

charged porphyrins. In agreement with this argument, no synthetic peripherally positively charged porphyrin has been found to aggregate in aqueous solution, to date. The only other peripherally positively charged porphyrin that has been shown to aggregate is a modified protoporphyrin^{17,18} (with only hydrogens at meso positions) that contained ethylenediammonium side chains attached to the vinyl groups. There is a recent fluorescence, nonkinetic study¹⁹ that suggests the stacking of the free base of tetrakis(*N*-methylpyridin-4-yl)porphyrin in water. The lack of quantitative information makes it difficult to compare with our results.

In spite of such steric as well as electrostatic factors, the fact that our silver(III) porphyrin aggregates in solution seems to indicate that its hydrophobicity, when compared to that of the free base, enhanced by the square-planar complex formation (which precludes solvation at the axial positions) is an important factor in aggregation, regardless of the type of charge at the peripheral positions. Furthermore, this dimerization of metalloporphyrins could be used as a guide in determining the coordination geometry of the central metal ion in solution as to whether it is square planar or not.

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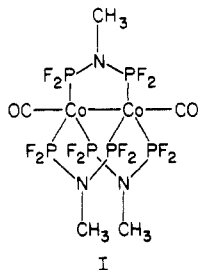
Contribution from the Laboratoire de Spectrochimie du Solide (LA 302), Université Paris VI, 75230 Paris Cedex 05, France, Department of Chemistry, University of Georgia, Athens, Georgia 30602, and Institut de Recherches sur la Catalyse, 69626 Villeurbanne Cedex, France

Spectroscopic Properties of a Mixed-Valence Binuclear Cobalt Complex: [CH₃N(PF₂)₂]₃Co₂(CO)₂⁻

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In recent years (alkylamino)bis(difluorophosphines) have been used as novel bidentate ligands for stabilizing low metal oxidation state and metal-metal bonded systems.¹ The binuclear cobalt derivative [CH₃N(PF₂)₂]₃Co₂(CO)₂ was obtained by the reaction of the bidentate fluorophosphine CH₃N(PF₂)₂ with Co₂(CO)₈ at room temperature and atmospheric pressure.^{2,3} X-ray diffraction studies on this complex reveal the presence of three CH₃N(PF₂)₂ ligands bridging the Co-Co bond, with each cobalt atom having an approximately trigonal-bipyramidal environment (I).



This binuclear cobalt compound (I) is quite interesting because of the high stability of its [CH₃N(PF₂)₂]₃Co₂ structural unit

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toward redox reactions. For example, this binuclear unit remains intact upon reaction with bromine to give a tetrabromide, [C-H₃N(PF₂)₂]₃Co₂Br₄.⁴ Moreover, electrochemical studies on this complex indicate reversible one- and two-electron reductions giving a green radical anion, [CH₃N(PF₂)₂]₃Co₂(CO)₂⁻, and a pale yellow dianion, [CH₃N(PF₂)₂]₃Co₂(CO)₂²⁻, respectively.⁵ Structural studies have not yet been performed on either the radical anion or the dianion owing to the difficulty of separating pure crystalline products from the supporting electrolyte. Nevertheless, the [CH₃N(PF₂)₂]₃Co₂ structural unit seems to be preserved in these reduction products. Thus the two reduction steps are perfectly reversible, not only electrochemically but also chemically. The spectroscopic study described in this paper confirms this assumption. In addition, the radical anion is of special interest in being an unusual mixed-valence d⁹-d¹⁰ cobalt dimer.

Other radical anions of dicobalt carbonyl derivatives have been reported in the literature. Thus Co₂(CO)₆(ER₃)₂⁻⁶⁻⁸ [ER₃ = (*n*-C₄H₉)₃P, (CH₃O)₃P, and (*i*-C₄H₉)₃As] are generated by irradiation of a frozen solution of Co₂(CO)₆(ER₃)₂ at 77 K. In addition, Co₂(CO)₆(RC₂R')⁷ can be produced by electrolysis in situ inside the ESR cavity usually at -60 °C. Both techniques lead to radicals having short lifetimes, which are therefore difficult to study by spectroscopic methods. An advantage of the radical anion [CH₃N(PF₂)₂]₃Co₂(CO)₂⁻ is its stability in an inert atmosphere at room temperature. This property allowed us to undertake a complete ESR study from 4 to 300 K and also to record its optical spectrum.

