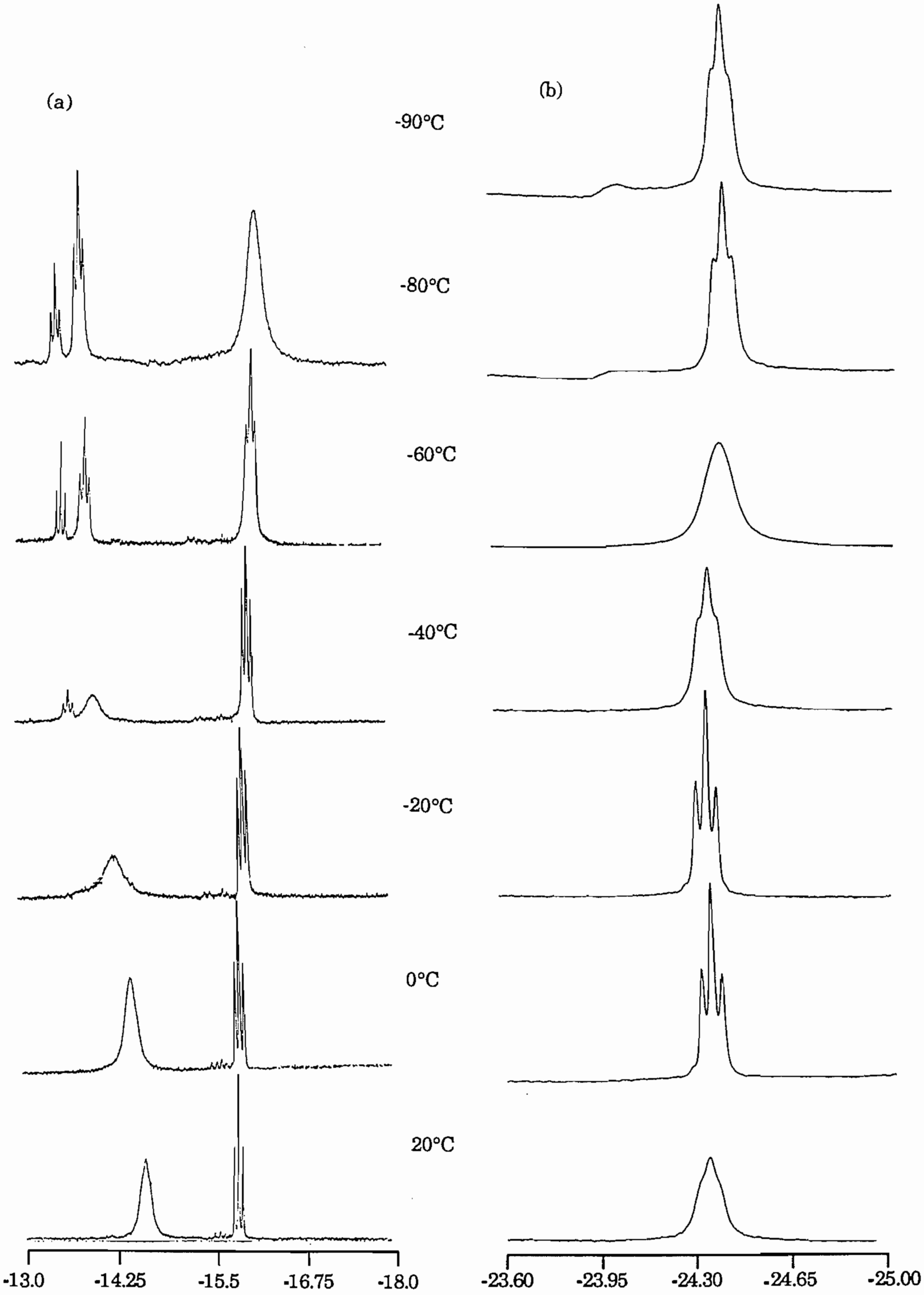
The hydride resonance of **2***b* in CD_2Cl_2 as a function of temperature is shown in Fig. 4(*b*). At least two exchange processes are apparent. The sharpening of the peak with cooling to around 0°C is probably due to the slowing of dissociation of the NH_3 ligand. The resonance for the five-coordinate product of this reaction is not visible in the ^{1}H NMR spectrum at low temperature and this indicates that the equilibrium greatly favors the six-coordinate complex **2***b*. There is no evidence for an isomer with ammine *cis* to hydride. In contrast, the complex $Ir(H_2)H(Cl)_2(P^iPr_3)_2$ is thermodynamically more stable with the π-acid dihydrogen ligand located *cis* to the hydride (22). A second broadening and then decoalescence occurs as the temperature is lowered below −60°C. The triplet at −24.4 ppm reappears along with an incompletely decoalesced, small, broad signal at −24.0 ppm. This might be due to the cyclohexyl groups taking up preferred positions in the complex, with the major species at −24.4 ppm having the conformation observed in the solid state (see the crystal structure presented below). No other isomers of **2***c*–*e* have been observed at low temperatures.

