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

Ligand	{Ligand}, MHz 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]

Acknowledgment. The valuable comments of Dr. G. M. Bancroft are gratefully acknowledged.

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.

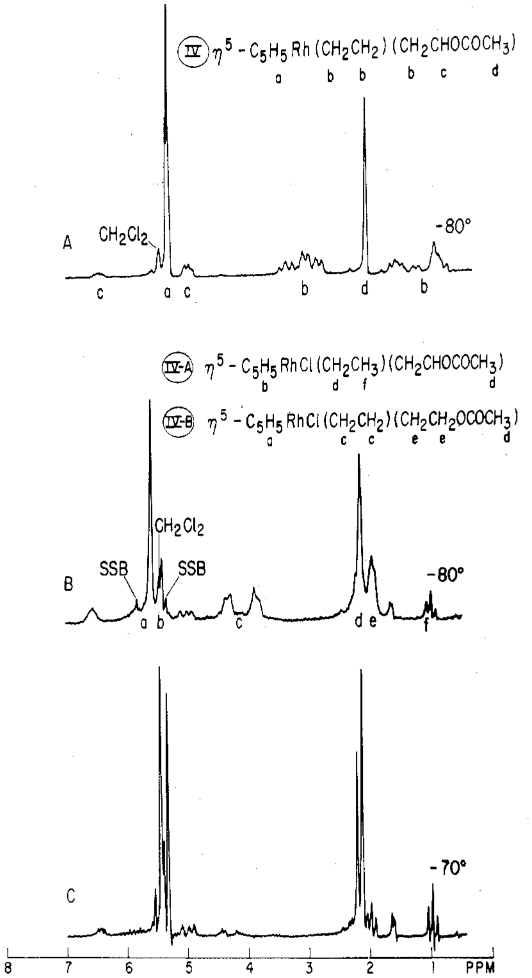

Figure 1. ^{1}H NMR spectrum at 100 MHz of η^5-$C_5H_5Rh(CH_2CH_2)(CH_2CHOCOCH_3)$ at −80 °C, A, and the variable-temperature spectra of the products from reaction of IV with HCl in CD_2Cl_2, B and C.

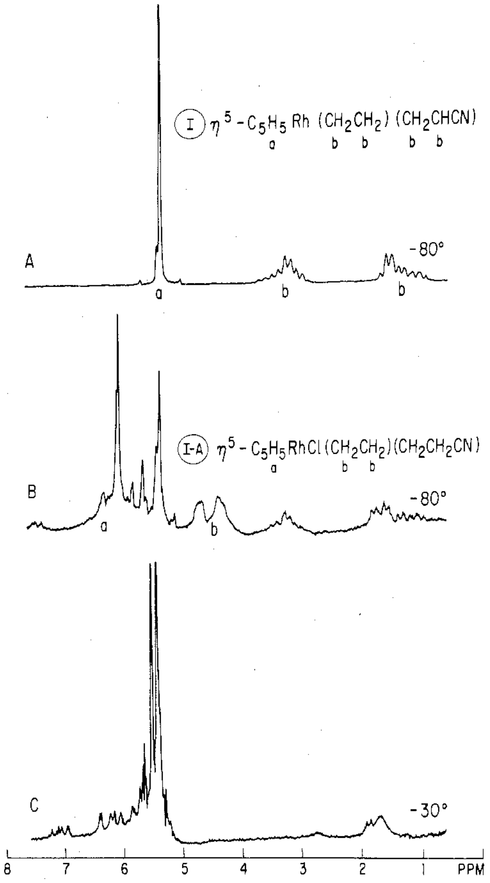

Figure 2. ^{1}H NMR spectrum at 100 MHz of η^5-$C_5H_5Rh(CH_2CH_2)(CH_2CHCN)$ at −80 °C, A, and the variable-temperature spectra of the products from reaction with HCl in CD_2Cl_2, B and C.