This paper presents the ESR and optical spectra of the mixed-valence complex [CH₃N(PF₂)₂]₃Co₂(CO)₂⁻. A detailed study of these experimental data show a strong electronic interaction between the two cobalt units so that this complex belongs to class III according to the classification of mixed-valence compounds of Robin and Day.⁹

Experimental Section

The complex [CH₃N(PF₂)₂]₃Co₂(CO)₂ was prepared according to the previously described procedure.³ Its electrochemical one-electron reduction was carried out under an argon atmosphere at -0.7 V vs. SCE. A mercury working electrode and an aluminum auxiliary electrode were used. Before use, the supporting electrolyte, [(*n*-C₄H₉)₄N][PF₆], was dehydrated by melting under vacuum. The solvent used, tetrahydrofuran, was freshly distilled over sodium benzophenone ketyl under an argon atmosphere.

The X-band ESR spectra were recorded on a Bruker 220D spectrometer supplied with a variable-temperature accessory in the range 4-293 K. For the Q-band, a Varian E09 spectrometer was used. The optical spectra were recorded from 10 000 to 40 000 cm⁻¹ on a UV-visible Beckman 5240 spectrophotometer. All ESR tubes and optical cells were filled under argon by using Schlenk techniques.

For analyses of the ESR spectra, a simulation program REPELEC¹⁰ was used, based on a second-order perturbation solution¹¹ of the spin Hamiltonian. For all simulations, the estimated errors are ±0.005 for the *g* values and ±1 G for the hyperfine parameters.

Results

(A) ESR. The room-temperature ESR spectrum of the radical anion [CH₃N(PF₂)₂]₃Co₂(CO)₂⁻ in tetrahydrofuran solution is shown in Figure 1a. This spectrum exhibits approximately 60 well-resolved lines centered around *g* = 2.025. Its relative com-

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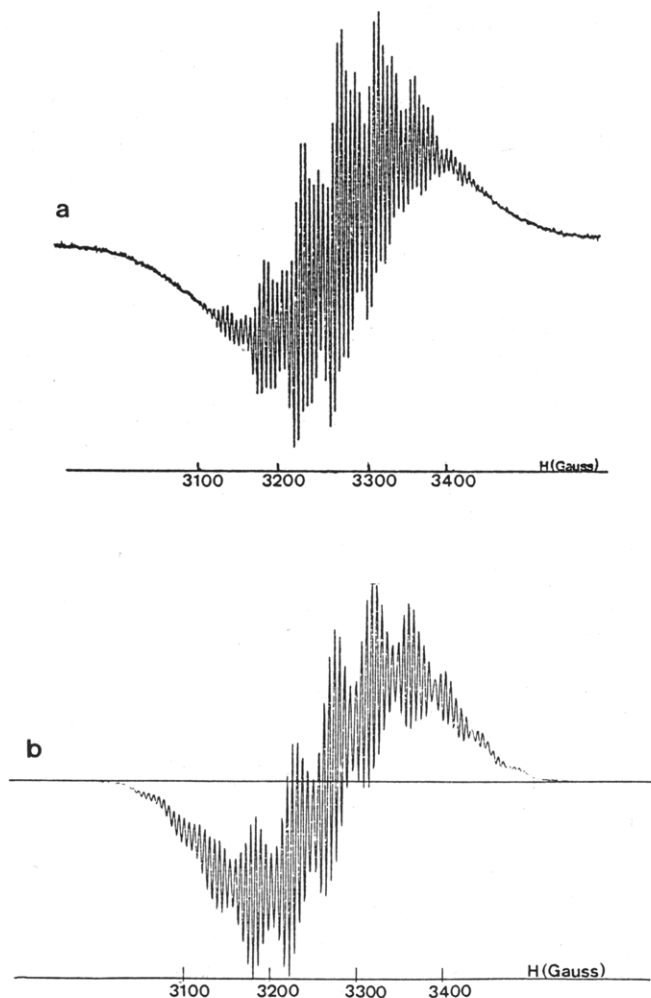


Figure 1. X-Band room-temperature ESR spectra of the radical anion $(\text{CH}_3\text{N}(\text{PF}_2)_2)_3\text{Co}_2(\text{CO})_2^-$ in THF ($c \approx 10^{-3}$ M): (a) experimental (microwave power 20 mW; field modulation intensity 0.5 G; gain 3.2×10^5); (b) simulated.

plexity arises from coupling of the electron spin with the variety of magnetic nuclei present, namely ^{59}Co , ^{31}P , ^{19}F , ^{14}N , and ^1H . Structural data on the corresponding neutral compound, $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$,² suggest that the predominant couplings should occur with the cobalt and phosphorus nuclei.

