An Investigation of 1:1 Adducts of Gallium Trihalides with Triarylphosphines by Solid-State ^{69/71}Ga and ³¹P NMR Spectroscopy

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Abstract: Several 1:1 adducts of gallium trihalides with triarylphosphines, $X_3Ga(PR_3)$ (X = Cl, Br, and I; PR₃ = triarylphosphine ligand), were investigated by using solid-state 69/71Ga and ³¹P NMR spectroscopy at different magnetic-field strengths. The 69/71Ga nuclear quadrupolar coupling parameters, as well as the gallium and phosphorus magnetic shielding tensors, were determined. The magnitude of the ⁷¹Ga quadrupolar coupling constants ($C_{0}(^{71}\text{Ga})$) range from approximately 0.9 to 11.0 MHz. The spans of the gallium magnetic shielding tensors for these complexes, $\delta_{11} - \delta_{33}$, range from approximately 30 to 380 ppm; those determined for phosphorus range from 10 to 40 ppm. For any given phos-

Introduction

Interest in the study of adducts formed by Group 13 Lewis acids with Group 15 Lewis bases dates back to the early 1800s with the first synthesis of F₃B·NH₃ by Gay-Lussac and Thénard.^[1] The preparation of adducts formed by the Group 13 (B, Al, Ga, In, Tl) trihalides or trialkyls with Lewis bases containing Group 15 elements (N, P, As, Sb, Bi)

phine ligand, the gallium nuclei are most shielded for X=I and least shielded for X=Cl, a trend previously observed for In^{III}-phosphine complexes. This experimental trend, attributed to spin-orbit effects of the halogen ligands, is reproduced by DFT calculations. The signs of $C_Q(^{69/71}Ga)$ for some of the adducts were determined from the analysis of the ³¹P NMR spectra acquired with magic angle spinning (MAS). The ¹J(^{69/71}Ga,³¹P) and $\Delta J(^{69/71}Ga,^{31}P)$ values, as well as their signs, were

Keywords: chemical shifts • coupling constants • density functional calculations • gallium • NMR spectroscopy • phosphorus

also determined; values of ${}^{1}J({}^{71}\text{Ga},{}^{31}\text{P})$ range from approximately 380 to 1590 Hz. Values of ${}^{1}J({}^{69/71}Ga, {}^{31}P)$ and $\Delta J(^{69/71}\text{Ga},^{31}\text{P})$ calculated by using DFT have comparable magnitudes and generally reproduce experimental trends. Both the Fermi-contact and spin-dipolar Fermi-contact mechanisms make important contributions to the ${}^{1}J({}^{69/71}Ga, {}^{31}P)$ tensors. The ${}^{31}P$ NMR spectra of several adducts in solution, obtained as a function of temperature, are contrasted with those obtained in the solid state. Finally, to complement the analysis of NMR spectra for these adducts, single-crystal X-ray diffraction data for $Br_3Ga[P(p-Anis)_3]$ and $I_3Ga[P(p-Anis)_3]$ were obtained.

has drawn considerable recent attention^[2] because they have many important applications, particularly in materials chemistry.^[3,4,5] For example, they are single-source precursors for preparing a wide range of semiconductors based on Group 13 and 15 elements.^[3] In the case of gallium, GaN and GaP are used extensively in light-emitting diodes (LEDs),^[5] GaSb is used in thermal-imagining devices^[5] and GaAs is widely used in solar cells.^[5] The gallium trihalide phosphine adducts were first prepared and characterized by Carty and co-workers,^[6] and have remained of interest because of their importance in the preparation of GaP-based semiconductors.^[7]

Gallium trihalide phosphine adducts have often been characterized by using single-crystal X-ray diffraction or vibrational spectroscopy.^[6,8–10] Herein, we show that solid-state ^{69/71}Ga and ³¹P NMR spectroscopy are excellent complementary techniques for characterizing 1:1 adducts of gallium trihalides with triarylphosphines. The information available from NMR spectroscopy includes the chemical shift (CS) tensors, indirect spin–spin coupling constants between ^{69/71}Ga and ³¹P, and the electric field gradient (EFG) tensors for the quadrupolar nuclei, ⁶⁹Ga and ⁷¹Ga. Previously, solid-state ^{69/71}Ga NMR spectroscopy has been used to determine the nuclear quadrupolar coupling constants (C_Q -(^{69/71}Ga)) for Ga₂O₃^[11] and various semiconductors, including

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201202954. It contains background information on nuclear quadrupole coupling, magnetic shielding, and indirect spin–spin coupling; sample preparation; quantum chemical calculations; single-crystal X-ray diffraction data for Br₃Ga[P(*p*-Anis)₃] and I₃Ga[P(*p*-Anis)₃]; a summary of 2*d* values; computational gallium magnetic shielding parameters; additional solid-state ³¹P and ^{69/71}Ga NMR spectra for all adducts at different magnetic-field strengths; and solution-phase ³¹P NMR spectra for all adducts at different temperatures.

GaN,^[12] GaP,^[13] and GaAs;^[14] nevertheless, the study of gallium complexes by using solid-state ^{69/71}Ga NMR spectroscopy is limited.^[15] Gallium isotropic chemical shifts (δ_{iso} (Ga)) range over approximately 1400 ppm;^[16] therefore, one might expect gallium chemical shift anisotropy (CSA) to be large. However, there have only been a few reports of gallium CSAs.^[11a,17]

Previously, we undertook a detailed solid-state NMR investigation of some related indium trihalide phosphine adducts.^[18,19] In those studies, we showed that a careful analysis of ¹¹⁵In and ³¹P NMR spectra could provide considerable information about these adducts. Hence, a goal of this study is to determine whether the similarity of the gallium trihalide triarylphosphines with the 1:1 indium-phosphine adducts investigated in the earlier studies will be reflected in their NMR properties. Specifically, 1:1 adducts of gallium trihalide with a triarylphosphine, $X_3Ga(PR_3)$ (X = Cl, Br, and I; PR_3 = triarylphosphine ligand), are characterized by using solid-state ^{69/71}Ga and ³¹P NMR spectroscopy; these NMR results are corroborated by the results of density functional theory (DFT) calculations. Possible causes for the observed sensitivity of the gallium CS tensors to the nature of the halogen ligands are considered. In addition, analyses of the 31 P NMR spectra allowed the determination of ${}^{1}J({}^{69/71}$ Ga, 31 P) and $\Delta J(^{69/71}Ga,^{31}P)$, that is, the anisotropy in ${}^{1}J(^{69/71}Ga,^{31}P)$. The signs for $\Delta J(^{69/71}\text{Ga},^{31}\text{P}), {}^{1}J(^{69/71}\text{Ga},^{31}\text{P}), \text{ and } C_{\Omega}(^{69/71}\text{Ga})$ were also determined for these adducts. In addition, since knowledge of the structures of the adducts under study is invaluable for a proper analysis of the 69/71Ga and 31P NMR spectra, single-crystal X-ray diffraction data for Br₃Ga[P(p-Anis)₃] and $I_3Ga[P(p-Anis)_3]$ (Anis=anisole, $C_6H_4(OCH_3))$) are also presented.

Gallium NMR spectroscopy: Gallium has two naturally occurring isotopes: ⁶⁹Ga and ⁷¹Ga. The nuclear-spin properties and natural abundance (NA) of the two isotopes, ⁶⁹Ga ($S = {}^{3}/_{2}$, $\Xi = 24.00 \%$, $Q = 17.1 \text{ fm}^{2}$, NA = 60.1 %) and ⁷¹Ga ($S = {}^{3}/_{2}$, $\Xi = 30.50 \%$, $Q = 10.7 \text{ fm}^{2}$ NA =

 $\Xi = 30.50\%$, Q = 10.7 fm², NA = 39.9%),^[20] make them potential candidates for NMR spectroscopic study. In the solid state, ⁷¹Ga is the preferred gallium NMR isotope because of its larger Larmor frequency and receptivity, as well as its smaller nuclear quadrupolar moment. Nevertheless, in many studies, including this work, both ⁶⁹Ga and ⁷¹Ga are investigated. In an applied magnetic field, \mathbf{B}_0 , the interactions involving the 69/ 71Ga nuclei of X3Ga(PR3) include the Zeeman, nuclear quadrupolar, and nuclear magnetic shielding interactions, as well as the direct dipolar and indirect nuclear spin-spin coupling interactions between ${}^{69/71}$ Ga and coupled 31 P nuclei $(I={}^{1}/_{2}, NA=100\%)$.