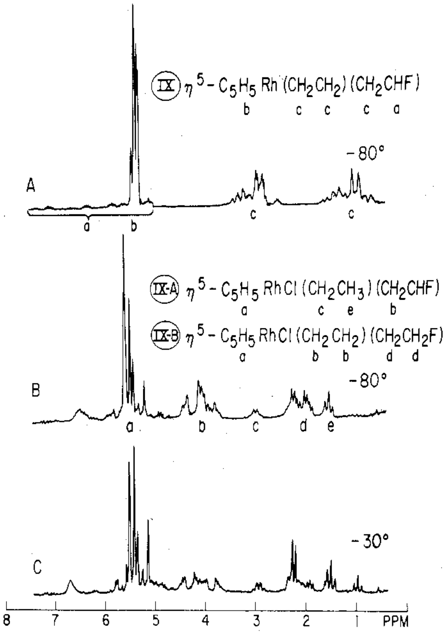

Figure 3. ^{1}H NMR spectrum at 100 MHz of η^5-$C_5H_5Rh(CH_2CH_2)(CH_2CHF)$ at −80 °C, A, and the variable-temperature spectra of the products from reaction of IX with HCl in CD_2Cl_2, B and C.

The complexes η^5-$C_5H_5Rh(CH_2CH_2)(CH_2CHF)$, IX, and η^5-$C_5H_5Rh(CH_2CHF)_2$, X, were prepared by Cramer.[8]

Reactions with HCl. A CD_2Cl_2 solution of 0.2 mmol of the rhodium complex with TMS as internal standard was charged to an NMR tube. The tube was chilled in liquid nitrogen and evacuated, 0.4 mmol of anhydrous HCl was added by syringe, and the tube was sealed. Prior to recording the spectrum, the tube was warmed to −80 °C, shaken, and placed in the NMR probe which was chilled to −80 °C. The ^{1}H NMR spectra were all recorded at 100 MHz.

Results and Discussion

The ^{1}H NMR spectra at −80 °C of the complexes which contain ethylene and a monosubstituted ethylene (IV, I, and IX) are shown in Figures 1, 2, and 3 along with the variable-temperature spectra of the products from the protonation of these complexes with HCl. Complete protonation of IV occurs on warming to −80 °C as evidenced by the absence of any resonances attributable to IV. The proton assignments for IV, shown in Figure 1A, are analogous to the assignments determined for η^5-$C_5H_5Rh(CH_2CH_2)(CH_2CHF)$.[8] "Inner" and "outer" isomers of IV give rise to the two resonances for proton C, the =CHO– proton. The two cyclopentadienyl resonances, separated by 3 Hz, are probably due to the two isomers rather than to coupling with rhodium since the rhodium coupling is usually small (0.7 Hz in η^5-$C_5H_5Rh(CH_2CH_2)_2$). The ^{1}H NMR spectrum resulting from reaction of IV with HCl, B of Figure 1, can be interpreted as arising from about 30% IV-A and 70% IV-B based on the proton assignments indicated in Figure 1. The assignment of the cyclopentadienyl and methyl protons of IV-A and IV-B is straightforward. The ethyl protons d and f of IV-A and the ethylene protons c of IV-B are assigned by analogy to η^5-$C_5H_5RhCl(CH_2CH_2)(CH_2CH_3)$ as well as comparison with the spectra of the products from reaction of complexes I and IX with HCl. A downfield shift of the ethylene protons on oxidation of rhodium from +1 to +3 is expected. The two