The ESR spectrum has been analyzed by trial-and-error comparison with simulated spectra obtained with the usual isotropic spin Hamiltonian. The best simulation was obtained by using a Lorentzian line shape with a pic-to-pic line width of 5 G (Figure 1b). It suggests that the unpaired electron is coupled with two equivalent cobalt nuclei, six equivalent phosphorus nuclei, and twelve equivalent fluorine nuclei. The following magnetic parameters are derived from this spectrum:

$$g_0 = 2.025 \quad |A(\text{Co})| = 18 \text{ G} \quad |A(\text{P})| = 42.7 \text{ G} \quad (1)$$

$$|A(\text{F})| = 5.3 \text{ G}$$

However, this simulation is not quite perfect for the following reasons: (1) The great number of magnetic nuclei coupled to the electron generate more than 1000 overlapping lines. (2) For simplification, the line width has been considered to be constant for each individual transition. In fact, the line width may vary with the quantum numbers m_i because of molecular tumbling in the solution.¹² This explains the poor resolution of the experimental spectrum on its wings at low and high magnetic fields, where the line width is greater than in the middle part.

From 150 K down to 4 K, the ESR spectrum remains unchanged (Figure 2a). Owing to the approximate D_{3h} symmetry

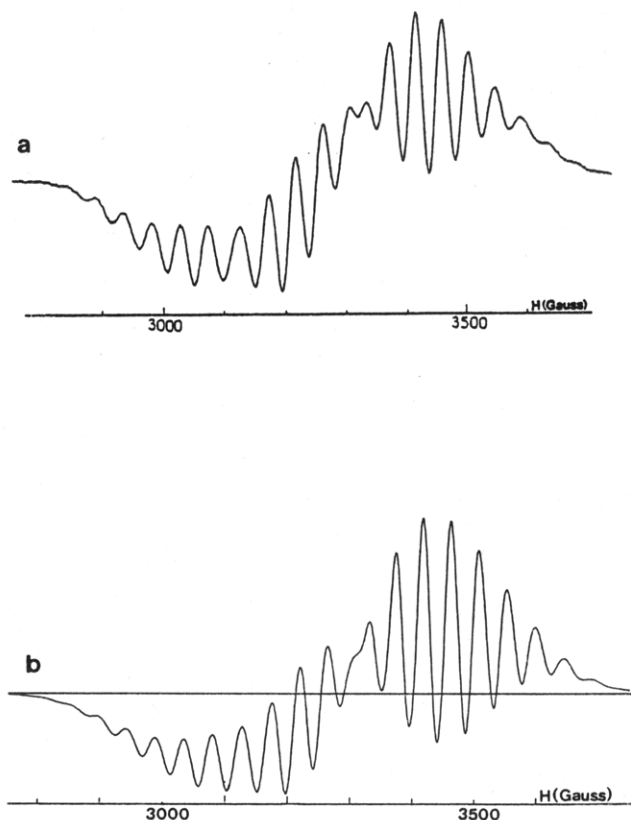


Figure 2. X-Band ESR spectra of the radical anion $(\text{CH}_3\text{N}(\text{PF}_2)_2)_3\text{Co}_2(\text{CO})_2^-$ in THF at 4 K ($c \approx 10^{-3}$ M): (a) experimental (microwave power 20 mW; field modulation intensity 8 G; gain 2×10^4); (b) simulated.

of the anion, the spin Hamiltonian used for simulation was assumed to be axial. The simulation reveals that at 4 K on the ESR time scale, the unpaired electron still remains equally delocalized onto the two magnetically equivalent cobalt nuclei and the six magnetically equivalent phosphorus nuclei (Figure 2b). The following magnetic parameters were determined by using a Lorentzian line shape ($\Delta_{\perp}^{\text{PP}} = 30$ G; $\Delta_{\parallel}^{\text{PP}} = 20$ G):

$$g_{\perp} = 2.03 \quad |A_{\perp}(\text{Co})| = 48 \text{ G} \quad |A_{\perp}(\text{P})| = 42.7 \text{ G} \quad (2a)$$

$$g_{\parallel} = 2.00 \quad |A_{\parallel}(\text{Co})| = 38 \text{ G} \quad |A_{\parallel}(\text{P})| = 42.7 \text{ G} \quad (2b)$$