The complexes $IrH(Cl)_2(PCy_3)_2(OCMeNMe_2)$ and $IrH(Cl)_2(PCy_3)_2(CO)$ with structures related to those of **2** have been reported (18). The first complex, which was only characterized as a solid, appears to exist as one isomer since only one IR absorption due to CO stretching is observed. The second complex formed as the isomer with *trans* PCy_3 groups and CO *trans* to hydride in the reaction of $IrH(Cl)_2(PCy_3)_2$ with CO. This compound, with a structure similar to **2***b*, isomerized to a second isomer and also eliminated HCl to give *trans*-$IrCl(CO)(PCy_3)_2$. Complexes **2** in solution do not readily eliminate HCl considering that they are prepared in the presence of excess amine base. Complexes **2***a* and **2***c* do appear to eliminate HCl in the gas phase under the conditions of FAB mass spectroscopy.

X-ray analysis of complex 2*b*

The X-ray diffraction study at 173 K reveals that the iridium atom of **2***b* is in a distorted octahedral environment surrounded by two *trans* PCy_3 ligands, two *trans* chlorine atoms, and one ammine *trans* to the hydride. Selected bond lengths and angles are listed in Table 2. The two tricyclohexylphosphine ligands are bent toward the hydride (P-Ir-P, 164.28(3)°). The Ir-H hydride and hydrogens on cyclohexyl groups are well defined in electron difference maps. The iridium–hydride distance of 1.49(4) Å is reasonable on the basis of distances determined by neutron diffraction studies (23). Interestingly, two cyclohexyl groups tilt toward the hydride and their four H-C protons embrace the Ir-H hydride with close CH···H(Ir) distances that fall between 2.21(1) and 2.35(1) Å (Fig. 5). Similarly the CH···HN distances from six hydrogens on two half-occupancy ammine ligands to cyclohexyl hydrogens in the structure have short contacts of 2.0–2.4 Å. Considering that the van der Waals radius of hydrogen is about 1.2 Å (24), these contacts, at less than twice this radius, might be weakly attractive. Such MH···HC interactions might be energetically favorable considering that CH···O (H···O at 2.1–2.4 Å) hydrogen bonds have been confirmed by neutron diffraction

Fig. 4. Variable temperature 400 MHz ^{1}H NMR spectra. (*a*) Spectra of **1***a* in CD_2Cl_2 in the hydride region (−13 to −18 ppm) and (*b*) spectra of **2***b* in CD_2Cl_2 in the hydride region (−23 to −25 ppm).



studies, and that NH···HIr (H···H at 1.7 Å) interactions have also been shown to be surprisingly strong (11). However, a more likely interpretation is that these short contacts are enforced by the steric bulk of the tricyclohexylphosphine ligands.

NMR studies

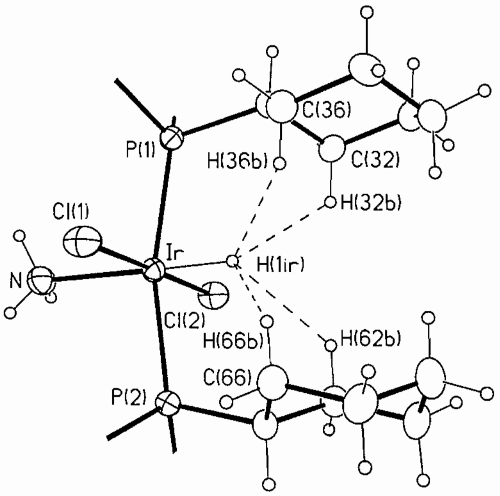
Complexes **1** and **2** were tested for the presence of intramolecular NH···HM or OH···HM interactions by use of ^{1}H NMR nOe difference experiments. Irradiation of the hydride resonance did not produce an enhancement in the NH resonance of

Table 3. List of minimum T_1 values (s, at 400 MHz), calculated H···H distances of four CH···HM interactions, and nOe enhancement of the hydride of complexes **1** and **2** when the isopropyl or cyclohexyl ^1H resonances around 1.8 ppm are irradiated.