β-olefin protons of coordinated vinyl acetate of IV-A are obscured by the coordinated ethylene protons of IV-B at 4.1 ppm. Their presence is indicated by integration, and, after loss of ethylene from IV-B at −70 °C, integration of the broad resonances at 4.1–4.5 ppm still shows two protons relative to the three methyl protons at 1 ppm. Unambiguous assignment of the resonance(s) of the α proton of coordinated vinyl acetate in IV-A is not possible. The proton assignments for IV-A and IV-B are supported by the integrated areas. Small amounts of such organic fragments as $CH_3CH{=}$ and $-CHO$ may be present as indicated by resonances at 1.6 and 9.55 ppm. No hydride signal was detected. At −70 °C, C of Figure 1, the resonances associated with coordinated ethylene and η^5-C_5H_5 of IV-B disappear, and sharp singlets at 5.32 and 5.44 ppm appear. These changes are attributed to a loss of ethylene by IV-B to form a new complex. (Ethylene was later isolated from this reaction.) Further changes in the spectrum on slowly warming to −10 °C are not readily explicable.

At −80 °C, B of Figure 2, there is incomplete reaction between I and HCl. The poor quality of the spectrum renders unambiguous proton assignments difficult, but the absence of a strong doublet suggests that the linear cyanoethyl complex, I-A, is formed. The ethylene protons of I-A are assigned analogous to IV-B and the integrated area between 0.8 and 1.9 ppm provides for two of the four cyanoethyl protons. The position of the remaining two cyanoethyl protons is uncertain. Some acrylonitrile may be present. A broad, weak hydride resonance at −13.4 ppm was present at −80 °C and disappeared at −50 °C. The spectrum remains essentially unchanged to −30 °C where the resonances for I as well as coordinated ethylene and η^5-C_5H_5 of I-A disappear. A sharp singlet at 5.52 ppm, assigned to ethylene, appears and resonances of acrylonitrile are present.

In Figure 3, the variable-temperature ^1H NMR spectrum of IX and HCl shows complete reaction at −80 °C to give about 30% IX-A and 70% IX-B based on the indicated assignments. The proton assignments for IX have been determined previously.[8] The protons a, c, e, and b of IX-A and a, b, and d of IX-B are assigned analogously to the assignments for IV-A and IV-B and the integrated areas are consistent with these assignments. While the fluorine–hydrogen couplings for the ethyl fluoride protons d of IX-B have not been determined, their values should be close to the values determined for ethyl fluoride where J_{H-F}(methyl) = 25.7 Hz and J_{H-F}(methylene) = 47.6 Hz.[9] Unambiguous assignment of the α vinyl fluoride hydrogen of IX-A is not possible. No hydride resonance was found.

There are changes in the spectrum as the temperature is raised, and at −30 °C, C of Figure 2, a new resonance at 5.52 ppm, assigned to ethylene, begins to appear.

These three complexes with ethylene and monosubstituted olefin as ligands all react rapidly with HCl at −80 °C, and protonation occurs preferentially on the α carbon of the substituted olefin to form the linear alkylrhodium. In contrast, the relative ease of reaction of η^5-$C_5H_5Rh(CH_2CHX)_2$ with HCl increases with the electron-releasing ability of X in the order $X = CN < CO_2CH_3 < OCOCH_3 \simeq F \simeq CH_3$; see Table I.

A reasonable mechanism for protonation could involve oxidative addition of HCl followed by olefin insertion into the rhodium–hydride bond. Presumably Cl^- is still within the coordination sphere of rhodium. Reaction is always accompanied by a color change from yellow to red, consistent with oxidation of Rh^+.

In contrast to facile insertion of coordinated C_2H_4 into the ethyl–rhodium bond in $[\eta^5\text{-}C_5H_5Rh(CH_2CH_2)(C_2H_5)]^+$ observed earlier,[1a] no concrete evidence for olefin insertion into the alkyl–rhodium bond was seen in this work. As the temperature is raised, the alkyl complexes lose olefin. Attempts to isolate with phosphine the rhodium complex remaining after olefin release were not successful. Heating η^5-$C_5H_5Rh(CH_2CHCN)_2$ and HCl to 100 °C gave $[\eta^5\text{-}C_5H_5RhCl_2]_2$. However, no products were isolated for the other complexes.

