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The ^{19}F Chemical Shifts of Fluorophenyl Phosphine Complexes of Group VIII Metals

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The ^{19}F chemical shifts for meta *and* para *fluorophenyl phosphines incorportated in a range of group VIII transition metal complexes are reported. The measured shifts are used to obtain values of the σ_I and σ_R° parameters used to correlate the electron withdrawing and donating parameters of aromatic compounds. It is concluded that the donor or acceptor properties of a metal ion containing moiety are determined more by the nature of the ligands present than by the formal oxidation state of the metal ion.*

Introduction

In a metal complex the ligand generally acts as an electron donor and the moiety containing the metal ion as an electron acceptor. The ability of different ligands and different metal ions to fulfil these roles varies widely. In some cases the reverse process of donation from the metal ion and acceptance by the ligand also contributes to the bonding. The stability and lability of a complex will depend on the donor and acceptor properties of the metal ion and the ligand. It is however not easy to obtain experimental data which can be directly related to these donor/acceptor properties. In the present study a possible approach to such data is explored.

Previously several physical techniques have been used to probe the charge distribution in metal complexes. A relatively early suggestion [1] involves the measurement of carbonyl stretching frequencies in the infrared but this is obviously limited to carbonyl complexes. The use of metal–ligand stretches [2, 3] has not been widespread and presents both theoretical and experimental difficulties. ESCA measurements have recently been applied to Pt complexes [4, 5] but the changes are not large and it is difficult to make comparisons between complexes of different metals. The ESR spectra of spin labelled ligands [6] have some potential use in this area.

The ^{19}F chemical shifts of fluoroaromatic compounds have been extensively correlated with the electron donating and withdrawing abilities of aromatic substituents. The initial investigations were carried out by Gutowsky *et al.* [7, 8] and the area has been further developed by Taft and his coworkers [9]. It is found empirically that the shifts of *meta* substituted fluorobenzenes reflect inductive effects in the σ system of the aromatic ring whereas those of *para* substituted fluorobenzenes reflect a combination of σ inductive and π resonance effects. Typically equations such as [10] have been found to represent

$$\delta_{meta} = -7.10\sigma_I + 0.60 \qquad (1)$$

$$\delta_{para} - \delta_{meta} = -29.5\sigma_R^\circ \qquad (2)$$

a large volume of chemical shift data. In these equations δ_{meta} and δ_{para} are the chemical shifts in ppm relative to the unsubstituted fluorobenzene and σ_I and σ_R° are parameters measuring the inductive and resonance effects of the substituent. The theoretical basis for these empirical relationships has been extensively discussed [11–13]. Although the theoretical arguments are not clearcut it seems apparent that parameters such as σ_I and σ_R° have much practical utility in correlating a large amount of physical data and that such parameters may be reliably derived from ^{19}F chemical shifts.

The question therefore arises as to the possible utility of such chemical shift data in probing the electron donating or accepting abilities of moieties containing transition metals. Several studies have explored this possibility. Parshall [14, 15] examined the ^{19}F NMR spectra of a series of Pt(II) complexes of the type *trans* $[(C_2H_5)_3P]_2Pt(C_6H_4F)X$ and found that the ^{19}F chemical shifts showed a marked dependence on the nature of the univalent anionic ligand X. He found that both σ_R° and σ_I were negative indicating that in these metal aryl compounds the metal containing group was an overall electron donor. Church and May [16] extended the study of platinum aryls to cationic complexes. Not surprisingly the NMR shifts indicated that the positively charged moieties were worse donors than the neutral species. These authors however raised several doubts about the detailed interpretation of this type of data. Similar studies of Co(III) aryls have been reported by Hill *et al.* [17] and of Au(I) complexes by Nichols [18].

TABLE I. ^{19}F Chemical Shifts[a] of Tri(fluorophenyl)phosphine Complexes.