Complexes	$T_{1\,min}$ s, IrH (Temp. K)	Calcd. $d_{CH\cdots HM}$ (Å)	nOe enhancement (%) of hydride
1*a*	0.17 ± 0.01 (183)[a]	2.0	12.5
2*b*	0.23 ± 0.01 (213)	2.1	13.5
2*c*	0.22 ± 0.01 (223)	2.1	11.5

[a] δ(H) −15.6.

Fig. 5. Part of the molecular structure of **2***b* showing the CH···HIr interactions. The non-interacting cyclohexyl groups are omitted for clarity.



any of the complexes. However, weak CH···HM interactions, as observed in the complex **2***b* by X-ray analysis, are detectable in ^1H NMR nOe difference experiments.

Selective irradiation of the hydride resonance of **2***b* leads to an nOe enhancement of C-H proton resonances at 1.8 and 1.9 ppm, but the magnitude of specific interactions could not be calculated due to the large number of non-interacting protons of the cyclohexyl groups that appear in the same region of the ^1H NMR spectrum. When the whole region of cyclohexyl resonances is saturated, an nOe enhancement of the hydride signal of over 10% is observed. The hydride of **2***b* has an unusually short minimum T_1 value of 0.23 s at 400 MHz and 213 K that is caused by the presence of CH···HIr interactions. An average H···H distance from the hydride to the closest H-C groups is calculated to be 2.1 ± 0.1 Å when the rate of dipole–dipole relaxation of the hydride is assumed to be made up of contributions from four cyclohexyl protons. The distance estimated by the T_1 method is slightly less than the average H···H distance revealed by the X-ray structure analysis.

The same CH···HM interactions have been observed for the other complexes **1** and **2** in solution. The T_1 and nOe data for selected complexes are listed in Table 3. In each case the minimum T_1 value can be interpreted in terms of a structure containing four CH···HM at 2.0–2.1 Å.

H/D exchange study

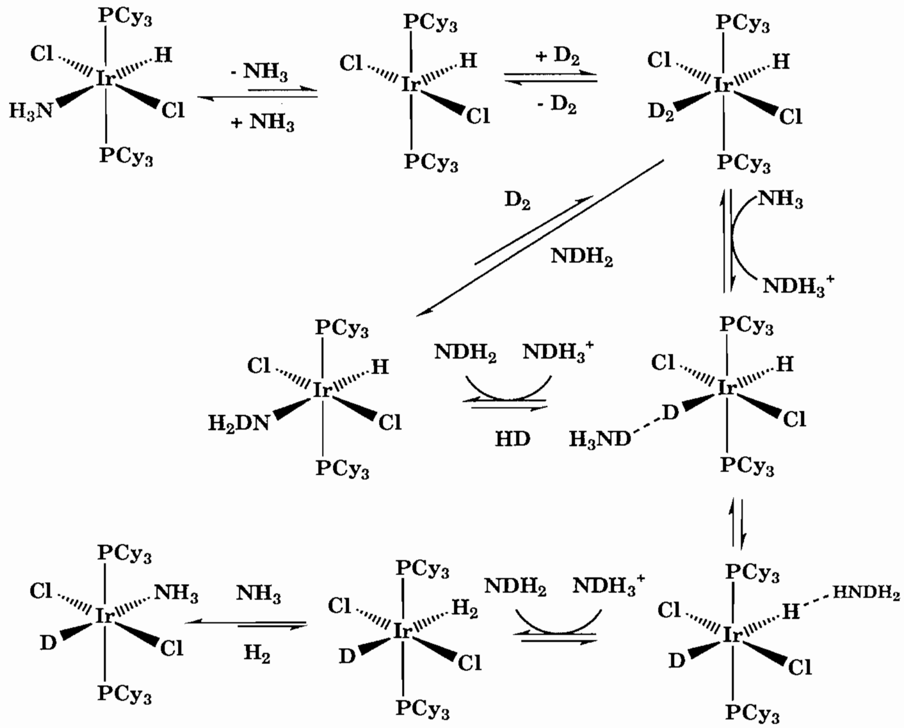
When a solution of complex **2***b* in CD_2Cl_2 is exposed to D_2 (1 atm), slow H–D exchange at the ammine and hydride sites is observed by use of ^2H NMR. The NH protons exchange with D_2 faster than does the hydride. After 24 h ca. 90% of both (N)H and (Ir)H positions have been deuterated. Since the dihydrogen complexes *trans*- and *cis*-$Ir(H)(H_2)Cl_2(PPr^i_3)_2$ (23, 25, 26) have been reported, it is quite possible that the deuteration is initiated by a short-lived, dideuterium intermediate *trans*-$Ir(H)(D_2)Cl_2(PCy_3)_2$, in spite of the fact that no trace of this complex or the H_2 analogue in solution is detected by NMR spectroscopy. The fast exchange between the acidic dideuterium ligand and the active protons of amines could result in the deuteration as suggested in Scheme 1 (5). The slower H–D exchange of the hydride might involve an initial intermolecular interaction between *trans*-$[Ir(H)_2(Cl)_2(PCy_3)_2]^-$ and NH_3D^+ as indicated. The CH···HIr interactions might make this exchange a slower process than expected because of steric interactions.