NMR spectroscopists typically measure chemical shifts, δ , the nuclear magnetic shielding of a given nucleus relative to that for a reference compound: $\delta \approx \sigma_{ref} - \sigma_{sample}$, in which the latter two terms refer to the magnetic shielding of the reference compound and of the sample, respectively.^[21] When discussing NMR spectra, it is convenient to use three chemical shift parameters: the isotropic chemical shift, $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, in which $\delta_{11} \ge \delta_{22} \ge \delta_{33}$, the span, $\Omega = \delta_{11} - \delta_{33}$, describing the maximum orientation dependence of the magnetic shielding interaction, and the skew, $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$, which is unitless with $-1 \le \kappa \le +1$;^[21] note that for an axially symmetric chemical shift tensor, $\kappa = \pm 1$.

The effects of the nuclear quadrupolar coupling interaction on solid-state NMR spectra of quadrupolar and spin-1/2nuclei have been discussed extensively;^[22] a summary is also presented in the Supporting Information. Likewise, readers are encouraged to consult the original literature^[22d,23,24] or Supporting Information for a detailed discussion of the effects of direct and indirect spin–spin interactions on NMR spectra.

³¹**P** NMR spectroscopy of the ^{69/71}Ga–³¹**P** spin pair: A ³¹**P** NMR spectrum spin–spin coupled to either ⁶⁹Ga or ⁷¹Ga should consist of four peaks (Figure 1).^[25] If $C_{\rm Q}$ is significant, the direct dipolar interaction for the ^{69/71}Ga–³¹**P** spin pair is not averaged to zero by magic angle spinning (MAS),^[25] a consequence of the fact that the gallium nuclei are not quantized exactly along **B**₀.^[26] In this case, one observes an uneven spacing between adjacent peaks (Figure 1); analysis of these spectra yield the residual dipolar coupling (*d*), which is directly related to $C_{\rm Q}$ and $R_{\rm eff}$. In favorable cases, such analyses will also yield the sign of $C_{\rm Q}$; see the Supporting Information for a presentation of the underlying theory.



Figure 1. Calculated splitting pattern in a ³¹P NMR spectrum of a MAS sample containing a ^{69/1}Ga–³¹P spin pair with d=0, d>0, and d<0. The spin states as indicated are those for a positive sign for ¹ $J(^{69/1}Ga,^{31}P)$, but the splitting pattern is invariant with this sign.

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Results and Discussion

Because of the importance of molecular structure in the analysis of the NMR results, those for the triarylphosphine gallium trihalide adducts are presented first, followed by a discussion of the solid-state ^{69/71}Ga NMR spectra of each adduct. Next, the ¹J(^{69/71}Ga,³¹P) and ΔJ (^{69/71}Ga,³¹P) values, as well as their signs, and the $C_{\rm Q}$ (^{69/71}Ga) values for all complexes, determined through ³¹P NMR spectroscopy, are reported. Finally, results of relativistic DFT calculations of the NMR parameters for these compounds are compared with experimental values and the causes of the observed sensitivity of the gallium CS tensors to the nature of the directly bonded halogen ligands are explored.

Structures of the triarylphosphine gallium trihalide adducts:

Structures for Cl₃Ga(PPh₃),^[8] Br₃Ga(PPh₃),^[8] and I₃Ga-(PPh₃),^[9] obtained from X-ray crystallography, have been reported; those for Br₃Ga[P(*p*-Anis)₃] and I₃Ga[P(*p*-Anis)₃] were determined as part of this study and are shown in Figure 2. See Tables S1 and S2 in the Supporting Information for more detailed X-ray diffraction data and for selected structural information. All five adducts studied by X-ray crystallography have approximately tetrahedral coordination about the Ga and P atoms; there is a C_3 axis along the Ga– P bond of I₃Ga(PPh₃) and Br₃Ga[P(*p*-Anis)₃] and an approximate C_3 axis along this bond for the other adducts.

We were unable to obtain crystals suitable for X-ray diffraction studies for the adduct of $GaCl_3$ with $[P(p-Anis)_3]$ and for the three adducts containing the tris(2,4,6-trimethoxyphenyl)phosphine (TMP) ligand. However, elemental analysis indicated that both moieties were present in a 1:1 ratio and solid-state ³¹P NMR spectroscopy confirmed the Ga–P connectivity.

^{69/71}Ga NMR of solid triarylphosphine gallium adducts: ^{69/71}Ga NMR parameters determined from analyses of the spectra for the triarylphosphine gallium trihalide adducts investigated herein are listed in Table 1. See Figures S1-S4 in the Supporting Information, as well as those shown below, for examples of Ga NMR spectra. The signs for $C_{\rm Q}(^{69/71}{\rm Ga})$ reported in this section were determined from an analysis of the ³¹P NMR spectra of MAS samples, or from the results of DFT calculations (see below).

Because $Br_3Ga[P(p-Anis)_3]$ has a C_3 symmetry axis along the Ga–P bond, the Ga CS and EFG tensors are axially symmetric with the unique compo-

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Table 1. Experimental $^{69/71}$ Ga NMR parameters for X₃Ga(PR₃) (X = Cl, Br, and I) adducts.

Gallium chemical shift tensor								
	$\delta_{ m iso}$	δ_{11}	δ_{22}		δ_{33}		Ω	κ
	[ppm]	[ppm]	[ppm]		[ppm]		[ppm]	
Cl ₃ Ga(PPh ₃)	260.0 ± 10.0	357.5 ± 10.0	215.0	± 10.0	207.5	± 10.0	150.0 ± 15.0	-0.90 ± 0.10
$Br_3Ga(PPh_3)$	137.0 ± 10.0	178.2 ± 10.0	119.7	± 10.0	113.2	± 10.0	65.0 ± 15.0	-0.80 ± 0.10
$I_3Ga(PPh_3)$	-150.0 ± 10.0	-30.0 ± 10.0	-30.0	± 10.0	-390.0	± 10.0	360.0 ± 15.0	1.00
Cl ₃ Ga[P(p-Anis) ₃]	256.0 ± 3.0	342.0 ± 3.0	220.0	± 3.0	207.0	± 3.0	135.0 ± 4.0	-0.80 ± 0.10
$Br_3Ga[P(p-Anis)_3]$	138.0 ± 7.0	164.7 ± 7.0	124.7	± 7.0	124.7	± 7.0	40.0 ± 10.0	-1.00
I ₃ Ga[P(p-Anis) ₃]	-135.0 ± 7.0	-10.0 ± 7.0	-31.0	± 7.0	-365.0	± 7.0	355.0 ± 10.0	0.88 ± 0.10
Cl ₃ Ga(TMP)	225.0 ± 10.0	295.0 ± 10.0	196.0	± 10.0	185.0	± 10.0	110.0 ± 15.0	-0.80 ± 0.10
Br ₃ Ga(TMP)	120.0 ± 10.0	140.0 ± 10.0	111.0	± 10.0	110.0	± 10.0	30.0 ± 15.0	-0.90 ± 0.10
I ₃ Ga(TMP)	-140.0 ± 10.0	-7.0 ± 10.0	-26.0	± 10.0	-387.0	± 10.0	380.0 ± 15.0	0.90 ± 0.10
Gallium quadrupola	ar coupling							
	$C_{\rm Q}(^{69}{\rm Ga})$	$C_{\rm Q}(^{71}{\rm Ga}$)	$\eta_{ m Q}$		α	β	γ
	[MHz]	[MHz]				[°]	[°]	[°]
Cl ₃ Ga(PPh ₃)	$+3.00\pm0.20$) +1.90=	±0.20	0.24	± 0.10	$65\pm$	$10 75 \pm 10$	32 ± 5
$Br_3Ga(PPh_3)$	$\pm 1.45 \pm 0.20$	$\pm 0.90 \pm$	10.20 €	0.10	± 0.10	$80\pm$	$10 50 \pm 10$	30 ± 10
$I_3Ga(PPh_3)$	$+5.20\pm0.20$	+3.30	10.20 €	0		0	0	0
$Cl_3Ga[P(p-Anis)_3]$	$+2.40\pm0.10$	+1.50	± 0.10	0.16	± 0.10	$80\pm$	$10 \qquad 85\pm5$	5 ± 10
Br ₃ Ga[P(p-Anis) ₃]	$\pm 1.60 \pm 0.10$	$\pm 1.00 \pm$	±0.10	0		-	90	0
I ₃ Ga[P(p-Anis) ₃]	-6.80 ± 0.20) -4.25 =	10.20 €	0.15	± 0.10	$75\pm$	$15 15 \pm 10$	45 ± 10
Cl ₃ Ga(TMP)	-14.30 ± 0.40) -9.00=	10.40 €	0.20	± 0.10	$80\pm$	$10 \qquad 85\pm5$	10 ± 10
Br ₃ Ga(TMP)	-17.40 ± 0.40	$-11.00 \pm$	± 0.40	0.24	± 0.10	$30\pm$	$10 85 \pm 5$	10 ± 10
I ₃ Ga(TMP)	-17.10 ± 0.40) -10.70	±0.40	0.35	± 0.10	$60\pm$	$10 10 \pm 10$	50 ± 10



