$In[Co(CO)_4]_3$, 15820-67-4; ^{71}Ga, 14391-03-8; ^{115}In, 14191-71-0; ^{69}Ga, 14391-02-7; ^{59}Co, 7440-48-4; ^{79}Br, 14336-94-8; ^{81}Br, 14380-59-7; ^{35}Cl, 13981-72-1.

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Notes

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Application of the Additive Electric Field Gradient Model to Nuclear Quadrupole Resonance Data in Indium(III) Compounds and the Relation to Tin(IV) Parameters

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Additive electric field gradient models have been the focus of recent attention in the effort to formalize and predict trends in Mössbauer quadrupole splittings[1,2] and nuclear quadrupole resonance data.[3,4] It has been possible to define individual ligand electric field gradient (EFG) contributions which, when combined appropriately, will approximate the EFG at a central atom. Sn(IV),[5] Sb(III),[6] Sb(V),[7] Ir(III),[8] and low-spin Fe(II)[9] complexes have been analyzed in this way using Mössbauer spectra. Nuclear quadrupole resonance data in five-[3,10] and six-coordinate[4] cobalt compounds have also been discussed in connection with partial ligand field gradients (PFG). There exist many specific exceptions to the PFG model because π bonding,[3,11] the assumption of constant PFG values for individual ligands,[12] secondary associations,[1,2] and geometry changes[1,2] all contribute significantly to the EFG. Moreover, Sternheimer factors (valence and core electron polarizations) are usually assumed to be, but may not be, constant for a particular geometry.[13] Exceptions not withstanding, the frequent success of the PFG model at least in rationalizing qualitative trends in the electric field gradient makes it of general value and utility.

The bonding in Sn(IV) and Sb(V) compounds seems to be dominated by σ-bonding terms, and they often have good agreement between calculated and observed electric field gradients. Similarly it should be possible to subject the In(III) atom to an additive ligand electric field gradient treatment. Only quite recently have enough ^{115}In nuclear quadrupole resonance data become available to permit a preliminary PFG analysis, and by no means is the present note meant to be a final description. It is unlikely, however, that modeling as extensive as has been possible for Sn(IV) will ever come about because the number of suitable In(III) compounds and their tractability seems more restricted. Also the sign of the ^{115}In nuclear quadrupole coupling constant cannot be obtained experimentally from NQR spectroscopy. Even under the best of circumstances important assumptions are always made in applying the PFG model. All of these considerations make the model for In(III) a necessarily crude one. Nevertheless, by making qualitative comparisons to Sn(IV) parameters as a guide, the EFG trends in In(III) complexes do seem understandable as arising mainly from ligand PFG contributions and coordination sphere geometry changes.

Discussion

Table I contains a number of inorganic and organometallic compounds for which nuclear quadrupole coupling constants, e^2Qq/h, and EFG asymmetry parameters, η, have been reported. In particular, these are compounds having roughly similar counterparts in Sn(IV) chemistry. The sample temperature differences do not cause shifts in the coupling constants that are large enough to warrant concern here.

The compounds referred to as "six-coordinate" are not in all cases proven to be so on the basis of crystal structure determinations. $(CH_3)_2InCl$,[14] $(CH_3)_2InBr$,[15] and $(CH_3)_2InOAc$[16] are known to contain six-coordinate In(III) atoms with approximately trans CH_3 groups and multiply associated anions. Other R_2InX compounds ($R = CH_3$, C_6H_5; X = F,

Table I. ^{115}In Nuclear Quadrupole Resonance Data

Compd no.		e^2Qq_{zz}/h, MHz	η	Ref
	"Six-Coordinate" Compounds			
1	$(CH_3)_2InInI_4$	1275^a	0.05	18, 19
2	$(CH_3)_2InF$	1048^a	0.185	18
3	$(CH_3)_2InCl$	1200^a	0.095	18
4	$(CH_3)_2InBr$	1222^a	0.00	18
5	$(CH_3)_2InI$	1186^a	0.00	18
6	$(CH_3)_2InOAc$	1038^a	0.265	18
7	$(C_2H_5)_2InCl$	1143^b	0.16	*c*
8	$(C_2H_5)_2InBr$	1158^b	0.12	*c*
9	$(C_6H_5)_2InCl$	1117^a	0.14	17
		1129^a	0.17	17
	"Four-Coordinate" Compounds			
10	CH_3InBr_2	590^a	0.56	18
11	$(CH_3)_3In\cdot N(CH_3)_3$	783^b	0.00	*d*
12	$(CH_3)_3In\cdot P(CH_3)_3$	643^b	0.07	*d*
13	$(CH_3)_3In\cdot As(CH_3)_3$	769^b	0.06	*d*
14	$(CH_3)_3In\cdot Sb(CH_3)_3$	838^b	0.03	*d*
15	$(C_2H_5)_3In\cdot O(C_2H_5)_2$	1024^b	0.04	*c*
16	$\{ClIn[Co(CO)_4]_2\}_x$	451^a	0.61	24
17	$\{BrIn[Co(CO)_4]_2\}_x$	428^a	0.65	24
18	$ClIn[Co(CO)_4]_2\cdot THF$	378^a	0.58	24
19	$BrIn[Co(CO)_4]_2\cdot THF$	369^a	0.67	24
20	$acacIn[Co(CO)_4]_2$	347^a	0.39	24