^2H NMR experiments indicate that the deuteration not only occurs at the hydride and ammine sites, but also at the cyclohexyl groups. When the amine ligand dissociates from complex **2***b* to generate a 16-electron intermediate, certain CH bonds could coordinate to the metal (27). Coordination of the CH bond makes it acidic and susceptible to proton exchange with the deuterated ammine as proposed in Scheme 2. An intramolecular example of H–D exchange between ammine and C—H bonds has also been reported (28) but the stereochemistry of the complexes involved is different than that of **2***b*. Another possible mechanism could involve the oxidative addition of carbon–hydrogen bonds of cyclohexyl groups to the complex $IrCl(PCy_3)_2$ (29). The latter complex might be produced from **2***b* by reductive elimination of NH_4Cl but we do not have evidence to support this idea.

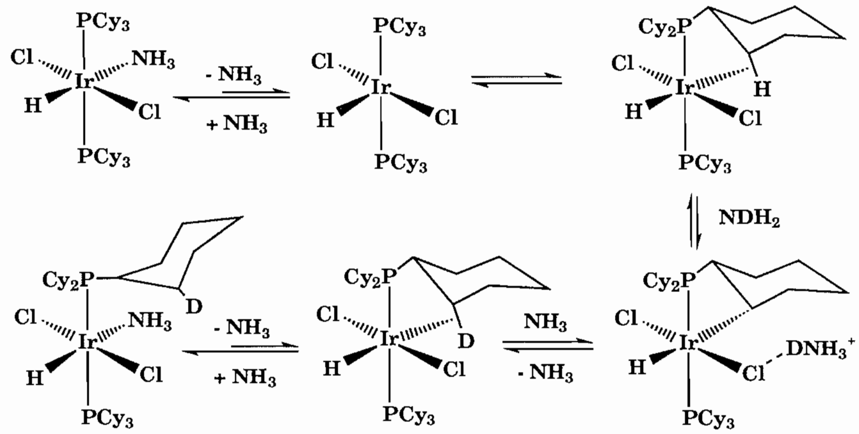
Conclusions

X-ray structural analysis and minimum T_1 and nOe techniques have revealed the presence of short CH···HM van der Waals contacts in complexes **1** and **2**. The H···H distances of 2.1–2.3 Å are less than the sum of the van der Waals radii of two hydrogens (2.4 Å), which might suggest that these interactions are favorable and might be similar to other hydrogen bonds formed by C-H hydrogen bond donors. However even in the absence of attractive interactions, the bulky cyclohexyl groups will probably occupy positions close to the small and polarizable hydride ligand for steric reasons alone. Therefore caution

Scheme 1.



Scheme 2.



is needed in claiming that CH···HM bonding is present because the size of van der Waals contact distances might vary depending on the steric pressures around the complex. Certainly the contributions of ligand hydrogens to hydride relaxation can be quite important, as suggested previously (8). Tricyclohexylphosphine ligands, when *cis* to a hydride, are likely to make a significant contribution to the relaxation. Such CH···H(Ir) interactions may also play an important role in H–D exchange and CH bond activation reactions. After the submission of this work, Crabtree's group reported that, on the basis of a survey of the Cambridge Crystallographic Database, CH...HM contacts (1.6–2.1 Å) commonly occur between arene CH bonds of phosphine ligands and hydride ligands and that such weak hydrogen bonds might influence the mechanism of cyclometallation of arenes (30).

No intramolecular NH···HIr interactions were observed for complexes **1** and **2**. Such interactions have been observed for ligands that can form six-membered HMXYZH rings. Only the thiourea ligand has the correct geometry to form such a ring; all the other amines would have to form four- (NH_3), five- (NH_2NH_2), or eight- ($NH_2CH_2CH_2CH_2NH_2$) membered rings. Thiourea and the other ligands might form stronger hydrogen bonds to the chloride ligand than to the hydride in these complexes.

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