Compound[b]	Method	δ_m^c	δ_p^c	σ_I	σ_R^o
L	d	−1.0	−1.0	0.23	0
LO	d	−2.9	−6.8	0.49	0.13
LMe^+I^-	d	−6.4	−13.5	0.99	0.24
L_2PtCl_2	d, g	−2.3	−5.9	0.41	0.12
L_2PtBr_2	g	−2.6	−6.0	0.45	0.12
L_2PtI_2	g	−1.6	−4.8	0.31	0.11
$L_2Pt(SCN)_2$	g	−3.4	−6.8	0.56	0.12
L_2PtO_2	d, e	−2.6	−8.3	0.45	0.19
L_2PtCS_2	d	−2.2	−4.4	0.39	0.08
L_2PtDPA	d, e	−1.0	−1.9	0.23	0.02
L_2PtHCl	d, e	−2.2	−5.0	0.39	0.10
$L_2PtRFCl^j$	d,e	−2.8	−6.3	0.48	0.12
L_2PdCl_2	d,e	−2.11	−5.41	0.38	0.11
L_2PdBr_2	d,e	−2.13	−4.84	0.38	0.09
L_2PdI_2	d,e	−2.00	−4.55	0.37	0.09
$L_2Pd(SCN)_2$	g	−3.4	−7.0	0.56	0.12
$L_2Ni(NCS)_2$	d	−2.4	−4.4	0.43	0.07
L_3RhCl	c	h	−2.1		
L_3RhBr	e	−2.9	−2.4	0.49	−0.02
L_3RhI	e	−2.5	−4.3	0.44	0.06
$L_2Rh(CO)Cl$	d	−1.99	−3.85	0.36	0.00
L_3RhCl_3	d	−1.4	−3.80	0.28	0.08
$L_2Ir(CO)Cl$	d	−1.95	−4.15	0.36	0.08
$L_2Ir(CO)ClHCl$	d	−2.61	−5.80	0.45	0.11
$L_2Ir(CO)Cl_3$	d	−2.84	−5.85	0.48	0.10
$L_2Ir(CO)ClMeI$	d	−2.73	−5.16	0.47	0.08
$L_2Ir(CO)ClO_2$	d	−2.38	−5.62	0.42	0.11
$L_2Ir(CO)BrO_2$	d	−2.39	−5.73	0.42	0.11
$L_2Ir(CO)IO_2$	d	−2.75	−5.75	0.47	0.10
L_3IrCl_3	d	−1.35	−3.25(2)	0.27	0.06
			−3.42(1)		0.07
$L_3Ir(CO)H$	e	−0.71	−0.23	0.18	−0.02

[a] Solvent $CDCl_3$. [b] L = *meta* or *para* tri(fluorophenyl)phosphine. [c] Shifts in ppm from fluorobenzene. [d] Compound synthesized directly. [e] Ligand exchange with triphenylphosphine complex. [g] Data from Ref. 19. [h] Exchange equilibrium too unfavourable to obtain data. [i] DPA = diphenylacetylene. [j] RF = CCl_2CClF_2.

In all of the work mentioned above the fluorophenyl group has been attached directly to the metal atom. The question arises as to whether similar studies would be possible in which the fluorophenyl group is part of a more common type of ligand such as an aryl phosphine. If the shifts are large enough and if they can reasonably be interpreted in terms of the electron donating or accepting abilities of the rest of the molecule there is a potential for obtaining information on the charge distributions of a wide range of interesting complexes including many pertinent to the area of homogeneous catalysis. Murray, Roberts and Walker [19] have reported the ^{19}F shifts of several platinum fluorophenyl phosphine complexes in the abstracts of a conference but little other data is available. It was the intent of the present study to examine the questions raised above.

Experimental

The ligands chosen for this study were *meta* and *para* trifluorophenyl phosphines. By using symmetrically substituted ligands possible complications arising from the tranfer of charge between inequivalent aromatic rings are avoided. The complexes studied were some thirty phosphine derivatives of platinum(0), platinum(II), palladium(II), nickel(II), rhodium(I), iridium(I), rhodium(III) and iridium(III). The complexes were prepared either by direct synthesis or by ligand exchange with the corresponding triphenylphosphine complexes *in situ*. The latter method has the advantage of experimental simplicity but also has a number of drawbacks. In some cases the equilibrium constant for ligand exchange may favour the triphenyl phosphine complex to the extent

TABLE II. ^{19}F Chemical Shifts[a] of Fluorophenyl Diphenyl Phosphine Complexes.