[a] Room temperature. [b] 77 K. [c] L. M. Golubinskaya, V. I. Bregadze, E. V. Bryukhova, V. I. Svergun, G. K. Semin, and O. Yu. Okhlobystin, *J. Organomet. Chem.*, 40, 275 (1972). [d] D. B. Patterson and A. Carnevale, *J. Chem. Phys.*, 59, 6464 (1973).

Cl, Br, I; but not all combinations) are believed to have similar structures based on vibrational, mass spectral, and NQR arguments.[17,18] The small but nonzero η values (0.00–0.265) suggest that the coordination sphere is often not perfectly symmetrical. The asymmetry parameter, considered along with the very large coupling constants, indicates that the R groups are situated roughly trans to one another on the indium atom. The crystal structures bear this out. $(CH_3)_2InOAc$ has η = 0.265 and the CH_3–In–CH_3 angle is 152°.[16] In $(CH_3)_2InCl$ the angle is 167° and η = 0.095.[14] In $(CH_3)_2InBr$, η = 0.00 and the angle is 180°.[15] Moreover, CH_3InI_2 is believed to contain approximately linear $(CH_3)_2In^+$ ions and InI_4^-.[18-20] The anion may weakly coordinate to the cation in the plane perpendicular to the $(CH_3)_2In^+$ linkage. The NQR parameters of CH_3InI_2 are quite similar to those in the R_2InX class of compounds as they should be.

Considering these "six-coordinate" complexes first, partial field gradients for the ligands can be calculated from the tensor components shown in Figure 1. PFG values will be calculated in MHz and in this sense are partial coupling constants. They have the same relative meaning as the PQS values derived for Sn(IV). The point of reference for PFG values for ligands L, here identified as $\{L\}$, is arbitrary. $\{X\} = 0$, where X = F, Cl, Br, or I was chosen. The sign of q_{zz} is no doubt negative[2] and since Q_{In} is probably positive,[21] the coupling constant should be negative. Using $(CH_3)_2InInI_4$ to illustrate a trans methyl group arrangement with weak equatorial halogen association and averaging its $\{CH_3^-\}$ value with those of $(CH_3)_2InX$, X = F, Cl, Br, or I, a $\{CH_3^-\}$ value of −300 MHz is obtained. The use of $\{F^-\} \simeq \{Cl^-\} \simeq \{Br^-\} \simeq \{I^-\} \simeq 0$ seems to be justified since the range of $\{CH_3\}$ from the average is only about ±30 MHz. Accordingly, $\{OAc^-\}$ must be approximately zero using the data for $(CH_3)_2InOAc$. These values are in line with those found in six-coordinate Sn(IV) compounds. For Sn(IV) using $\{X^-\} = 0$ where X = F, Cl, or Br, the PQS values for I^- [2] and oxygen donors[22] fall into a small range around 0. Some of the EFG differences in R_2InX compounds certainly come from coordination sphere geometry differences. The nonzero η values for $(CH_3)_2InF$ and $(CH_3)_2InCl$ and the crystal structure of $(CH_3)_2InCl$ indicate that the CH_3–In–CH_3 linkage is nonlinear and this will lower the EFG at indium by a factor of $(1 - 3\cos^2\theta\sin^2\theta)$ where θ is the angle between the In–CH_3 bond vector and the collinear axis.[23] A CH_3–In–CH_3 angle of 160° corresponds to a 4–5% decrease in the EFG while a 140° angle leads to a 15–20% decrease. As noted earlier, these angles are in the range of those found for several of these compounds.[14-16]

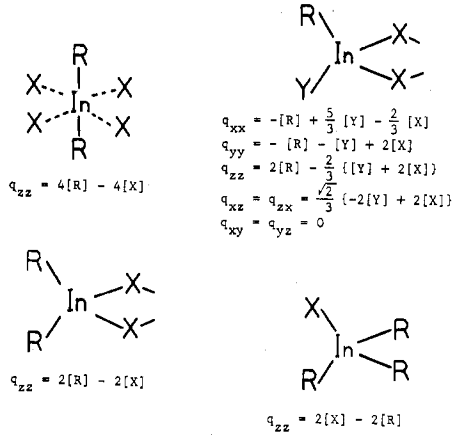

Figure 1. Geometries of complexes of In(III). The electric field gradient tensor components are found in ref 2.