Figure 2. Molecular structures of $Br_3Ga[P(p-Anis)_3]$ (top) and $I_3Ga[P(p-Anis)_3]$ (bottom). For clarity, the hydrogen atoms are not shown.

nent of each tensor along the Ga–P bond; hence $\eta_{\rm Q} = 0$ and $\kappa = \pm 1$. The central transition peaks in the ⁷¹Ga NMR spectra of MAS and stationary samples of Br₃Ga[P(*p*-Anis)₃], shown in Figure 3a and b, respectively, are broad and featureless; the broadening, attributed to the ⁷¹Ga–^{79/81}Br residual dipolar interactions (⁷⁹Br: $I={}^{3}/_{2}$, $\Xi=25.05$ %, NA= 50.69%; ⁸¹Br: $I={}^{3}/_{2}$, $\Xi=27.01$ %, NA=49.31%),^[20] leads to difficulties in determining the $C_{\rm Q}({}^{71}{\rm Ga})$ value. The value for $C_{\rm Q}({}^{71}{\rm Ga})$, (+1.00±0.10) MHz, was obtained by analyzing the full ⁷¹Ga NMR spectrum of a MAS sample, including

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Figure 3. Experimental (lower traces) and calculated (upper traces) central transition in the ⁷¹Ga NMR spectra of a) MAS and b) stationary powder samples of Br₃Ga[P(p-Anis)₃] acquired at 11.75 and 21.14 T. c) The NMR spectrum of the central and satellite transitions for a MAS sample (20.0 kHz) acquired at 21.14 T is shown in the lower trace with the simulated spectrum of a stationary sample shown in the upper trace; the peak arising from the central transition has been truncated in these images to emphasize the line shape of the spectrum arising from the satellite transitions.

the satellite transitions, as shown in Figure 3c. The small value for $C_{\rm Q}(^{71}\text{Ga})$ is consistent with the ³¹P NMR spectra, that is, a negligible *d* value (see below). Powder line shapes

arising from quadrupolar coupling cannot be discerned in these spectra, but the ⁷¹Ga NMR spectrum of a stationary sample obtained at 21.14 T (Figure 3b) is asymmetric; this is attributed to anisotropic gallium magnetic shielding. This allowed the determination of the span of the gallium CS tensor, (40.0±10.0) ppm, and of κ , -1.00. Thus, the unique components of the Ga CS and EFG tensors, δ_{11} and V_{ZZ} , respectively, are along the C_3 axis, in agreement with results of the DFT calculations.

The central transition peaks in the ⁷¹Ga NMR spectra of both MAS and stationary samples (Figure S3 in the Supporting Information) of Br₃Ga(PPh₃) are similar to those of Br₃Ga[P(*p*-Anis)₃], and thus were analyzed in the same manner. The broad and featureless peaks are also attributed to the ⁷¹Ga^{-79/81}Br residual dipolar interactions. This adduct has an approximate C_3 symmetry axis about the Ga–P bond.^[8] Analysis of the ⁷¹Ga NMR spectra yielded similar values as for Br₃Ga[P(*p*-Anis)₃]: $C_Q(^{71}Ga) = (\pm 0.90 \pm$ 0.20) MHz, $\eta_Q = (0.10 \pm 0.10)$, $\Omega = (65.0 \pm 15.0)$ ppm, and $\kappa =$ (-0.80 ± 0.10). Hence, the EFG and CS tensors are almost axially symmetric with V_{ZZ} coincident with δ_{11} , both aligned approximately along the Ga–P bond.

Ga NMR spectra of the central transition of stationary samples of $I_3Ga(PPh_3)$ obtained at different magnetic-field strengths are shown in Figure 4. From the simulations, it is apparent that for ⁷¹Ga at 7.05 T, the broadening arising from the magnetic shielding anisotropy is somewhat greater than that arising from the second-order nuclear quadrupolar interaction, the opposite of what is observed for the ⁶⁹Ga



Figure 4. Experimental (lower traces) and calculated (upper traces) central transition in the a) 71 Ga and b) 69 Ga NMR spectra of stationary powder samples of I₃Ga(PPh₃) acquired at 7.05, 11.75, and 21.14 T.

Chem. Eur. J. 2013, 19, 2826-2838

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nuclei of this sample. For 69Ga NMR spectra acquired at 11.75 T, the broadening arising from these two interactions is comparable. The contribution from the second-order quadrupolar interaction is negligible for ⁷¹Ga NMR spectra acquired at 21.14 T. The differences discussed above arise because ⁶⁹Ga has a larger nuclear quadrupole moment and a smaller magnetic moment, combined with the fact that, in frequency units, the effects of the second-order quadrupolar interaction are inversely proportional to \mathbf{B}_0 , whereas those of the magnetic shielding anisotropy are proportional to \mathbf{B}_{0} . The value of $C_0(^{71}\text{Ga})$ is $(+3.30\pm0.20)$ MHz and $\Omega =$ (360.0 ± 15.0) ppm. Both the EFG and CS tensors at Ga in I₃Ga(PPh₃) are axially symmetric, as expected from the presence of a C_3 symmetry axis, with $\eta_0 = 0$ and $\kappa = 1.00$. The skew indicates that δ_{33} is oriented along the Ga-P bond, in contrast to Br₃Ga(PPh₃) and Br₃Ga[P(p-Anis)₃] in which δ_{11} is parallel or approximately parallel to the this bond. DFT calculations reproduce these orientations (see below).

The Ga NMR spectra of the central transition of stationary samples of I₃Ga[P(*p*-Anis)₃], obtained at three different magnetic-field strengths (Figure 5), are similar to those of I₃Ga(PPh₃). The $C_Q(^{71}$ Ga) value is (-4.25 ± 0.20) MHz and $\Omega = (355.0\pm10.0)$ ppm; both the EFG and CS tensors at Ga in I₃Ga[P(*p*-Anis)₃] are close to axially symmetric ($\eta_Q =$ (0.15 ± 0.10) and $\kappa = (0.88\pm0.10)$), as expected from the approximate C_3 symmetry axis that includes the gallium atom. The values of the asymmetry parameters indicate that δ_{33} and V_{ZZ} are oriented approximately along the Ga–P bond.

 $^{69/71}$ Ga NMR spectra of Cl₃Ga[P(*p*-Anis)₃] are shown in Figure 6. The splitting in the ⁷¹Ga NMR spectrum of a MAS sample obtained at 11.75 T is attributed to ¹*J*(⁷¹Ga,³¹P). The



Figure 6. Experimental (lower traces) and calculated (upper traces) central transition in the ⁷¹Ga NMR spectra of a) MAS and b) stationary powder samples of $Cl_3Ga[P(p-Anis)_3]$ acquired at 7.05 and 11.75 T. The corresponding ⁶⁹Ga spectra of this compound are shown in c) (MAS) and d) (stationary).

 $C_{\rm Q}(^{71}{\rm Ga})$ value, (+1.50±0.10) MHz, was determined from an analysis of the ⁷¹Ga spectra of a MAS sample. The breadth of the peaks in the ⁷¹Ga NMR spectra of a stationary sample, acquired at 7.05 and 11.75 T, plotted on the ppm scale in Figure 6b, are almost equal; this observation is a clear indication that magnetic shielding anisotropy dominates the ⁷¹Ga NMR spectra of Cl₃Ga[P(*p*-Anis)₃]. The span of the Ga CS tensor is (135.0±4.0) ppm. The gallium $\eta_{\rm Q}$ and κ values, (0.16±0.10) and (-0.80±0.10), respectively,



Figure 5. Experimental (lower traces) and calculated (upper traces) central transition in the a) 71 Ga and b) 69 Ga NMR spectra of stationary powder samples of I₃Ga[P(*p*-Anis)₃] acquired at 7.05, 11.75, and 21.14 T.

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indicate that the EFG and CS tensors at Ga are close to axially symmetric with δ_{11} and V_{ZZ} both approximately in the direction of the Ga–P bond.

⁷¹Ga NMR spectra of Cl₃Ga-(PPh₃) (Figure S4 in the Supporting Information) are similar to those of $Cl_3Ga[P(p-Anis)_3]$. The $C_{\rm Q}(^{71}{\rm Ga})$ value, $(+1.9\pm$ 0.2) MHz, is slightly larger in magnitude than that for the latter, as is the span of the Ga CS tensor, (150 ± 15) ppm. The gallium $\eta_{\rm O}$ and κ values, (0.24 \pm 0.10) and (-0.9 ± 0.1) , respectively, indicate that the EFG and CS tensors at Ga have a similar orientation to those for $Cl_3Ga[P(p-Anis)_3],$ discussed above.