Compound[b]	δ_m	δ_p	σ_I	σ_R^0
L	−0.4	−0.4	0.14	0.0
L_2PdCl_2	−1.2	−4.0	0.25	0.09
L_2PtO_2	−2.0	−6.1	0.37	0.14
L_2PtCl_2	−1.6	−4.6	0.31	0.10

[a] Solvent $CDCl_3$. [b] L = *meta* or *para* fluorophenyl diphenyl phosphine.

that resonances from the complexed fluorophenyl phosphine cannot be observed. If ligand exchange is fast on the NMR time scale only an averaged resonance will be observed and a knowledge of the equilibrium constant is required to find the shift of complexed ligand. There is also the possibility of reactions other than simple ligand exchange occurring, *e.g.* halide ions may be displaced by a phosphine to give cationic complex. For these reasons in most cases the fluorophenyl phosphine complexes have been prepared by direct synthesis. For a number of complexes the results from ligand exchange reactions have been compared with the shifts obtained by direct synthesis of the compound. In each instance satisfactory agreement was obtained.

Table I presents the observed ^{19}F chemical shifts for some 28 complexes of both *meta* and *para* trifluorophenyl phosphine. Shifts are given in parts per million relative to fluorobenzene and the method used to obtain the data is indicated. Equations 1 and 2 have been used to calculate σ_I and σ_R^0. The solvent used throughout was $CDCl_3$ since this appears to be considerably purer than commercially available spectroscopic grade $CHCl_3$. This table also includes some data from Murray, Roberts and Walkers [19] results. Table II gives similar data for three complexes of *meta* and *para* fluorophenyl diphenyl phosphine.

Discussion

We note initially that the chemical shifts extend over a range of approximately 7 ppm. Since the shifts can be measured with an accuracy of ±0.02 ppm these ^{19}F shifts provide a potentially sensitive probe for the donor/acceptor properties of the metal containing moiety. This range of 7 ppm may be compared with the range of 25 ppm observed for substituted fluorobenzenes for which the substituent is one atom closer to the ^{19}F nucleus.

It is convenient to discuss these results in terms of the σ_I and σ_R^0 values given in Table I. A positive σ value is indicative of an electron withdrawing substituent. The general expectation is that donation of electrons from the phosphorus atom to the metal will leave a greater positive charge on the phosphorus and hence enhance its electron withdrawing properties with respect to the aromatic ring. This will be reflected in a more positive value for σ_I. It is also recognized though that the phosphine ligands can function as electron acceptors from the metal if metal–ligand π bonding is present. Such bonding will decrease the positive charge on the phosphorus and hence make σ_I more negative. In general, it is expected that σ_I will depend upon both of these effects. The interpretation of σ_R^0 is not straightforward. As pointed out by Rakshys *et al.* [10] in the parent phosphines, both donation of electrons to the π system of the ring from the phosphorus lone pair and acceptance of electrons from the π system of the ring into the empty phosphorus d orbitals can be envisaged. The observation of a small or zero σ_R^0 indicates that these effects either cancel each other out or are negligibly small. If the phosphine is complexed to a metal, the lone pair will no longer be available for donation to the ring. Any excess positive charge on the phosphorus will also tend to enhance donation to the empty d orbitals. Both of these effects will give rise to the positive σ_R^0. It might be expected that the increase in σ_R^0 would parallel that in σ_I. However, the further possibility of donation from the metal d orbitals to the phosphorus d orbitals exists. This could lead to the subsequent donation from the phosphorus d orbitals to the aromatic system. Such a process would make a negative contribution to σ_R^0. There are obviously some steric restrictions on the conjugation of this type. In most cases, it is not clear whether the aromatic rings will or will not be suitably oriented.

Methyltriphenyl phosphonium iodide provides a qualitative indication of the magnitude of the effects to be expected in the absence of metal d orbitals. Compared to triphenyl phosphine, the σ_I value has increased by 0.76 units (from +0.23 to +0.99) and σ_R^0 has increased by 0.24 units. This can be taken as a measure of the effect of placing a full positive charge on the phosphorus atom. A rather closer analogy to complex formation (again without the added complication of d orbitals) is provided by the phosphine oxide results. In this case, σ_I has increased by 0.26 units and σ_R^0 by 0.13 units. This result would indicate about 1/3 or 1/2 of a positive charge on the phosphorus.