The simulation thus did not give any evidence of an anisotropic hyperfine interaction with the phosphorus nuclei. Furthermore, fluorine hyperfine interactions did not appear in the anisotropic spectrum because of the rather large line widths. ENDOR experiments have been performed in order to determine these parameters.¹³

The Q-band spectrum recorded at 77 K could be simulated with the same parameters by using a greater line width ($\Delta_{\perp}^{\text{PP}} = \Delta_{\parallel}^{\text{PP}} = 45$ G) (Figure 3).

(B) Electronic Spectroscopy. The optical spectrum has been recorded at room temperature in both tetrahydrofuran and dichloromethane. The positions and extinction coefficients of the maxima are the same in each of these solvents and appear at $15\,300 \text{ cm}^{-1}$ ($\epsilon \approx 970 \text{ M}^{-1} \text{ cm}^{-1}$) and $29\,200 \text{ cm}^{-1}$ ($\epsilon \approx 5700 \text{ M}^{-1} \text{ cm}^{-1}$) (Figure 4).

Discussion

The most important feature deduced from the ESR spectra is the complete electronic delocalization over the two cobalt sites of the radical anion, even at 4 K. This indicates that the hopping frequency in such a dimer is higher than 10^8 Hz, $\tau \approx 10^{-8}$ s being the ESR time scale. This radical anion is therefore a class III

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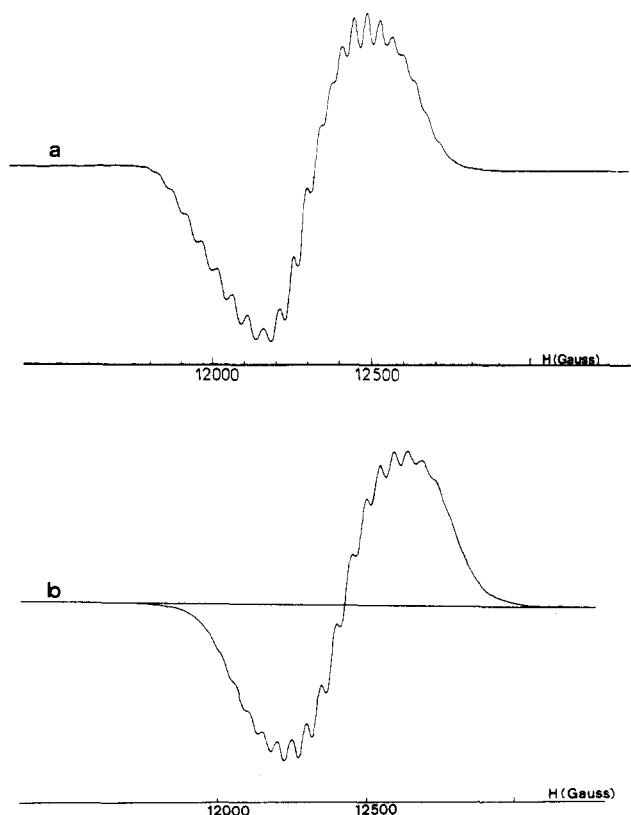


Figure 3. Q-Band ESR spectra of the radical anion $(\text{CH}_3\text{N}(\text{PF}_2)_2)_3\text{Co}_2(\text{CO})_2^-$ in the THF at 77 K ($c \ 10^{-1}$ M): (a) experimental (microwave power 5 mW; field modulation intensity 10 G; gain 8×10^2); (b) simulated.

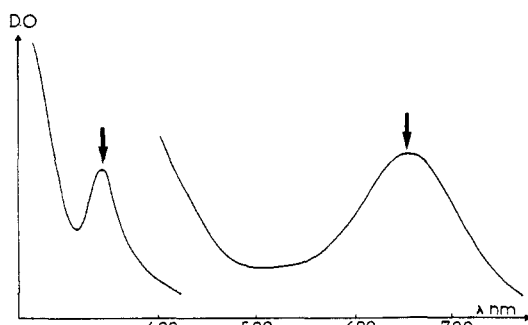


Figure 4. Optical spectrum of the radical anion $(\text{CH}_3\text{N}(\text{PF}_2)_2)_3\text{Co}_2(\text{CO})_2^-$ in THF solution ($c \ 2 \times 10^{-3}$ M).