The Ga NMR spectra of the central transition of stationary samples of X_3 Ga(TMP) (X = Cl, Br and I), obtained at 11.75 T, are shown in Figure 7; the results of the analyses are summarized in Table 1. For a given adduct, the Ga NMR spectra have similar line shapes apart from the positions of the discontinuities in each spectrum, suggesting that they have similar Ga EFG tensors, but different Ga CS tensors.

The $|C_Q(^{71}Ga)|$ values for the gallium complexes investigated herein range from 0.9 to 11.0 MHz (Table 1). These are greatest for the adducts containing the bulky TMP ligand, but otherwise there is no clear relationship between the gallium C_Q value and the structures of the adducts. A comparison of adducts with the same triaryl-phosphine ligand indicates that



Figure 7. Experimental (lower traces) and calculated (upper traces) central transition in the 71 Ga (left) and 69 Ga NMR (right) spectra of stationary powder samples of a) Cl₃Ga(TMP), b) Br₃Ga(TMP), and c) I₃Ga(TMP), acquired at 11.75 T.



Figure 8. Spans of the CS tensors for X₃Ga(TMP), X₃Ga[P(*p*-Anis)₃], and X₃Ga(PPh₃).

the gallium nuclei are most and least shielded for X = I and Cl, respectively, as shown in Figure 8 and summarized in Table 1; this has been attributed to the spin-orbit effect of the halogen ligand.^[27] Reported Ga chemical shift values for $X_3Ga(PPh_3)$ (X = Cl, Br, and I) in CD₂Cl₂ are 264, 152, and -151 ppm, respectively.^[8] similar to the values and the trend obtained in this study. The same trend in indium chemical shifts has also been observed for the indium(III) trihalide triarylphosphine adducts.^[18] The spans of the gallium magnetic shielding tensors for the adducts considered herein are

largest for X=I (355 to 380 ppm) and smallest for X=Br (30 to 65 ppm).

Solid-state ³¹**P NMR spectroscopy**: With a couple of exceptions, the ${}^{1}J({}^{69/71}\text{Ga},{}^{31}\text{P})$ and $R_{\text{eff}}({}^{69/71}\text{Ga},{}^{31}\text{P})$ values for the adducts considered herein are too small to be extracted from the Ga NMR spectra of stationary samples, but are available from ${}^{31}\text{P}$ NMR spectra acquired with MAS. Figures 9–11 provide examples of ${}^{31}\text{P}$ NMR spectra for several X₃Ga-(PR₃) adducts. From the relative magnetogyric ratios for



Figure 9. Experimental (lower traces) and calculated (upper traces) 31 P NMR spectra of MAS powder samples of a) Cl₃Ga[P(*p*-Anis)₃], b) Cl₃Ga(TMP), c) I₃Ga[P(*p*-Anis)₃], and d) Br₃Ga(TMP) acquired at 7.05 T.

 $d = (3C_0R_{\rm eff})/(10v_s)^{[18]}$ (see also the Supporting Information). Table S3 in the Supporting Information summarizes the 2d values obtained in this study. With $C_{\rm Q}$ determined from the Ga NMR spectra and d determined from the ³¹P NMR spectra of MAS samples, $R_{\rm eff}(^{69/71}{\rm Ga},^{31}{\rm P})$ values can be determined from analyses of the ³¹P NMR spectra. In our earlier work,^[18] we also demonstrated that a 2.5% correction for librational effects^[28] on measured values of $R_{\rm eff}$ or $R_{\rm DD}$ was sufficient for heavier atoms such as those in the Ga-P spin pairs considered herein. Hence, experimental dipolar couplings

rect spin-spin coupling to ⁶⁹Ga and ⁷¹Ga, with an intensity ratio of 3:2, respectively, based on the natural abundances of the two gallium isotopes. Thus, one may expect to see eight peaks in the isotropic region of a ³¹P NMR spectrum, as shown in Figure 9a. However, in most cases, not all the peaks are resolved as a consequence of the similar magnetogyric ratios for ⁶⁹Ga and ⁷¹Ga, combined with relatively small ${}^{1}J({}^{69/71}\text{Ga}{}^{31}\text{P})$ values and in some cases, broad peaks. Another important spinspin parameter for the present work, $R_{\rm eff}(^{69/71}{\rm Ga},^{31}{\rm P})$, may be estimated from ³¹P NMR spectra of either stationary or MAS samples. The parameters derived from analyses of the ³¹P NMR spectra are summarized in Table 2.

From the values for $R_{\rm eff}$ (^{69/71}Ga,³¹P) and $R_{\rm dd}$ (^{69/71}Ga,³¹P), the latter of which can be calculated from the Ga–P bond length, ΔJ (^{69/71}Ga,³¹P) may in some cases be estimated. In an earlier study, we showed that if the **J** and dipolar tensors are coincident with an exact or approximate C_3 symmetry axis incorporating the spin pair, then

⁶⁹Ga and ⁷¹Ga, ³¹P NMR spectra of MAS samples are expected to consist of two 1:1:1:1 quartets, arising from indi-

obtained from 31 P NMR spectra have been reduced by 2.5%.

Table 2.	Experimental	³¹ P NMR	parameters	for	$X_3Ga(1)$	PR_3)	(X =	Cl, Br	, and I)	adducts.
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Phosphorus chemica	l shift tensor					
	$\delta_{ m iso}$	δ_{11}	δ_{22}	δ_{33}	Ω	κ
	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	
Cl ₃ Ga(PPh ₃)	-8.1 ± 1.0	5.6 ± 1.0	-14.4 ± 1.0	-15.4 ± 1.0	21.0 ± 2.0	-0.90 ± 0.10
Br ₃ Ga(PPh ₃)	-13.5 ± 1.0	0.2 ± 1.0	-19.8 ± 1.0	-20.8 ± 1.0	21.0 ± 2.0	-0.90 ± 0.10
$I_3Ga(PPh_3)$	-28.5 ± 1.0	-15.2 ± 1.0	-35.2 ± 1.0	-35.2 ± 1.0	20.0 ± 2.0	-1.00
Cl ₃ Ga[P(p-Anis) ₃]	-18.9 ± 1.0	5.8 ± 1.0	-30.3 ± 1.0	-32.2 ± 1.0	38.0 ± 2.0	-0.90 ± 0.10
Br ₃ Ga[P(p-Anis) ₃]	-26.6 ± 1.0	0.1 ± 1.0	-39.9 ± 1.0	-39.9 ± 1.0	40.0 ± 2.0	-1.00
I ₃ Ga[P(p-Anis) ₃]	$-32.4 \pm\! 1.0$	-13.9 ± 1.0	-39.4 ± 1.0	-43.9 ± 1.0	30.0 ± 2.0	-0.70 ± 0.20
Cl ₃ Ga(TMP)	-41.4 ± 1.0	-27.5 ± 1.0	-47.3 ± 1.0	-49.5 ± 1.0	22.0 ± 2.0	-0.80 ± 0.10
Br ₃ Ga(TMP)	-41.7 ± 1.0	-32.2 ± 1.0	-45.7 ± 1.0	-47.2 ± 1.0	15.0 ± 2.0	-0.80 ± 0.10
I ₃ Ga(TMP)	-54.1 ± 1.0	-47.8 ± 1.0	-56.8 ± 1.0	-57.8 ± 1.0	10.0 ± 2.0	-0.80 ± 0.10
⁶⁹ Ga- ³¹ P spin-spin co	oupling					
* *	¹ J(⁶⁹ Ga, ³¹ P	')	$R_{\rm eff}(^{69}{\rm Ga},^{31}{\rm P})$	$R_{\rm dd}(^{69}{\rm Ga},^{31}{ m Ga})$	P)	$\Delta J(^{69}\text{Ga},^{31}\text{P})$
	[Hz]		[Hz] ^[a]	[Hz]		[Hz]
Cl ₃ Ga(PPh ₃)	780 ± 20		650 ± 50	860 ± 20		630 ± 150
Br ₃ Ga(PPh ₃)	620 ± 20		550 ± 50	840 ± 20		870 ± 150
I ₃ Ga(PPh ₃)	300 ± 20		550 ± 50	810 ± 20		780 ± 150
$Cl_3Ga[P(p-Anis)_3]$	$770\pm\!20$		750 ± 50	$860 \pm 20^{[b]}$		330 ± 150
$Br_3Ga[P(p-Anis)_3]$	640 ± 20		580 ± 50	$730\pm\!20$		450 ± 150
$I_3Ga[P(p-Anis)_3]$	480 ± 20		700 ± 50	830 ± 20		390 ± 150
Cl ₃ Ga(TMP)	$1250\pm\!20$		520 ± 50	$860 \pm 20^{[b]}$		1020 ± 150
Br ₃ Ga(TMP)	$1120\pm\!20$		520 ± 50	$730 \pm 20^{[b]}$		630 ± 150
I ₃ Ga(TMP)	$850\pm\!20$		500 ± 50	$810 \pm 20^{[b]}$		930 ± 150
⁷¹ Ga- ³¹ P spin-spin co	oupling					
1 1	¹ <i>J</i> (⁷¹ Ga, ³¹ P	')	$R_{\rm eff}(^{71}{\rm Ga},^{31}{\rm P})$	$R_{\rm dd}(^{71}{\rm Ga},^{31}{\rm Ga})$	P)	$\Delta J(^{71}\text{Ga},^{31}\text{P})$
	[Hz]	, 	[Hz] ^[a]	[Hz]	,	[Hz]
Cl ₃ Ga(PPh ₃)	990 ± 20		830 ± 50	1090 ± 20		780 ± 150
Br ₃ Ga(PPh ₃)	780 ± 20		700 ± 50	1060 ± 20		1080 ± 150
I ₃ Ga(PPh ₃)	380 ± 20		700 ± 50	1030 ± 20		990 ± 150
$Cl_3Ga[P(p-Anis)_3]$	980 ± 20		950 ± 50	$1090 \pm 20^{[b]}$]	420 ± 150
$Br_3Ga[P(p-Anis)_3]$	810 ± 20		740 ± 50	930 ± 20		570 ± 150
$I_3Ga[P(p-Anis)_3]$	$610\pm\!20$		890 ± 50	1050 ± 20		480 ± 150
Cl ₃ Ga(TMP)	$1590\pm\!20$		660 ± 50	$1090 \pm 20^{[b]}$]	1290 ± 150
Br ₃ Ga(TMP)	$1420\pm\!20$		660 ± 50	$930 \pm 20^{[b]}$		810 ± 150
I ₃ Ga(TMP)	$1080\pm\!20$		$630\!\pm\!50$	$1030 \pm 20^{[b]}$]	1200 ± 150
5 7 - (60/71 - 21-)						