Using the same analysis on $(C_6H_5)_2InCl$ gives $\{C_6H_5^-\}$ = −280 MHz assuming that $\{Cl^-\} = 0$. These values of $\{CH_3^-\}$ and $\{C_6H_5^-\}$ for In(III) seem reasonable by comparison to the much more extensively tested Sn(IV) quantities. $\{C_6H_5^-\}/\{CH_3^-\}$ = 0.93 in six-coordinate In(III), while $\{C_6H_5^-\}/\{CH_3^-\}$ = 0.92 in six-coordinate Sn(IV).[2] $\{C_2H_5^-\} \simeq \{CH_3^-\}$ using compounds **3** and **7** in Table I.

The compounds referred to in Table I as "four-coordinate" are more varied in their ligand selections but are by no means all proven to have this coordination number based on x-ray data. Assignment of four-coordination is based on spectroscopic information[18,24] and is supported in the cobalt carbonyl compounds by crystal structure data for the peripherally related complexes $In_3Br_3Co_4(CO)_{15}$[25] and $(C_2H_5)_4NBr_2In[Co(CO)_4]_2$.[26] CH_3InBr_2 has been proposed to be four-coordinate based on NQR analogies.[18] The crystal structure is needed to provide firm support because CH_3InCl_2, for which no NQR data have been reported, crystallizes with five-coordinate In(III) atoms.[27] It should be emphasized that only qualitative trending in ligand PFG values can be expected anyway because, even in four-coordinate Sn(IV) compounds, significant differences can exist between predicted and observed quadrupole splittings.[5] To compute the partial ligand electric field gradients, q_{zz} was assumed to be negative in all compounds except those of the R_3InX stoichiometry. No corrections were made for η, and in all cases the geometry was assumed to be tetrahedral. $\{acac^-\}$ was set equal to 0 as a bench mark so that $\{Co(CO)_4^-\}$ = −170 MHz is obtained using compound **20**. Using the equations in Figure 1, $\{Cl^-\}$, $\{Br^-\}$, and $\{THF\}$ will take on small values in the 0 to −50 MHz range using compounds **16–19**. The partial electric field gradients for oxygen and halogen donors are also very similar in Sn(IV) compounds.[28] Using compounds **10–14** a range of values for $\{CH_3^-\}$ of −370 ± 50 MHz is obtained if it is assumed that group 5 atom Lewis base donors have PFG values of ≃0 MHz. All of these values are summarized in Table II. Only compound **15** gives unsatisfactory results because $\{(C_2H_5)_2O\}$ would have to take on an unreasonably large value in order to fit the experimental coupling constant. It seems plausible that this compound involves only a very weak donor–acceptor interaction such that the In(III) coordination sphere is better approximated as a trigonal-planar three-coordinate complex rather than a tetrahedral four-coordinate complex.

Table II. Some Partial Quadrupole Coupling Constants for Ligands Bound to In(III)

	{Ligand}, MHz	
Ligand	Four-coordination[a]	Six-coordination[b]
$CH_3^- \simeq C_2H_5^-$	−370 ± 50	−300 ± 30
$C_6H_5^-$		−280
THF	~−10	
$Co(CO)_4^-$	−170	
Cl^-, Br^-	−45 ± 10	
CH_3COO^-		~0

[a] Calculated on the basis of $\{acac^-\} = 0$. [b] Calculated on the basis of $\{X\} = 0$ (X = F, Cl, Br, I).

Three notable features emerge from the PFG values in Table II. First, the trend in the PFG values is qualitatively the parallel of that found[2] for four-coordinate Sn(IV), namely, $\{CH_3^-\} > \{Co(CO)_4^-\} > \{\text{oxygen donors}\} \simeq \{\text{halogen donors}\}$. Second, $\{Co(CO)_4^-\}/\{CH_3^-\} = 0.52$ for Sn(IV) and 0.47 for In(III). This ratio is in quite good agreement considering the limited number of In(III) compounds with which to work. Third, $\{CH_3^-\}$ takes on a trend in In(III) which is comparable to that in Sn(IV) upon going from four- to six-coordination. That is, $\{CH_3^-\}_{O_h}/\{CH_3^-\}_{T_d}$ for Sn(IV) is 0.75,[2] while in In(III) the value is 0.81. The error in this In(III) ratio is possibly large because the error in $\{CH_3^-\}_{T_d}$ is significant, and the reference ligands, although giving similar PFG values, are different.