Table I. Protonation of Rhodium–Olefin Complexes with HCl

Complex[a]	Temp, °C	Results
$CpRh(PR)_2$, VIII	−80	$CpRhCl(PR)(CH_2CH_2CH_3)$, $CpRhCl(PR)(CH(CH_3)_2)$, propylene; warming gives propylene at expense of rhodium alkyls
$CpRh(VF)_2$, X	−80	Vinyl fluoride; no $CpRh(VF)_2$; other components unknown; protonation at <−80 °C
$CpRh(VA)_2$, V	−80	Vinyl acetate; no $CpRh(VA)_2$; other components unknown; protonation at <−80 °C
$CpRh(MA)_2$, VI	−80	No reaction
	−20	Methyl acrylate, methyl propionate, some $CpRh(MA)_2$; other components unknown
$CpRh(AN)_2$, II	+40	No evidence for protonation
$CpRh(DMFU)_2$, VII	+30	No evidence for protonation

[a] Abbreviations: Cp, η^5-C_5H_5; AN, CH_2CHCN; VF, CH_2CHF; VA, $CH_2CHOCOCH_3$; PR, CH_2CHCH_3; MA, $CH_2CHCO_2CH_3$; DMFU, *trans*-$CH_3O_2CCHCHCO_2CH_3$.

HCl adds preferentially to η^5-$C_5H_5Rh(CH_2CH_2)(CH_2CHOCOCH_3)$, IV, in a mixture with η^5-$C_5H_5Rh(CH_2CH_2)_2$, III, at −80 to −60 °C. There is, however, no evidence that the reaction of III with HCl is reversed by IV. After 0.1 mmol of III had reacted with 0.1 mmol of HCl at −80 °C to give η^5-$C_5H_5RhCl(CH_2CH_2)(CH_2CH_3)$, 0.1 mmol of IV was added at −80 °C. There was no evidence for reaction of IV. Likewise, there was no evidence for reaction of III when 0.1 mmol was added at −80 °C to a CD_2Cl_2 solution of η^5-$C_5H_5RhCl(CH_2CH_2)(CH_2CH_2OCOCH_3)$ and η^5-$C_5H_5RhCl(CH_2CH_3)(CH_2CHOCOCH_3)$. Aqueous NaOH does appear to reverse the reaction of III with HCl in methanol at 25 °C.[10]

There is evidence for interaction between HCl and η^5-$C_5H_5Rh(CH_2CHCN)_2$, II, η^5-C_5H_5Rh(*trans*-$CH_3O_2CCHCHCO_2CH_3)_2$, VII, and η^5-$C_5H_5Rh(CH_2CHCO_2CH_3)_2$, VI, even at temperatures where alkylrhodium complexes were not detected. The ^1H NMR signal of HCl in CD_2Cl_2 solutions of these complexes reversibly moves upfield and broadens as the temperature is raised. At −80 °C, the chemical shift of HCl in a CD_2Cl_2 solution of 0.2 mmol of VI and 0.4 mmol of HCl is 9.9 ppm with a width at half-height of 22 Hz; at −60 °C, 8.8 ppm, 14 Hz; at −20 °C, 6.3 ppm, 8 Hz; at 0 °C, 4.4 ppm, 10 Hz. In contrast, the chemical shift of HCl in CD_2Cl_2 moves from 1.60 ppm at −80 °C to 1.28 ppm at 0 °C. The width at half-height is constant at 4 Hz. Although no hydride signal was detected for these systems, the reversible shifts of the HCl signal suggest an equilibrium, possibly involving a hydride, or some other species, and free HCl. With strong electron-withdrawing substituents on both olefin ligands, rhodium may not be basic enough to completely abstract hydrogen from HCl. An equilibrium may exist between the rhodium complex and HCl which does not involve H–Cl bond cleavage,[11] i.e.