[a] $R_{\rm eff}^{69/71}$ Ga,³¹P) values were obtained by correcting the observed values by -2.5%. [b] Estimated (see text).

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Figure 10. Experimental (lower traces) and calculated (upper traces) 31 P NMR spectra of a) MAS and b) stationary powder samples of Br₃Ga[P(*p*-Anis)₃] acquired at 4.70, 7.05, and 11.75 T.

A detailed discussion of the analysis of the data for the $Br_3Ga[P(p-Anis)_3]$ adduct (Figure 10) is presented as an example. The equally spaced peaks in this spectrum indicate that d is negligible and therefore that the gallium C_0 values are very small, precluding an experimental assignment of a sign for this interaction; these were thus assigned from the DFT calculations (see below). Values of (810 ± 20) and (740 ± 50) Hz for ${}^{1}J({}^{71}\text{Ga}, {}^{31}\text{P})$ and $R_{\text{eff}}({}^{71}\text{Ga}, {}^{31}\text{P})$, respectively, were obtained from analyses of the spectra of MAS and stationary samples (Figure 10). From the known Ga-P bond length, 2.500 Å, an uncorrected value of (950 ± 20) Hz was obtained for $R_{\rm DD}$; this is reduced to (930±20) Hz after applying the correction for librational motion discussed above. Furthermore, since this adduct contains a C_3 symmetry axis along its Ga-P bond, ΔJ can be calculated by using $\Delta J =$ $3(R_{\rm DD}-R_{\rm eff})$, allowing an estimate of $\Delta J(^{71}{\rm Ga},^{31}{\rm P})$, which depends on the sign of R_{eff} . Values for ΔJ of $(+570 \pm 150)$ or $(+5010\pm150)$ Hz are thus obtained. An analysis of ³¹P NMR spectra of stationary samples showed that ¹J- $(^{71}\text{Ga}, ^{31}\text{P})$ and $R_{\text{eff}}(^{71}\text{Ga}, ^{31}\text{P})$ have the same sign. Since onebond spin-spin coupling constants in analogous compounds are positive, $[^{18,29,30]} I J(^{71}\text{Ga},^{31}\text{P})$ and R_{eff} are expected to be positive^[31,32] and thus, the smaller of the two possible values for ΔJ is more probable. Hence, $\Delta J({}^{71}\text{Ga}, {}^{31}\text{P})$ and ${}^{1}J$ -(⁷¹Ga,³¹P) are both positive and have similar magnitudes. This conclusion is supported by calculations (see below).

The I₃Ga(PPh₃) adduct also has a C_3 axis along the Ga–P bond.^[9] Analyses of the ³¹P NMR spectra of MAS and stationary samples (Figure 11) are similar to those of Br₃Ga[P-(*p*-Anis)₃]. However, in this case, the 2*d* value obtained at 4.70 T, +20 Hz, is apparent; the C_0 (⁷¹Ga) value is thus relatively large and had to be included in the analysis, which indicates that the sign of C_0 (⁷¹Ga) is positive, as for C_0 (⁶⁹Ga). These results agree with those obtained from DFT calculations (see below). A comparable analysis was performed for Cl₃Ga(PPh₃) and I₃Ga[P(*p*-Anis)₃].

The analysis outlined above assumes that the **J** and dipolar tensors are coincident and axially symmetric. Significant differences between R_{eff} and R_{DD} must be a consequence of $\Delta J(^{69/71}\text{Ga},^{31}\text{P})$, and since the analysis yields comparable values of $\Delta J(^{69/71}\text{Ga},^{31}\text{P})$ for closely related adducts, the deviation from axial symmetry is not thought to be sufficient to



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Figure 11. Experimental (lower traces) and calculated (upper traces) 31 P NMR spectra of a) MAS and b) stationary powder samples of I₃Ga(PPh₃) acquired at 4.70 and 7.05 T.

significantly affect the values obtained. As discussed above, these analyses assumed that the signs of ${}^{1}J({}^{69/71}\text{Ga},{}^{31}\text{P})$ for these adducts are positive; DFT calculations (see below) support this assumption.

Although Ga–P bond lengths are unavailable for several adducts considered herein, examination of the data for similar adducts in References [8] and [9] and in this study (Table S2 in the Supporting Information) indicate that there is little variation in the Ga–P bond lengths for a given halide. Since $R_{\rm eff}$ values, determined for all adducts, are of comparable magnitudes (Table 2), $\Delta I(^{69/71}\text{Ga},^{31}\text{P})$ is expected to be significant in all cases considered herein. Hence, values for $\Delta I(^{69/71}\text{Ga},^{31}\text{P})$ have been estimated based on the smallest corrected value of $R_{\rm DD}$ (and thus the smallest value for $\Delta I(^{69/71}\text{Ga},^{31}\text{P})$) predicted from the Ga–P bond lengths for a given halide; these are summarized in Table 2.

Previously, the nature of the bond between a spin-spin coupled pair has been explained based on the assumption that the coupling is dominated by the Fermi-contact mechanism.^[33] Although a similar conclusion appears to be consistent with the results of DFT calculations discussed below, it is important to consider that the Fermi contact term does not contribute to ΔJ ;^[23,24] hence the observation of ΔJ (^{69/}⁷¹Ga,³¹P) for these adducts indicates that mechanisms other than the Fermi-contact term also make significant contributions to ¹J(^{69/71}Ga,³¹P).^[24]

To summarize, ${}^{1}J({}^{69/71}Ga,{}^{31}P)$ and $\Delta J({}^{69/71}Ga,{}^{31}P)$ values, as well as their signs, have been determined for all X₃Ga(PR₃) adducts investigated herein. These are of comparable magnitude and are positive. Signs for $C_{\rm Q}({}^{69/71}Ga)$ have also been determined for those adducts that have $C_{\rm 3}$ symmetry and for which the ${}^{69/71}Ga-{}^{31}P$ residual dipolar coupling was observable.

Solution-phase ³¹**P NMR spectroscopy**: ³¹**P**{¹**H**} NMR spectra of Br₃Ga[P(*p*-Anis)₃] dissolved in deuterated chloroform and acquired at various temperatures are shown in Figure S9 of the Supporting Information. At 323 K, two overlapping multiplets due to ¹*J*(⁶⁹Ga,³¹P) and ¹*J*(⁷¹Ga,³¹P) are apparent. The value of ¹*J*(⁷¹Ga,³¹P) is approximately 810 Hz (estimated error 10%) in agreement with the value obtained in the solid state, (810±20) Hz (see Table 2). At temperatures less than 300 K, the ^{69/71}Ga-³¹P spin–spin coupling splitting pat-

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terns collapse as a result of rapid ^{69/71}Ga spin-lattice relaxation.^[34] At 213 K, the ^{69/71}Ga nuclei are essentially self-decoupled from the ³¹P nuclei (i.e., $\{2\pi[J(^{69/71}\text{Ga},^{31}\text{P})][T_1(^{69/71}\text{Ga})]\}^2 \ll 0.1).^{[34,35]}$ Similar results were obtained for $I_3\text{Ga}[P(p\text{-Anis})_3]$ (see Figure S10 in the Supporting Information) and for $I_3\text{Ga}(P\text{Ph}_3)$.