In summary, the additive electric field gradient model seems to have application to In(III) complexes along the same lines as have been applied to Sn(IV). By the same token, one can infer that in a general sense the ligand factors which dictate the electronic structure of In(III) in these geometries are the same as those that would apply to Sn(IV).[29]

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Registry No. In(III), 22537-49-1; CH_3^-, 15194-58-8; $C_2H_5^-$, 25013-41-6; $C_6H_5^-$, 30922-78-2; THF, 109-99-9; $Co(CO)_4^-$, 14971-27-8; Cl^-, 16887-00-6; Br^-, 24959-67-9; CH_3COO^-, 71-50-1; ^{115}In, 14191-71-0.

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(29) While this paper was in the reviewal stage, we became aware of a similar partial electric field gradient analysis on In(III) by G. M. Bancroft and T. K. Sham (*J. Magn. Reson.*, in press), which was also in the reviewal stage. The conclusions of these two papers, where they overlap, are in accordance with one another.

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Protonation of Rhodium–Olefin Complexes

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The postulated mechanism for many transition metal catalyzed reactions of olefins involves protonation of coordinated olefin to give coordinated alkyl.[1] An ethylrhodium complex from reaction of diethylenerhodium complexes with HCl has been identified by Cramer.[1a] Recently, Osborn has reported reversible protonation of molybdenum– and tungsten–ethylene complexes.[2] Studies of the reactions of other transition metal–olefin complexes with protonic acid have generally involved only alkyl-substituted olefins,[3] although some work has been reported on the protonation of vinyl halide–rhodium complexes.[4] In view of the importance of catalytic reactions involving substituted olefins and the significant role of protonation in these reactions, a study was made of the reactions with HCl of some η^5-$C_5H_5Rh(olefin)_2$ complexes where the olefin ligands are substituted ethylenes.

Experimental Section

Synthesis of η^5-$C_5H_5Rh(olefin)_2$. A mixture of η^5-$C_5H_5Rh(CH_2CH_2)(CH_2CHCN)$, I, and η^5-$C_5H_5Rh(CH_2CHCN)_2$, II, plus unreacted η^5-$C_5H_5Rh(CH_2CH_2)_2$, III, was obtained by heating for 1 h at 130 °C six evacuated, sealed 20-ml tubes each containing 0.448 g (2.0 mmol) of III (prepared by King's procedure[5]) and 3.0 ml of CH_2CHCN. The contents of the six tubes were combined and the acrylonitrile was evaporated to give 4.17 g of yellow residue which was chromatographed on alumina. The first fraction, eluted with benzene, gave 0.67 g of III. The second and third fractions were eluted with 4:1 and 2:1 benzene–ethyl acetate. The second fraction was crystallized from *n*-hexane at −80 °C to give 0.27 g of I as a pale yellow solid, mp 54–56 °C. The third fraction was rechromatographed to give 1.99 g of II as a yellow solid, mp 109.5–112 °C.[6]

A similar procedure with a 2-h reaction time was followed to synthesize η^5-$C_5H_5Rh(CH_2CH_2)(CH_2CHOCOCH_3)$, IV, mp 40–41.5 °C, and η^5-$C_5H_5Rh(CH_2CHOCOCH_3)_2$, V, mp 82.5–86 °C. Compound IV was eluted with 1:1 benzene–*n*-hexane, crystallized from methanol at −80 °C, and sublimed at 40 °C (0.2 mmHg). Compound V was eluted with 2:1 benzene–ethyl acetate and crystallized from ethanol.

The complexes η^5-$C_5H_5Rh(CH_2CHCO_2CH_3)_2$, VI, mp 103–106 °C, and η^5-$C_5H_5Rh(\textit{trans}\text{-}CH_3O_2CCHCHCO_2CH_3)_2$, VII, mp 195–199 °C were synthesized by a similar procedure in tubes containing 2 mmol of III, 4–5 mmol of substituted olefin, and 3 ml of benzene with reaction times of 2 and 1 h, respectively.

A solution of 1.78 g (6.2 mmol) of $acacRh(CH_2CHCH_3)_2$[7] in 10 ml of THF at −40 °C was treated with 5.5 ml of 18% NaC_5H_5 in THF. The mixture was warmed to 25 °C, the solvent removed, and the residue washed with benzene and CH_2Cl_2. The product, η^5-$C_5H_5Rh(CH_2CHCH_3)_2$, VIII, distilled as an orange liquid at 60 °C (0.2 mmHg) to give 1.3 g (83%). Satisfactory elemental analyses were obtained for all of the complexes.