For the metal complexes studied, σ_I is, in all cases except one, equal to or greater than σ_I for the free ligand, *i.e.*, the phosphine is behaving as a Lewis base. The magnitude of the enhancement (0 to 0.33 units) provides a very rough measure of the positive charge on the phosphorus. Turning to specific compounds, the series of diminishing σ_I values provided by the various platinum complexes is noted.

$L_2Pt(SCN)_2 > L_2PtO_2 \sim L_2PtCl_2 \sim L_2PtBr_2 >$

$L_2PtHCl \sim L_2PtCS_2 > L_2PtI_2 > L_2Pt(DPA)$

(DPA = diphenylacetylene)

There is no obvious trend between *cis* and *trans* complexes. The range of σ_I values (σ_I = 0.56 to 0.33) covered by this series indicates substantial differences in the amount of negative charge donated to the metal. This series is expected to parallel the charge on the metal. It may be noted that formally Pt(II) complexes tend to occur at the high end of the series and the formally Pt(0) complexes at the low end. There is, however, no sharp line between these two oxidation states. In cases where analogous compounds are involved these results parallel nicely the ESCA energies reported by Cook *et al.* [4], *i.e.*,

$L_2PtCl_2 > L_2PtO_2 > L_2PtCS_2 > L_2PtDPA$

$(L = (C_6H_5)_3P)$

Notable in this series is the high σ_I value for the oxygen complex. McGinnety and Ibers [20] have suggested that the formation of such stable oxygen complexes required donation of π electrons to the oxygen moiety which implies that these electrons are less available for donation to other ligands. This would seem to be reflected in the high σ_I value. A similar argument could be applied to the thiocyanate complex. It is also interesting that the hydride complex has a relatively low σ_I, in accord with the lack of π acceptor properties of the hydride ligand. In cases where the change in σ_I is close to zero., it is inferred that the negative charge lost from the phosphorus by sigma donation is balanced by the gain from backbonding. Thus, for the diphenylacetylene complex (and probably also for the tetrakis phosphine complex – see *Experimental*) σ and π bonding are both important. It is thus suggested that σ_I values derived in this manner provide an empirical measure of the electron affinity of the metal atoms in differing ligand environments. It would be natural to associate the "electron affinity of the metal" with the positive charge on the metal. This, however, is probably an excessive simplification since the effect of charge transfer from one ligand may be enhanced or diminished by charge transfer from other ligands so that any measurement involving only one ligand will not reflect the true metal charge.

It would be desirable to compare σ_I values for the Pt complexes with those of analogous square planar complexes of Pd and Ni. Unfortunately, the data on hand does not allow direct comparison. Many Ni(II) phosphine complexes are tetrahedral and paramagnetic. Interaction with the unpaired electrons prevent analysis of the chemical shifts in the above manner. The Ni(II) isothiocyanate complex cannot be compared directly with the Pd and Pt thiocyanate complexes. From the results for the chloride and the bromide complexes, it would appear that the electron affinity of Pt is rather greater than that of Pd but the iodide gives the opposite indication. However, the Pt complexes have *cis* geometry and the analogous Pd complexes have *trans* geometry. The results may, therefore, arise more from extra electron withdrawing ability of a *trans* halide ion than any intrinsic difference between Pt and Pd. It is, however, interesting to note that in the square planar d^8 complexes the formally singly charged Rh and Ir do not have notably lower electron affinities than the formally doubly charged Pd and Pt.

Perhaps the most interesting comparisons are between the four coordinate Rh(I) and Ir(I) complexes and the six coordinate Rh(III) and Ir(III) compounds. Oxidative addition to Vaska's compound ($L_2IrCOCl$), for example, is accompanied by a formal increase in the oxidation state of the metal from +1 to +3 so that it might be expected that there would be an increase in the positive charge on the metal, and hence an increase in σ_I for the phosphine ligand. On the other hand, it could be argued that these compounds tend to be covalent rather than ionic and that the relevant change is an increase in the number of electrons from 16 in the valence shell of the four coordinate compounds to 18 electrons in the six coordinate compounds. This would imply an increase in the negative charge on the metal and hence a decrease in σ_I for the coordinated phosphine. Examination of the results of Table I shows both type of behaviour. Thus, the σ_I value for Vaska's compound is 0.36. The addition compounds with HCl, Cl_2, CH_3I, and O_2 have values of 0.45, 0.48, 0.47 and 0.42, respectively. In these cases, σ_I has clearly increased. On the other hand, L_3RhCl_3 and L_3IrCl_3 both have σ_I values of 0.27 which are significantly less than observed for any of the four coordinate Rh(I) or Ir(I) complexes. It is possible that this difference in behaviour is associated with the presence or absence of π accepting carbonyl ligand. Thus, L_3IrCl_3 (σ = 0.27) may be compared with $L_2Ir(CO)Cl_3$ (σ = 0.48) and the large difference rationalized in terms of the greater π accepting ability of a carbonyl ligand relative to a phosphine. This increases the positive charge on the metal and hence the demand for electrons from the phosphine. However, perhaps the most significant conclusion is that the electron affinity of the metal is much more sensitive to the nature of the ligands than it is to the formal oxidation state.