mixed-valence compound according to the classification of Robin and Day.⁹

This electronic delocalization leads us to describe the energy levels of the system with a set of molecular orbitals delocalized over the two cobalt units. Such molecular orbital (MO) diagrams have been used to interpret the electronic spectra of several binuclear cobalt carbonyl complexes of the type $\text{Co}_2(\text{CO})_6\text{L}_2$ having D_{3d} symmetry.^{14,15} The observed structure of the neutral $[\text{C}-\text{H}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ molecule² suggests D_{3h} symmetry for the corresponding radical anion. The MO diagram¹⁴ (Figure 5) shows that the unpaired electron is in the σ^* level of the cobalt-cobalt bond built on the antibonding combination of the d_{z^2} orbitals of each cobalt atom. This is consistent with the ESR results. Thus the shift of the g -tensor components from the free-spin value, $g_e = 2.0023$, arises from spin-orbit coupling of the molecular orbital containing the unpaired electron with filled molecular orbitals. For an electron in a d_{z^2} orbital, a shift is predicted for the per-

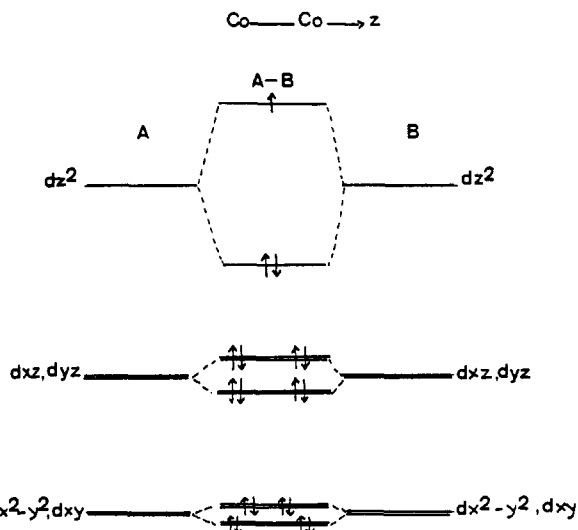


Figure 5. Schematic MO diagram for the radical anion $(\text{CH}_3\text{N}(\text{PF}_2)_2)_3\text{Co}_2(\text{CO})_2^-$.

pendicular component g_{\perp} but not for the parallel component g_{\parallel} ,¹⁶ i.e.

$$g_{\perp} = g_e + \frac{6\lambda}{\Delta(E(\sigma^*) - E(\pi^*))} \quad (3a)$$

$$g_{\parallel} = g_e \quad (3b)$$

These predictions are quite consistent with the experimental data: $g_{\perp} = 2.03$ and $g_{\parallel} = 2.00$.

Owing to the small value of the isotropic parameter for cobalt, it is obvious that the parallel and perpendicular hyperfine coupling constants have opposite signs. This result is consistent with the proposed σ^* ground state: the odd electron density ρ on the cobalt $3d_{z^2}$ atomic orbitals may be correlated with the experimental cobalt splitting tensor as in¹⁶

$$A_{\parallel}(\text{Co}) = A(\text{Co}) + 2\rho(\text{Co } d_{z^2}) B(\text{Co } d_{z^2}) \quad (4a)$$

$$A_{\perp}(\text{Co}) = A(\text{Co}) - \rho(\text{Co } d_{z^2}) B(\text{Co } d_{z^2}) \quad (4b)$$

$A(\text{Co})$ is the isotropic coupling term for the cobalt nucleus and $B(\text{Co } d_{z^2})$ is an anisotropic splitting constant of a cobalt nucleus with an unit $3d_{z^2}$ odd-electron density. $B = 62$ G for a Co^0 .¹⁶ In (4a) and (4b), the second-order effects have been ignored. Such formulas indicate that A_{\parallel} is positive while A_{\perp} is negative and lead to an estimation of $\rho(\text{Co } d_{z^2}) = 0.46$. So the odd-electron density seems to be mainly localized in the σ^* molecular orbital with a small extension over the axial carbonyls and the equatorial di-fluorophosphines.