$$\eta^5\text{-}C_5H_5Rh(ol)_2 + HCl \rightleftharpoons \eta^5\text{-}C_5H_5Rh(ol)_2(HCl)_x$$

The reversible absorption of HCl by II is further evidence of an equilibrium. At 0 °C, 1.0 mmol of II in $CHCl_3$ or

CH_2Cl_2 absorbs 4–5 mmol of HCl and changes color from light to dark orange. On applying a vacuum, the color change is reversed and all of the HCl is released. Examination of the residue by ^1H NMR shows only II. It may also be that N (or O) protonation is occurring. The infrared spectrum of a solution of HCl and II at 25 °C contains new absorptions at 1615 and 1930 cm^{-1} which cannot be attributed to starting materials. Infrared experiments with DCl have thus far been inconclusive because of overlap.

The results of this work suggest that rhodium may be a poor catalyst for reactions of some substituted olefins with mechanisms which involve olefin insertion into an alkyl–rhodium bond. On the other hand it is a good catalyst for reactions involving alkylmetal formation such as the hydrogenation of 1,4-dicyano-2-butene.[12] In addition, a strong preference for linear alkyl formation was found.

Registry No. I, 59831-04-8; I-A, 59831-05-9; II, 52367-67-6; III, 12211-95-9; IV, 59831-06-0; IV-A, 59831-07-1; IV-B, 59831-08-2; V, 59831-09-3; VI, 52367-68-7; VII, 59831-10-6; VIII, 36312-12-6; IX, 59872-34-3; IX-A, 59831-11-7; IX-B, 59831-12-8; X, 36118-17-9; HCl, 7647-01-0.

Supplementary Material Available: Table II, showing elemental analyses of the new complexes (1 page). Ordering information is given on any current masthead page.

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Novel Triaryloxo- and Triaroyloxostannyl Transition Metal Complexes

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Many transition metal complexes are known which have SnX_3^- as a monodentate ligand.[1-3] X is usually halogen, but several complexes are known where X is alkyl or aryl. In contrast, transition metal complexes with tin ligands of the type $Sn(OR)_3^-$ or $Sn(NR_2)_3^-$ are rare.[4] We now report the preparation and some properties of a novel series of platinum(II) and palladium(II) complexes which have either $Sn(OC_6H_5)_3^-$ or $Sn(O_2CC_6H_5)_3^-$ as ligands.

Table I. Melting Point and Infrared Data for *trans*-$L_2M(X)Y$ ($L = PEt_3, P(OC_6H_5)_3$; M = Pd, Pt)

X	Y	Mp, °C	ν_{PtX},[e] cm^{-1}
	trans-$(PEt_3)_2Pt(X)Y$		
Cl	$Sn(OC_6H_5)_3$	92–93	302
Cl	$SnCl_3$[a]		339,[c] 315[d]
Cl	$Sn(CH_3)_3$[a]		278[f]
Cl	$Sn(C_6H_5)_3$[a]		298[c]
Cl	$Sn(O_2CC_6H_5)_3$	141	280
Cl	$Sn(OC_6H_5)_3$[b]	151–152	288
Br	$Sn(OC_6H_5)_3$	90–91	187
$Sn(OC_6H_5)_3$	$Sn(OC_6H_5)_3$	152–153	
$Sn(OC_6H_5)_3$	$Sn(OC_6H_5)_3$[b]	177–180	
	trans-$(PEt_3)_2Pd(X)Y$		
Cl	$Sn(OC_6H_5)_3$	94–95	*g*
Cl	$Sn(O_2CC_6H_5)_3$	144–146	286
$Sn(OC_6H_5)_3$	$Sn(OC_6H_5)_3$	141–142	

[a] Complex where PEt_3 is replaced by $P(C_6H_5)_3$. [b] Complex where PEt_3 is replaced by $P(OC_6H_5)_3$. [c] R. V. Parish and P. J. Rowbotham, *J. Chem. Soc., Dalton Trans.*, 38 (1973). [d] M. C. Baird, *J. Inorg. Nucl. Chem.*, 29, 367 (1967). [e] Duplicate determinations of the stretching frequencies on the new complexes gave values within 3–5 cm^{-1} of each other. [f] D. J. Cardin and M. F. Lappert, *Chem. Commun.*, 506 (1966). [g] Assignment uncertain due to interference by other absorptions.