There have been a number of infrared studies of metal complexes containing triphenylphosphine and carbonyl ligands [21, 22]. High carbonyl stretching frequencies have been associated with diminished back-donation to the carbonyl and hence increased positive charge on the metal. By and large, the carbonyl stretching frequencies correlate reasonably

TABLE III. Carbonyl Stretching Frequencies.

Compound	σ_I	ν_{CO}	Reference
L = $(C_6H_5)_3P$			
$L_2Ir(CO)Cl$	0.36	1950	21
$L_2Ir(CO)I$	0.44	1975	21
$L_2Ir(CO)HCl_2$	0.45	2024	22
$L_2Ir(CO)Cl_3$	0.48	2078	22
$L_2Ir(CO)ClMeI$	0.47	2048	21
		2054	22
$L_2Ir(CO)ClO_2$	0.42	2000	21
$L_2Ir(CO)BrO_2$	0.42	1996	21
$L_2IrCOIO_2$	0.47	1995	21
$L_3Ir(CO)H$	0.18	1930	33
$L_2Rh(CO)Cl$	0.36	1960	21

well with the σ_I parameters derived from this present work. This is illustrated in Table III. The very low σ_I for the five coordinate $L_3Ir(CO)H$ is particularly notable and is paralleled by a low carbonyl stretching frequency. A quantitative correlation would not be expected since σ_I is associated with σ bonding where the carbonyl stretching frequencies are associated with changes in π bonding.

A limited study of complexes of $C_6H_4F(C_6H_5)_2P$ was undertaken, and the results of these measurements are shown in Table II. These results closely parallel the results for the corresponding tris fluorophenylphosphines but the magnitudes of the values of σ_I and σ_R° are somewhat reduced. From this it may be deduced that the metal ion withdraws charge phenylphosphines but the magnitude of the values of reducing the effect on the fluorinated moiety. This result is consistent with the report that carbonyl containing complexes involving fluorophenylphosphines have higher CO stretching frequencies than the phenylphosphine compounds [23].

The discussion to this point has omitted the σ_R° values, since they do not provide a direct measure of π donation from the metal to the phosphorus d orbitals and hence to the aromatic π system. This is due to the fact that the molecular framework is not planar as is required for direct conjugation. As indicated previously, the value of σ_R° are expected to be positive and to parallel the σ_I values. Donation from the phosphorus lone pair to the ring π system is no longer possible and acceptance into the phosphorus d orbitals will be enhanced by increasing positive charge on the phosphorus, both effects leading to a more positive σ_R°. A negative contribution could arise from electron donation from the phosphorus d orbitals to the π system if the phosphorus d orbitals are partly filled by donation from the metal. In general, the σ_R°'s are positive and parallel the σ_I's quite closely. The notable exceptions are the square planar Rh(I) complexes which have large σ_I's but small or even slightly negative σ_R°,s. It is quite possible that back-donation can be important in these complexes. On the other hand, the platinum oxygen complex has the highest observed σ_R° which is consistent with the suggestion made above that donation to the oxygen molecule inhibits donation to other ligands. It cannot be claimed, however, that the σ_R°'s provide any quantitative measure of back-bonding since they obviously represent the relatively small difference between several competing processes.

Experimental

The synthesis of $(m\text{FC}_6H_4)_3P$ and $(p\text{FC}_6H_4)_3P$ followed conventional methods. The reaction of the appropriate bromofluorobenzene with dry magnesium in THF produced the Grignard reagent, which was reacted with an equivalent amount of PCl_3 to yield the desired product, in about 20% yield, after recrystallization from the hot ethanol.