In some cases, we observed broadening of the overlapping 1:1:1:1 multiplets with increasing temperature, which we attribute to ligand exchange at higher temperatures. Likewise, Cheng et al. found that it was necessary to cool samples below room temperature to decrease the rate of ligand exchange sufficiently to observe ${}^{1}J({}^{69/71}Ga, {}^{31}P)$ for X₃Ga(PPh₃) (X=Cl and Br) dissolved in CH₂Cl₂.^[8] Clearly, an interplay of the magnitude of the 69/71Ga nuclear quadrupolar coupling constants, rotational correlation times, rate of ligand exchange, and the magnitude of ${}^{1}J({}^{69/71}Ga, {}^{31}P)$ will dictate exactly what line shape one will observe in solution as a function of temperature. To obtain accurate values of ${}^{1}J({}^{69/}$ ⁷¹Ga,³¹P) from ³¹P NMR spectra acquired in solution, it would be necessary to carry out detailed line-shape analyses as outlined in the review by Mlynárik,^[34] but we were able to obtain reasonable estimates of these values for the X₃Ga(PR₃) adducts (see Table 3). As shown in Tables 2 and 3, the same trend is observed for solid samples and for samples in solution. ¹*J*(^{69/71}Ga,³¹P) values decrease slightly as X changes from Cl to Br and more dramatically as X changes from Cl or Br to I.

Table 3. Solution-phase ^{31}P NMR parameters for $X_3Ga(PR_3)$ (X = Cl, Br, and I) adducts.

	$\delta_{iso}(^{31}P)$	${}^{1}J({}^{71}\text{Ga},{}^{31}\text{P})$	Т
	[ppm]	[Hz]	[K]
Cl ₃ Ga(PPh ₃)	-5.5 ± 0.2	721 ± 10	183 ^[a]
	-5.6 ± 0.2	793 ± 10	193
Br ₃ Ga(PPh ₃)	-10.7 ± 0.2	693 ± 10	273 ^[a]
	-10.3 ± 0.2	696 ± 10	193
$I_3Ga(PPh_3)$	-29.7 ± 0.2	466 ± 10	273 ^[a]
	-28.7 ± 0.2	470 ± 10	253
Cl ₃ Ga[P(p-Anis) ₃]	-18.8 ± 0.2	970 ± 10	RT
$Br_3Ga[P(p-Anis)_3]$	-24.8 ± 0.2	810 ± 10	323
$I_3Ga[P(p-Anis)_3]$	-31.4 ± 0.2	535 ± 10	333
Cl ₃ Ga(TMP)	-41.7 ± 0.2	[b]	193
Br ₃ Ga(TMP)	-45.8 ± 0.2	[b]	233
I ₃ Ga(TMP)	-52.8 ± 0.2	[b]	193

[a] Reference [8]. [b] Only one broad peak was observed and the ${}^{1}J({}^{71}\text{Ga}, {}^{31}\text{P})$ values could not be resolved.

These results demonstrate that, because of the competing mechanisms occurring for samples in solution, it generally is easier to characterize indirect spin–spin coupling constants involving quadrupolar nuclei in the solid state.

DFT calculations—Comparison with experiment: Calculated Ga NMR parameters are summarized in Table 4. A compar-

Table 4. Calculated $^{6971}Ga~NMR$ parameters for $X_3Ga(PR_3)$ and model $X_3Ga(PMe_3)~(X\,{=}\,Cl,\,Br,\,and~I)$ adducts $^{[a]}$

Gallium chemical shift tensors							
	$\delta_{ m iso}$	δ_{11}	δ_{22}	δ_{33}	Ω		κ
	[ppm]	[ppm]	[ppm]	[ppm]	[pi	om]	
Cl ₃ Ga(PPh ₃)	344	473	291	270	203	3	-0.79
Br ₃ Ga(PPh ₃)	171	205	156	153	52	2	-0.89
I ₃ Ga(PPh ₃)	-212	-30	-30	-575	545	5	1.00
Cl ₃ Ga[P(p-Anis) ₃]	344	468	295	268	200)	-0.73
Br ₃ Ga[P(p-Anis) ₃]	130	152	119	119	33	3	-1.00
I ₃ Ga[P(p-Anis) ₃]	-189	$^{-8}$	-34	-525	51'	7	0.90
Cl ₃ Ga(TMP)	313	409	278	253	150	5	-0.69
Br ₃ Ga(TMP)	101	140	86	78	62	2	-0.75
I₃Ga(TMP)	-190	31	-87	-515	54′	7	0.57
Cl ₃ Ga(PMe ₃)	354	469	304	288	180)	-0.83
Br ₃ Ga(PMe ₃)	135	144	138	122	22	2	0.44
I ₃ Ga(PMe ₃)	-178	37	-15	-555	59	1	0.82
Gallium quadrupolar	coupling						
	$C_{\rm Q}(^{69}{\rm Ga})$	C_{Q}	(⁷¹ Ga)	$\eta_{ m Q}$	α	β	γ
	[MHz]	[M	[Hz]		[°]	[°]	[°]
Cl ₃ Ga(PPh ₃)	+8.3	+:	5.2	0.17	73	88	17
Br ₃ Ga(PPh ₃)	+4.6	+3	2.8	0.39	80	84	50
I ₃ Ga(PPh ₃)	+5.6	+3	3.5	0.00	0	0	0
Cl ₃ Ga[P(p-Anis) ₃]	+5.9	+:	3.7	0.47	83	88	10
Br ₃ Ga[P(p-Anis) ₃]	+11.0	+	6.9	0.00	90	90	0
I ₃ Ga[P(p-Anis) ₃]	-3.3	-2	2.1	0.52	85	37	47
Cl ₃ Ga(TMP)	-6.8		4.3	0.36	79	77	11
Br ₃ Ga(TMP)	-11.4	—′	7.1	0.04	27	87	0
I₃Ga(TMP)	-3.2	-1	2.0	0.32	72	46	30
Cl ₃ Ga(PMe ₃)	+6.6	+	4.1	0.11	84	73	6
Br ₃ Ga(PMe ₃)	+12.7	+	8.0	0.01	17	89	18
I ₃ Ga(PMe ₃)	-4.2	-2	2.6	0.17	86	30	30

[a] Chemical shifts converted from shielding values according to $\delta_{iso}(Ga) = 1814 - \sigma_{iso}(Ga)$ (see text).

ison of experimental and calculated $C_{\rm O}(^{69/71}{\rm Ga})$ values (Tables 1 and 4) shows that the DFT calculations do not reproduce experimental trends, but they do correctly predict that these values are small (e.g., for the diatomic gallium(I) halides, $C_0(^{69}\text{Ga})$ ranges from -106.6 for GaF to -81.1 MHz for GaI, an order of magnitude larger than the values for the gallium(III) adducts investigated herein).^[36] In addition, the calculated sign for $C_{\rm O}(^{69/71}{\rm Ga})$ is reproduced for the seven adducts for which it is known from experiments. Furthermore, the calculated relative orientations of the gallium EFG and shielding tensors, given by the Euler angles α , β , and γ , are in qualitative agreement with experimental values. For example, consider the two complexes that have an exact C_3 axis along the Ga-P bond, Br₃Ga[P(p-Anis)₃] and I₃Ga(PPh₃). Despite the small gallium and phosphorus spans, calculations correctly predict that the unique components of the EFG and CS tensors are V_{ZZ} and δ_{11} for the former and V_{ZZ} and δ_{33} for the latter.

Converting calculated shielding into chemical shifts requires the establishment of an absolute shielding scale for the nucleus of interest.^[37] Since no such scale has been established for gallium, the gallium shielding constant for [Ga-(H₂O)₆]³⁺ was calculated to approximate that of the accepted gallium chemical shift reference, Ga(NO₃)₃ (1.0 m).^[20] This value, σ =1814 ppm, was set to δ_{iso} (Ga)=0 ppm and thus the calculated chemical shift values in Table 4 were obtained from calculated magnetic shielding values by using the relationship $\delta(Ga)_{calcd} = 1814 - \sigma(Ga)_{calcd}$.

