to describe its electronic structure including ENDOR experiments and LCAO–MO calculations.

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Contribution from the Department of Chemistry,
Yale University, New Haven, Connecticut 06511

T_1's and Proton NMR Integration in Metal Hydride Complexes

Robert H. Crabtree,* Brigitte E. Segmuller,
and Richard J. Uriarte[1]

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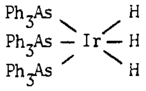
It is sometimes difficult to determine the number of hydrides present in a transition-metal hydride complex.[2] Microanalysis, hydrogen evolution studies, and X-ray crystallography can all be misleading.[2b] Integration of the proton NMR resonances might seem to be the most direct approach. Unfortunately, as inorganic chemists have long been aware, metal hydrides sometimes give anomalous integration.[2c] The most reasonable explanation involves differences between the relaxation times (T_1) of the hydride and those of the other ligand protons; an unusually long MH relaxation time could easily lead to low MH integrals. This problem seems to have rarely received attention in the literature,[2c] and no MH relaxation times seem to have been reported.

Difficulties in integrating spectra of certain metal hydride complexes led us to measure T_1 values, to see if they are unusually large, and to compare both bridging and terminal hydrides and hydrides coordinated to different platinum isotopes.

The complex *fac*-$[Ir(AsPh_3)_3H_3]$ (**1**)[3] gave the anomalous integration results recorded in Table I. It can be seen that shorter pulses and longer delay times give the magnetization a better chance to recover and so, as expected, produce better integration values. We were surprised to find that at short delay times the integration ratio was *smaller* than the theoretical. This implies that the ligand protons, not the hydrides, have the longer relaxation times and so were taking longer to recover their full magnetization. In order to confirm this picture, we measured the T_1 values of this complex and of three others. The results are given in Table II.



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Contrary to our expectation, in no case is the MH proton relaxation the slowest in the molecule. The Mo and Ir hydrides seem to relax faster than the Pt hydrides by a factor of 5–10. It is not clear why this is so. These results show that our own recently suggested method[2c] by which the hydride in one hydride complex is integrated against a second hydride complex as internal standard may work well because hydride relaxation times tend to be short. Apart from the Pt case, the MH relaxation times were unusually fast and faster than those of any other protons in the molecule.

Table I. Integration Data for *fac*-$[Ir(AsPh_3)_3H_3]$

pulse,[a] deg	interval between pulses, s	integral[b]
90	1.14	7.46
	2.1	11.57
	4.1	14.8
	9.1	15
60	2.1	13.7
	4.1	15

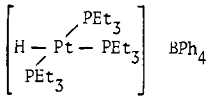
[a] The tip angle corresponding to the pulse width used (36 μs = 90°) on the FX-90 Q spectrometer. CD_2Cl_2 solvent; 26 °C. [b] ±1%; theoretical value 15. Reported as $AsPh_3/IrH$.

Table II. Apparent T_1 Values for the Compounds Studied[a]

compd	H resonances	shift, δ	T_1, s
fac-$[Ir(AsPh_3)_3H_3]$ (**1**)	IrH	−14.4	0.38
	AsPh, *o*	{6.99	1.55
	m	{7.08	2.06
	p	7.18	2.59
$[Pt(PEt_3)_3H]BPh_4$ (**2**)	^{195}PtH	−6.19	2.03
	PtH[b]	−6.19	2.38
	PCH_2	2.00[c]	1.30
		1.90[d]	1.05
	PCH_2CH_3	1.14	1.91
	BPh, *o*	{6.90	3.39
	m	{7.05	3.94
	p	7.34	4.87
$[(IrH(PPh_3)_2)_2(\mu\text{-}H)(\mu\text{-}Cl)_2]BF_4$ (**3**)	IrH (terminal)	−23.37	0.37
	IrH (bridging)	−12.00	0.48
	PPh, *o*	{7.20	0.81
	m	{7.35	0.95
	p	7.40	0.75
$[(MoH_2(PMePh_2)_3)_2(\mu\text{-}F)_3]BF_4$ (**4**)	PPh, *o*	{7.13	0.93
	m	{7.20	1.32
	p	7.32	1.73
	PMe	1.36	0.41
	MoH	−1.90	0.21

[a] Under argon in CD_2Cl_2 at 30 °C using a 180°–τ–90° pulse sequence (490 MHz). Where ^1H–^1H dipolar coupling from different protons contributes to relaxation, nonexponential relaxation can give rise to errors in T_1's. Experimentally, however, relaxation was exponential to the accuracy of our measurements over five T_1's. Our values are probably accurate to 2% for comparisons within the same complex and to 5% as an absolute value. [b] ^{192}Pt, ^{194}Pt, ^{196}Pt, and ^{198}Pt. [c] PR_3 trans to H. [d] PR_3 cis to H.