Experimental Section

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox. Elemental analyses were performed in house. Tin was determined by ASTM method E54-60T. An important starting material in this work, $Sn(OCH_3)_2$, was prepared from $SnCl_2$, $N(C_2H_5)_3$, and methanol following the procedure described by Morrison.[6] All NMR spectra were referenced to tetramethylsilane. The far-infrared spectra were taken in Nujol mulls between CsI plates. Molecular weights were determined cryoscopically in benzene under N_2.

Preparation of $NaSn(OC_6H_5)_3 \cdot THF$. Addition of 30 ml of tetrahydrofuran to a mixture of phenol (3.03 g, 32 mmol), $Sn(OCH_3)_2$ (2.84 g, 16 mmol), and $NaOC_6H_5$ (1.87 g, 16 mmol) produced a clear solution. Evaporation of volatiles under vacuum (10 mmHg) produced a white amorphous solid which was then dissolved in 25 ml of benzene. This mixture was filtered and 1 ml of tetrahydrofuran was added to the filtrate. Rapid addition of 40 cm^3 of hexane to the filtrate followed by 1 h of standing yielded 4.93 g (63% yield) of white crystals, mp 122.5–124 °C.

NMR (60 MHz, DMSO): δ (ppm) 1.60–1.90 and 3.50–3.75 (8 H, multiplet), 6.35–7.20 (15 H, aromatic, multiplet). Anal. Calcd for $C_{22}H_{23}O_4SnNa$: C, 53.58; H, 4.70; Sn, 24.05. Found: C, 53.75; H, 4.78; Sn, 22.67.

Preparation of $NaSn(O_2CC_6H_5)_3 \cdot 0.5THF$. Following the procedure described for the preparation of $NaSn(OC_6H_5)_3 \cdot THF$ the analogous $NaSn(O_2CC_6H_5)_3 \cdot 0.5THF$ was prepared in 80% yield. This material did not melt below 230 °C.

NMR (60 MHz, DMSO): δ (ppm) 8.05 and 7.50 (15 H, multiplet, $-C_6H_5$), 3.60 and 1.75 (4 H, multiplet, THF). Anal. Calcd for $C_{23}H_{19}O_{6.5}SnNa$: C, 51.11; H, 3.54; Sn, 21.96. Found: C, 51.57; H, 4.07; Sn, 21.58.

Preparation of *trans*-$(PEt_3)_2Pt[Sn(OC_6H_5)_3]Cl$. A solution of $NaSn(OC_6H_5)_3 \cdot THF$ (4.93 g, 10.0 mmol) in 35 ml of THF was added to a solution of *trans*-$(PEt_3)_2PtCl_2$ (5.03 g, 10.0 mmol) in 20 ml of THF. A white precipitate formed on mixing. The mixture was filtered and the filtrate evaporated to dryness under vacuum (12 mmHg) to give an oily yellow residue. This residue was taken up in 10 ml of THF and then 50 ml of hexane was added. On standing of the mixture at 0 °C yellow needles formed (5.96 g); mp 90–91 °C. Recrystallization from 5 ml of THF and 7 ml of hexane gave 4.22 g (50% yield), mp 92–93 °C.

NMR (60 MHz, CD_2Cl_2): δ (ppm) 2.25 and 1.15 (30 H, multiplet, $-C_2H_5$), 7.05 (15 H, multiplet, $-C_6H_5$).

Tables I and II give the elemental analyses[15] and physical measurements for this complex and related ones prepared by this procedure.