Plots of experimental versus calculated $\delta_{iso}(Ga)$, κ , and Ω values are shown in Figure 12; these indicate that the calculated chemical shift parameters are qualitatively in agreement with the corresponding experimental values. For the three series of complexes studied, X₃Ga(PPh₃), X₃Ga[P(p-Anis)₃], and X₃Ga(TMP), δ_{iso} is greatest for X = Cl and least for X=I, in agreement with experiments; this is illustrated in Figure 13. Likewise, calculated and experimental Ω values are in agreement (compare Figure 13 with Figure 8). To investigate the origin of the increased gallium shielding as the atomic number of the halogen atom increases, the socalled normal halogen effect (NHE), the diamagnetic (σ_{dia}), paramagnetic (σ_{para}), and spin-orbital ($\sigma_{spin-orbit}$) contributions to the gallium isotropic magnetic shielding constants were calculated (see Table S4 in the Supporting Information). The value of σ_{dia} is virtually independent of the halogen, and σ_{para} tends to decrease slightly as X changes from Cl to I; however, it is clearly $\sigma_{\text{spin-orbit}}$ that is responsible for the observed NHE, with contributions from $\sigma_{\rm spin-orbit}$ to the isotropic shielding of gallium of approximately 160, 370, and 745 ppm for X=Cl, Br, and I, respectively. Significantly, although both σ_{para} and $\sigma_{\text{spin-orbit}}$ are significantly anisotropic, there is little variation in the anisotropy of the former, regardless of the halogen atom. In contrast, the anisotropy in $\sigma_{\rm spin-orbit}$ varies from less than 30 ppm for the trichloro adducts to more than 700 ppm for the triiodo adducts (Table S4 in the Supporting Information). Hence, $\sigma_{spin-orbit}$ is also responsible for the large spans in the gallium chemical shift tensors for the triiodo adducts in comparison with those for the tribromides and trichlorides.

In contrast to the Ga^{III} adducts, Ga^I monohalides exhibit an inverse halogen dependence (IHD).^[38] Likewise, we re-

cently reported an NHE for a series of In^{III} trihalides in contrast to the IHD found for some In^I monohalides.^[18] In both the gallium and indium series of compounds, a large paramagnetic term (largest for X = I and smallest for X = CI) is mainly responsible for the IHD of the isotropic chemical shifts monohalides for the (see Table S5 in the Supporting Information).

Calculated ${}^{1}J({}^{69/71}Ga, {}^{31}P)$ and $\Delta J({}^{69/71}Ga, {}^{31}P)$ values for the X₃Ga(PR₃) adducts are listed in Table 5. The former are generally smaller than the observed values; nevertheless the experimental trend that ${}^{1}J({}^{69/71}Ga, {}^{31}P)$ is greatest for X = Cl and smallest for X = I is reproduced by the calculations. Calculated

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X₃Ga(PMe₃).

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(a) 350

Figure 12. Experimental versus calculated gallium CS tensor values a) δ_{iso} , b) κ , and c) Ω for the gallium trihalide triarylphosphine adducts X₃Ga(PR₃). The solid line indicates perfect agreement between experimental and calculated values. The standard deviations ($s = [\Sigma(\text{calcd}-\text{exptl})^2/(n-1)]^{1/2}$ in which n is the number of data points) are 64 ppm, 0.14, and 111 ppm for δ_{iso} , κ , and Ω , respectively.



Table 5. Calculat	ed ¹ <i>J</i> (^{69/71} Ga, ³¹ P) a	and $\Delta J(^{69/71}\text{Ga},^{31}$	P) for X ₃ Ga(PR ₃)	and
model X ₃ Ga(PM	e_3) (X = Cl, Br, and	d I) adducts.		

	¹ <i>J</i> (⁶⁹ Ga, ³¹ P) [Hz]	¹ <i>J</i> (⁷¹ Ga, ³¹ P) [Hz]	$\Delta J(^{69}\text{Ga},^{31}\text{P})$ [Hz]	$\Delta J(^{71}\text{Ga},^{31}\text{P})$ [Hz]
Cl.Ga(PPh.)	± 3//	±/137	±511	±650
$Br_3Ga(PPh_3)$	+211	+268	+484	+615
I ₃ Ga(PPh ₃)	+6	+8	+391	+496
Cl ₃ Ga[P(p-Anis) ₃]	+404	+513	+536	+682
$Br_3Ga[P(p-Anis)_3]$	+218	+277	+480	+609
I ₃ Ga[P(p-Anis) ₃]	+89	+114	+448	+569
Cl ₃ Ga(TMP)	+469	+596	+555	+705
Br ₃ Ga(TMP)	+254	+322	+471	+598
Cl ₃ Ga(PMe ₃)	+388	+492	+549	+697
Br ₃ Ga(PMe ₃)	+181	+229	+469	+596
I ₃ Ga(PMe ₃)	+52	+66	+466	+592

values of $\Delta J(^{71}\text{Ga}, ^{31}\text{P})$ are positive and range from approximately 500 to 700 Hz, whereas the experimental values range for (420 ± 150) to (1290 ± 150) Hz. Although the errors in the experimental values are large, it is clear that the anisotropies in the indirect Ga-P spin-spin coupling tensors are on the same order of magnitude as the isotropic values. The calculated contribution of the Fermi-contact mechanism to ${}^{1}J({}^{69/71}\text{Ga},{}^{31}\text{P})_{iso}$ (not shown) for the model adducts is approximately 99%. The calculations indicate that the nonzero $\Delta J(^{69/71}\text{Ga},^{31}\text{P})$ values result from the spin-dipolar Fermi-contact (SD×FC) cross term. Thus, both the Fermi-contact and spin-dipolar Fermi-contact mechanisms make important contributions to the $J(^{69/71}Ga, {}^{31}P)$ tensors in these adducts. A similar effect was noted for the J(113/¹¹⁵In,³¹P) tensors of indium(III) trihalide phosphine adducts.[18]

Conclusion

The results of an investigation of several triarylphosphine gallium trihalide adducts, $X_3Ga(PR_3)$ (X=Cl, Br, or I; PR_3 =triarylphosphine ligand) by using solid-state ^{69/71}Ga and ³¹P NMR spectroscopy and single-crystal X-ray diffraction has been presented. The experimental $C_Q(^{71}Ga)$ values for these adducts range from (+3.3±0.2) to (-11.0±0.4) MHz; the signs of $C_Q(^{69/71}Ga)$ for some adducts with an exact or approximate C_3 axis were determined from analyses of the ³¹P NMR spectra. The ^{69/71}Ga nuclear quadrupolar coupling constants reported herein are small compared with others that we have previously measured in our lab. The relatively small EFGs at the gallium nuclei in these compounds are in agreement with the predictions of Bancroft and coworkers.^[39]

Trends observed in this study are similar to those observed for the related In-phosphine adducts.^[18] In particular, the gallium nuclei are most shielded for X=I and least shielded for X=Cl, that is, the normal halogen effect. The anisotropic gallium magnetic shielding is measurable for all adducts, with spans as large as (380 ± 15) ppm. Similar to observations for the In-phosphine adducts, the spans are greatest for the adducts with X=I; for ^{69/71}Ga spectra acquired at

21.14 T, the contribution from this interaction to the NMR line shape of the central transition is of the same magnitude or greater than that from $C_{\rm O}(^{69/71}\text{Ga})$. Values for ${}^{1}J(^{69/71}\text{Ga},^{31}\text{P})$ were determined for all adducts investigated herein. In addition, $\Delta J(^{69/71}\text{Ga},^{31}\text{P})$ values and their signs are reported; these were derived from known or estimated values for $R_{\rm DD}$. As for the ${}^{115}\text{In}{-}^{31}\text{P}$ J tensors,^[18] the ${}^{1}J(^{69/71}\text{Ga},^{31}\text{P})$ values are comparable in magnitude and positive.

Solution-phase ³¹P NMR spectroscopic results indicate that the gallium T_1 relaxation times for I₃Ga(PPh₃), Br₃Ga[P(*p*-Anis)₃], and I₃Ga[P(*p*-Anis)₃] are very short at lower temperatures, whereas those for Cl₃Ga(PPh₃), Br₃Ga-(PPh₃), and Cl₃Ga[P(*p*-Anis)₃] do not change significantly in comparison to changes in the Ga–phosphine exchange rates. The differences between the solution-phase ³¹P NMR spectra for these adducts at different temperatures are attributed to a competition between variations in the ^{69/71}Ga T_1 values and in the Ga-phosphine exchange rates. The ³¹P NMR parameters, ¹J(⁷¹Ga,³¹P) and δ_{iso} (³¹P), measured in solution, are generally in agreement with those obtained from solid-state NMR spectroscopy.