The compound $[(FC_6H_4)_3P]_2PtCl_2$ was prepared by the literature method [24]. The addition of an ethanolic solution of $(FC_6H_4)_3P$ to a stirred aqueous solution of K_2PtCl_4 caused immediate precipitation of white crystals. After stirring for 10 minutes, the product was filtered and washed with water and hot ethanol. The product was recrystallized from boiling chloroform. The corresponding dibromide and diiodide complexes were prepared from the dichloride complex by stirring for 24 hours in an acetone solution containing a large excess of KBr or KI.

The palladium complexes were prepared by the addition of ethanolic $(FC_6H_4)_3P$ to a stirred aqueous solution of $Pd(NO_3)_2$ to which had been added a large excess of KX. The remainder of the synthesis followed closely the preparation described for the platinum(II) complexes, except that the crude product was recrystallized from chloroform by the addition of hexane.

The tetrakis platinum(0) complex $[(FC_6H_4)_3P]_4Pt$ was prepared by the reaction of $[(FC_6H_4)_3P]_2PtCl_2$ with hydrazine [25] in the presence of excess $(FC_6H_4)_3P$.

The complexes $[(FC_6H_4)_3P]_2PtDPA$ (DPA is diphenylacetylene) [26] and $[(FC_6H_4)_3P]_2PtCS_2$ were prepared *in situ* by addition of DPA and CS_2 to the tetrakis complex [27]. The compound $[(FC_6H_4)_3P]_2PtO_2$ was prepared by passage of air through a chloroform solution of the tetrakis complex followed by precipitation with hexane [28]. The complex $[(FC_6H_4)_3P]_2PtHCl$ was prepared by the passage of gaseous HCl through a solution of $[(FC_6H_4)_3P]_4Pt$ followed by precipitation and recrystallization from boiling chloroform [29].

The complexes $[(FC_6H_4)_3P]_3RhCl_3$ and $[(FC_6H_4)_3P]_3IrCl_3$ were prepared by literature methods [30, 31] from the appropriate phosphine and the hydrated metal trichloride.

The rhodium(I) and iridium(I) complexes were prepared according to the literature methods [27] from the hydrated metal trichloride and the appropriate phosphine in refluxing N,N-dimethylformamide. The oxidative addition products of the iridium(I) complexes $[(FC_6H_4)_3P]_2Ir(CO)HCl_2$, $[(FC_6H_4)_3P]_2Ir(CO)Cl_3$, $[(FC_6H_4)_3P]_2IrCH_3ClI$, and $[(FC_6H_4)_3P]_2Ir(CO)ClO_2$ were prepared by literature methods by the addition of HCl, Cl_2, CH_3 to $[(FC_6H_4)_3P]_2Ir(CO)Cl$ [32].

The triphenylphosphine complexes used in the exchange experiments were purchased from Strem Chemical Company and were used without further purification.

The NMR spectra were recorded using a Varian DP60 NMR spectrometer operating at 56.4 MHz using a locked frequency sweep mode. Internal C_6H_5F was used as an internal lock and spectra were recorded using a proton decoupling frequency of 59,995,200 Hz. Deuterochloroform $CDCl_3$ was used throughout. Observed chemical shifts are reproducible to within ±0.02 ppm. All samples were prepared under a nitrogen atmosphere using $CDCl_3$ previously flushed with nitrogen. In spite of these precautions, small resonances attributed to the phosphine oxides $(C_6H_5)_3PO$ were observed. These were identified by comparison with genuine samples of the phosphine oxides prepared by oxidation of the phosphines by alcoholic potassium hydroxide. In no case was there any evidence for the formation of phosphine oxide complexes.

The tetrakis platinum complex presented some difficulties and the shifts are not reported. Solutions of this complex give ^{19}F resonances at the free ligand position. The complex is known to be dissociated in solution. Addition of free ligand does not cause any shift in position. The most likely interpretation is that there is no chemical shift difference between free and complexed ligand (which would put the $[(FC_6H_4)_3P]_4Pt$ in the expected position in the series of platinum complexes discussed above), but lacking any external probe for complexation it could also be argued that only free ligand is observed with the complex resonance being missed by reason of low intensity or broadening due to rapid exchange.

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