From (3a) and (3b), it is also possible to estimate the energy difference between the $\sigma^*(d_{z^2})$ and $\pi^*(d_{xy}, d_{yz})$ orbitals. The spin-orbit coupling constant λ depends upon the charge of the metal ion and the covalency of the metal-ligand bonds: λ can be written as $\alpha^2\beta^2\lambda^0$, where λ^0 is the spin-orbit coupling constant for a free Co^0 ion ($\lambda^0 = 390$ cm^{-1}) and α^2 and β^2 are the electronic densities on the metal in the ground state σ^* and in the excited state π^* . α^2 from the previous calculation is 0.46. β^2 may be assumed to be close to 0.5: the energy difference $\Delta[E(\sigma^*) - E(\pi^*)]$ is found to be 19400 cm^{-1} . This should be the maximum value expected since β^2 may be smaller than 0.5 because of electronic delocalization over the ligands. These calculations suggest that the bands at 15300 and 29200 cm^{-1} in the optical spectrum can be assigned to $\pi^* \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ transitions, respectively. This agrees with previous assignments in the literature¹⁴ for other binuclear cobalt carbonyl complexes.

Given the wealth of information on the nuclear hyperfine couplings in this complex, a more detailed study will be published

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

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Registry No. $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2^-$, 73988-94-0.

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T_1 's and Proton NMR Integration in Metal Hydride Complexes

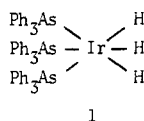
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It is sometimes difficult to determine the number of hydrides present in a transition-metal hydride complex.² Microanalysis, hydrogen evolution studies, and X-ray crystallography can all be misleading.^{2b} Integration of the proton NMR resonances 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(AsPh₃)₃H₃] (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.

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.

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Table I. Integration Data for *fac*-[Ir(AsPh₃)₃H₃]

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

^aThe tip angle corresponding to the pulse width used (36 μs = 90°) on the FX-90 Q spectrometer. CD_2Cl_2 solvent; 26 °C. ^b $\pm 1\%$; theoretical value 15. Reported as AsPh₃/IrH.

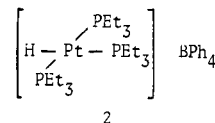
Table II. Apparent T_1 Values for the Compounds Studied^a

compd	H resonances	shift, δ	T_1 , s
<i>fac</i> -[Ir(AsPh ₃) ₃ H ₃] (1)	IrH	-14.4	0.38
	AsPh, <i>o</i>	{6.99	1.55
	<i>m</i>	{7.08	2.06
	<i>p</i>	7.18	2.59
[Pt(PEt ₃) ₃ H]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 ₂ CH ₃	1.14	1.91
	BPh, <i>o</i>	{6.90	3.39
<i>m</i>	{7.05	3.94	
<i>p</i>	7.34	4.87	
[(IrH(PPh ₃) ₂) ₂ (μ -H)(μ -Cl) ₂]BF ₄ (3)	IrH (terminal)	-23.37	0.37
	IrH (bridging)	-12.00	0.48
	PPh, <i>o</i>	{7.20	0.81
	<i>m</i>	{7.35	0.95
[(MoH ₂ (PMePh ₂) ₃) ₂ (μ -F) ₃]BF ₄ (4)	<i>p</i>	7.40	0.75
	PPh, <i>o</i>	{7.13	0.93
	<i>m</i>	{7.20	1.32
	<i>p</i>	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. ^b¹⁹²Pt, ¹⁹⁴Pt, ¹⁹⁶Pt, and ¹⁹⁸Pt. ^cPR₃ trans to H. ^dPR₃ cis to H.

Apart from the Pt case, the MH relaxation times were unusually fast and faster than those of any other protons in the molecule.

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(PEt₃)₃]BPh₄ (2),⁴ we find that hydrides coor-



minated 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 BPh₄⁻ ($T_1 \approx 4$ 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(PPh₃)₂)₂(μ -H)(μ -Cl)₂]BF₄ (3)⁸ show that the

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(5) (a) ¹⁹⁴Pt, 32.9%, $I = 0$; ¹⁹⁶Pt, 25.3%, $I = 0$; ¹⁹⁰Pt, 0.01%, ¹⁹²Pt, 0.79%, and ¹⁹⁸Pt, 7.2%, I unknown. (b) ¹⁹⁵Pt, 33.8%, $I = 1/2$.

(6) Unexpectedly the ¹⁹⁵PtH satellites are broader than the central PtH resonances at fields lower than 490 MHz; we have not been able to explain this satisfactorily.

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