The experimental results have been complemented by relativistic DFT calculations. These calculations qualitatively reproduce the available experimental ^{69/71}Ga EFG and CS tensors, including their relative orientations, and they also reproduce the normal halogen effect observed between the isotropic gallium magnetic shielding and the halogen ligands; calculations confirm that this effect is due to the spin-orbital effect of the halogen ligand. Although calculated values of ${}^{1}J({}^{69/71}\text{Ga},{}^{31}\text{P})$ and $\Delta J({}^{69/71}\text{Ga},{}^{31}\text{P})$ are generally lower than the experimental values, calculations undertaken for the $X_3Ga(PR_3)$ adducts confirm that ${}^{1}J({}^{69/71}Ga, {}^{31}P)$ and $\Delta J(^{69/71}\text{Ga},^{31}\text{P})$ are comparable in magnitude with positive signs. Calculations indicate that both the Fermi-contact and spin-dipolar Fermi-contact mechanisms are important factors when considering the J tensor between coupled gallium and phosphorus nuclei.

We have provided herein an interpretation of solid-state $^{69/71}$ Ga NMR spectra for some gallium–phosphine complexes. The conclusions reached in this study are comparable to those reached in an earlier study of indium–phosphine complexes:^[18] one may not ignore the effects of gallium magnetic shielding anisotropy, particularly for spectra acquired at high magnetic-field strengths; relativistic DFT calculations are helpful in the analysis of $^{69/71}$ Ga NMR spectra; and NMR investigations of spin- $^{1}/_{2}$ nuclei, such as 31 P, coupled to gallium complement the $^{69/71}$ Ga NMR studies.

Experimental and Computational Details

Sample preparation: Gallium(III) chloride $(GaCl_3)$, gallium(III) bromide $(GaBr_3)$, gallium(III) iodide (GaI_3) , triphenylphosphine (PPh₃), tris-*para*methoxyphenylphosphine (P(*p*-Anis)₃), and tris(2,4,6-trimethoxyphenyl)phosphine (TMP) were purchased from either Aldrich or Strem and used as received. Owing to the ease of hydrolysis of the anhydrous halides and oxidation of the phosphine ligands, all operations were carried out in a

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dry glovebox filled with argon. See the Supporting Information for more details of these syntheses and of the syntheses of the $X_3Ga(TMP)$ compounds, X = Cl, Br, and I, which have not previously been reported.

Single-crystal X-ray diffraction: Single crystals of $Br_3Ga[P(p-Anis)_3]$ and I₃Ga[P(p-Anis)₃] suitable for X-ray diffraction were grown by very slow evaporation of solutions of these complexes in a 1:1 mixture of ethyl acetate and dichloromethane. Suitable crystals were mounted on glass fibers by means of paratone-N oil, and data were collected at 193 K by using graphite-monochromated $Mo_{K\alpha}$ radiation (0.71073 Å) on a Bruker PLAT-FORM/SMART 1000 CCD diffractometer. The structures were solved by direct methods using SHELXS-97^[40] and refined using full-matrix least-squares on F² (SHELXL-97).^[40] All nonhydrogen atoms in the compounds were refined with anisotropic displacement parameters. Selected crystal data and structure refinement details for $Br_3Ga[P(p-Anis)_3]$ and I₃Ga[P(p-Anis)₃] are listed in Tables S1 and S2 in the Supporting Information. CCDC-896761 $(Br_3Ga[P(\textit{p-Anis})_3])$ and CCDC-896762 $(I_3Ga[P-Mathematical Amplitude Amplitude$ (p-Anis)₃]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

NMR spectroscopy: Solution-phase ³¹P{¹H} NMR spectra were acquired at 161.902 MHz on a three-channel Varian Inova 400 MHz (¹H) spectrometer by using a pulsed field gradient direct detection broadband switchable probe. Reported temperatures are based on a calibration curve for that probe. The low-temperature portion of the calibration curve was constructed by using a standard methanol sample from Varian. The solvent used for the X₃Ga(PPh₃) and X₃Ga(TMP) adducts was CD₂Cl₂ whereas CDCl₃ was used for the X₃Ga[P(*p*-Anis)₃] complexes.

Solid-state ³¹P NMR spectra of MAS and stationary samples were acquired on a Chemagnetics CMX Infinity 200 (B_0 =4.70 T), as well as Bruker Avance 300 and 500 NMR spectrometers by using the combination of standard cross-polarization (CP) with proton TPPM decoupling.^[41] Samples were packed in 4 mm o.d. rotors. Proton 90° pulse widths of 4.0 µs, contact times of 5 to 10 ms, and pulse delays of 4 to 60 s were used to acquire most ³¹P NMR spectra. ³¹P chemical shifts were referenced with respect to 85% aqueous phosphoric acid by setting the isotropic peak of an external solid ammonium dihydrogen phosphate sample to 0.81 ppm.^[42] Spectra of MAS samples were acquired at ambient temperature with a spinning frequency of 8.0 to 15.0 kHz.

^{69/71}Ga NMR spectra of MAS and stationary samples were acquired on Bruker Avance 300 (B_0 =7.05 T), 500 (B_0 =11.75 T) and Avance II 900 MHz (B_0 =21.14 T) NMR spectrometers by using Bruker 4 mm MAS probes. Spectra of MAS samples were acquired at ambient temperature with a spinning frequency of 12.5 to 20.0 kHz. A $\pi/2-\tau_1-\pi/2-\tau_2-$ ACQ echo sequence was used to acquire all Ga NMR spectra, with pulse lengths ($\tau_{p(sel)}$) that selectively excited the central transition, $\tau_{(sel)} = \tau_{(non-sel)}/(S+1/2) = \tau_{(non-sel)}/2$ for ^{69/71}Ga.^[43] Proton TPPM decoupling^[41] was used to acquire all spectra. Each step of the Ga NMR spectra acquired at 7.05 or 11.75 T is the sum of 4096 to 72000 scans. Ga NMR chemical shifts were referenced with respect to an external solution of Ga(NO₃)₃ (1.0 M).^[20]

³¹¹P and ^{69/71}Ga NMR parameters were determined by visual comparison of experimental NMR spectra with those simulated by using the WSolids software package.^[44] This software includes the quadrupolar interaction to second-order perturbation theory for simulations of ^{69/71}Ga NMR spectra, and includes spin-spin interactions with these nuclei for simulations of ³¹P NMR spectra of MAS samples.

Quantum chemical calculations: DFT calculations of gallium EFG^[45] and $CS^{[46]}$ tensors, as well as ${}^{1}J({}^{69/71}Ga, {}^{31}P)$ and $\Delta J({}^{69/71}Ga, {}^{31}P)$ values, ${}^{[47]}$ were performed by using the Amsterdam Density Functional (ADF) program. ${}^{[48]}$ Geometries used for calculations for the $Cl_3Ga(PPh_3)$, ${}^{[8]}$ Br₃Ga(PPh₃), ${}^{[8]}$ I₃Ga(PPh₃), ${}^{[9]}$ Br₃Ga[P(p-Anis)₃], and I₃Ga[P(p-Anis)₃] adducts were those obtained from X-ray diffraction, except for the C–H bond lengths, which were fixed at 1.08 Å. Because single-crystal structure data for $Cl_3Ga[P(p-Anis)_3]$, $Cl_3Ga(TMP)$, Br₃Ga(TMP), and I₃Ga[P(p-Anis)₃], and I₃Ga[P(p-Anis)₃], were unavailable, the geometries for $Cl_3Ga(PPh_3)$, Br₃Ga[P(p-Anis)₃], and I₃Ga[P(p-Anis)₃] were used, with the H atoms replaced by a methoxy group where needed (e.g., the *para*-H atom of PPh₃ was replaced with a methoxy group to model the P(p-Anis) ligand). To investigate the effects

of the halides on the gallium magnetic shielding, CS tensors for model $X_3Ga(PMe_3)$ (X=Cl, Br, or I) adducts were also calculated. See the Supporting Information for more details.

Acknowledgements

We thank Victor Terskikh and Shane Pawsey for helpful comments and for acquiring some NMR spectra at 21.14 T. We are very grateful to Jason Clyburne, Gang Wu, Neil Burford, Klaus Eichele, Chris Kirby, Mike Lumsden, and Kenneth Wright for early contributions to this project. Access to the 900 MHz NMR spectrometer was provided by the National Ultrahigh-Field NMR Facility for Solids (Ottawa, Canada), funded by the Canada Foundation for Innovation, the Ontario Innovation Trust, Recherche Québec, the National Research Council of Canada, and Bruker BioSpin and managed by the University of Ottawa (www.mmr900.ca). R.G.C. and R.E.W. thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support through the Discovery Grant Program and for a Major Resources Support grant. R.E.W. also thanks the Canada Research Chairs program for research support.

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Received: August 19, 2012 Published online: January 10, 2013

Chem. Eur. J. 2013, 19, 2826-2838

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