For complex **1**, the ligand protons relax more slowly by a factor of 5. This is consistent with the integration values of Table I. In the case of $[PtH(PEt_3)_3]BPh_4$ (**2**),[4] we find that hydrides coordinated to the $I = 0$ platinum nuclei[5a] relax more slowly (T_1 = 2.38 s) than those coordinated to the $I = {}^1/_2$ isotope[5b] (2.03 s). The additional relaxation no doubt arises by the dipolar mechanism.[6,7] Once again, the most slowly relaxing nuclei are the aromatic CH groups of BPh_4^- ($T_1 \approx 4$ s), not the metal hydrides at all. Adjusting the instrumental conditions to allow for the relaxation of the hydride proton therefore does not guarantee that all the protons present will relax satisfactorily. Results for the complex $[(IrH(PPh_3)_2)_2(\mu\text{-}H)(\mu\text{-}Cl)_2]BF_4$ (**3**)[8] show that the



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[1] Visting Associate Professor, Yale University. Permanent address: St. Peter's College, Jersey City, NJ.

[2] (a) Green, J. C.; Green, M. L. H. In "Comprehensive Inorganic Chemistry"; Pergamon Press: London, 1973. (b) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.*, in press. (c) Crabtree, R. H.; Hlatky, G. G.; Holt, E. M. *J. Am. Chem. Soc.* **1983**, *105*, 7302.

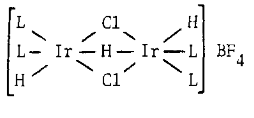
[3] (a) Canziani, F.; Zingales, F. *Rend.—Ist. Lomb. Accad. Sci. Lett., A: Sci. Mat., Fis., Chim. Geol.* **1962**, *96*, 513. (b) As this compound contains no phosphine, the $\{^1H\}^{31}P$ NMR methods for determining the number of hydrides are not applicable.

[4] Clark, H. C.; Dixon, K. R. *J. Am. Chem. Soc.* **1969**, *91*, 596.

[5] (a) ^{194}Pt, 32.9%, $I = 0$; ^{196}Pt, 25.3%, $I = 0$; ^{190}Pt, 0.01%, ^{192}Pt, 0.79%, and ^{198}Pt, 7.2%, I unknown. (b) ^{195}Pt, 33.8%, $I = {}^1/_2$.

[6] Unexpectedly the ^{195}PtH satellites are broader than the central PtH resonances at fields lower than 490 MHz; we have not been able to explain this satisfactorily.

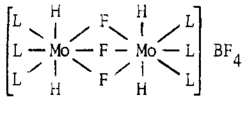
[7] Boere, R. T.; Kidd, R. G. *Annu. Rep. NMR Spectrosc.* **1982**, *13*, 319.



3 ($L = PPh_3$)

hydride protons, like those of **1**, relax relatively rapidly. The data also show there is a difference between the relaxation times of the bridging and terminal hydrides. Possibly the ligand protons make a greater contribution to the relaxation of the latter.[9]

Our final example[2c] is $[(MoH_2(PMePh_2)_3)_2(\mu\text{-}F)_3]BF_4$ (**4**). Here the hydride proton relaxes faster (0.21 s) than any of the



4 ($L = PMePh_2$)

hydride protons in **1**–**3**, about 2 times as fast as the PMe protons and about 8 times as fast as the PC_6H_5 protons in **4**.

We conclude that hydrides can indeed have a relaxation time different, either faster or slower, from those of other protons in a metal complex. This can lead to integration anomalies, but careful control of the experimental conditions (in particular a sufficiently long delay time) can alleviate these problems. Satisfactory integrals for **1**–**4** (theoretical ±1%) can be obtained at 490 MHz with a 5° pulse and 4-s delay time.

Experimental Section

Complexes **1**,[3] **2**,[4] **3**,[8] and **4**[2c] were obtained by literature methods. T_1 measurements were made at 490 MHz as described in Table II. All relaxation times are the result of a computer fitting of ca. 20 observations over the range of $0.1T_1$–$5T_1$ and allowing 30-s recovery time between acquisitions. In all cases strict first-order behavior was observed in the recovery of magnetization. Integration measurements on **1** were made at 90 MHz on an FX-90 Q instrument (see Table I).

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Registry No. **1**, 75494-79-0; **2**, 22276-37-5; **3**, 96149-07-4; **4**, 87656-09-5.

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(9) Chemical shift anisotropy (CSA) does not contribute significantly to relaxation, because we find that T_1 for MH is no slower for **3** at 250 MHz than at 490 MHz; any CSA contribution[7] should vary as H_0^2. Efficient dipolar relaxation is therefore presumably the factor responsible for the rapid relaxation observed.

Contribution from the School of Science,
Griffith University, Nathan, Queensland 4111, Australia,
and Department of Physical and Inorganic Chemistry,
University of Western Australia,
Nedlands, Western Australia 6009, Australia

Lewis Base Adducts of Group 11 Metal Compounds.† 14. Crystal Structures of the 1:2 Binuclear Adducts of Copper(I) Halides with Some 2(4)-Mono- and Dimethyl-Substituted Pyridine Bases and Quinoline

Jeffrey C. Dyason,[1a] Lutz M. Engelhardt,[1b] Peter C. Healy,[1a] Chaveng Pakawatchai,[1b] and Allan H. White*[1b]

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Coinage metal halides, MX, may, in many cases, be recrystallized from solution in nitrogen base, L, to yield adducts, MXL_n. Where the ligand bulk of the base is small, *n* may be as high as 3, as has been demonstrated structurally for nitrogen rather than phosphine base complexes, by structure determination of the adducts obtained by recrystallizing copper(I) chloride, bromide, and iodide from 3-methylpyridine.[2] With increased steric bulk, as when, e.g., 2- rather than 3-methylpyridine is used, *n* is reduced to 2, leading, in the case of copper(I) iodide with 2-methylpyridine, to the formation of a bis(μ-halo)-bridged dimer[3] in which the coordination number of the metal remains at 4 but now comprises two halogen and two base ligands, rather than yielding a monomeric species with a 1:3 copper halide to ligand base ratio. With a further increase in steric bulk of the base, as e.g., to 2,6-dimethylpyridine, the coordination number attainable by the metal is reduced to 3 as in, e.g., mononuclear iodobis(2,6-dimethylpyridine)copper(I) on the one hand[3] from neat base or binuclear bis(μ-iodo)bis(2,6-dimethylpyridine)dicopper(I) from acetone solution on the other.[4] In the latter sterically uncrowded species, the copper–copper distance is very short (2.586 (5) Å); as steric crowding and coordination number about the copper rise, the copper–copper distance is observed to increase, being 2.866 (3) Å in the binuclear 1:2 adduct of copper(I) iodide with quinoline[3] and 3.083 (3) Å in the adduct with 2-methylpyridine.[3] For the 1:1 adducts of copper(I) chloride, bromide, and iodide with 2,9-dimethyl-1,10-phenanthroline, a hiatus is observed, the chloride being mononuclear with a three-coordinate copper atom and the bromide and iodide binuclear with four-coordinate copper.[5] Elsewhere, we show chloro-, bromo- and iodobis(2,6-dimethylpyridine)copper(I) to be mononuclear;[2] the iodo/2-methylpyridine analogue is binuclear, but with the longest copper–copper distance (3.083 (3) Å) hitherto observed in complexes of that type. Given the nature of the result with the 2,9-dimethyl-1,10-phenanthroline adducts, and the meager structural information on analogous chloride and bromide systems, we considered it not unlikely that a similar discontinuity might be observed throughout the copper(I) chloride, bromide, and iodide series of 1:2 adducts with 2-methylpyridine or a similar base, providing an opportunity to examine more closely the factors leading to dissociation in complexes with monodentate ligands of this type. Accordingly, we report in this paper the synthesis and structure determinations of the 1:2 copper chloride and bromide adducts with 2-methylpyridine (**1** and **2**) (the iodide has been already determined),[3] the chloride, bromide, and iodide series with 2,4-dimethylpyridine (**3**–**5**), and the chloride and bromide adducts with quinoline, (**6** and **7**), the iodide having already been determined[3] to display an intermediate Cu···Cu distance (see above).

Experimental Section

In the work described in this and the following paper, complexes were prepared in all cases by recrystallization under argon of the parent halide from its solution in hot pure base as off-white or fluorescent crystals; because of the air-sensitive nature of the compounds and the readiness with which base is readily lost in compounds such as these with high copper(I) halide:ligand base ratios, their characterization depends primarily on the crystallographic work.

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† In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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