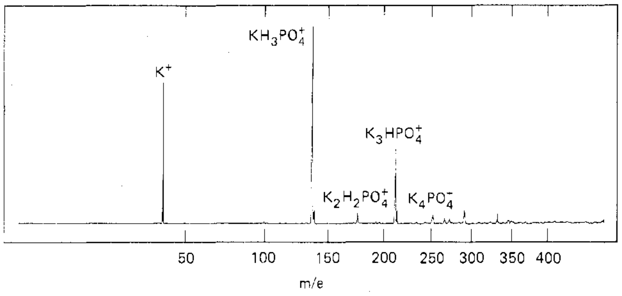

Figure 5. Field desorption spectrum of potassium dihydrogen phosphate, 306 °C.

mental conditions result in the formation of Al^+ and Fe^+ ions from the cathode surface, in addition to Na^+ and Mg^+ ions present as impurities. This spectrum, obtained at a higher field strength, is therefore not a pure field desorption spectrum but a composite of field desorption and ion bombardment. We may be observing here behavior similar to that observed under secondary ion mass spectrometry (SIMS).[12,13]

An FD spectrum of potassium phosphate, a material containing a polyvalent anion, is shown in Figure 5. Here we can identify, in addition to K^+ ions, $KH_3PO_4^+$, $K_2H_2PO_4^+$, $K_3HPO_4^+$, and $K_4PO_4^+$. Analogously, the analysis of K_2CO_3 showed only $K_3CO_3^+$ ions in addition to K^+. In contrast, under electron impact one might observe a minute yield of $K_2CO_3^+$ [14] but no $K_3CO_3^+$.

Again it should be emphasized that these are merely rudimentary illustrations of the type of chemistry that can be studied by field desorption mass spectrometry. Unlike classical electron impact mass spectrometry, which is highly useful in the study of the concentration and the structure of inorganic species in the gas phase, and in contrast to SIMS, which is highly useful in determining the elemental composition of thin solid layers, field desorption can teach us about the structure of inorganic solids. This technique could demonstrate nearest neighbor relations in solutions of inorganic materials and provide information on the relative stability of cluster ions. It could also indicate charge-transfer processes in solution, in addition to allowing the assessment of the isotopic composition of oxy anions, PO_4^{3-} in particular, using ^{18}O as a tracer. The great number of possible applications of this technique and its potential as a novel research tool are the main reasons for bringing it this early to the attention of the inorganic chemistry research community.

Registry No. Potassium iodide, 7681-11-0; potassium fluoride, 7789-23-3; ammonium chloride, 12125-02-9; potassium chloride, 7447-40-7; lithium iodide, 10377-51-2; potassium bromide, 7758-02-3; sodium iodide, 7681-82-5; ammonium nitrate, 6484-52-2; calcium fluoride, 7789-75-5; calcium chloride, 10043-52-4; magnesium chloride, 7786-30-3; uranium fluoride, 10049-14-6; potassium dihydrogen phosphate, 7778-77-0.

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Zerovalent Triarylstibine Complexes of Nickel, Palladium, and Platinum

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Although $Pd(PPh_3)_4$,[2] $Pt(PPh_3)_4$,[3] and $Ni(PPh_3)_4$ have been known for some time, the nature of the species present in solution remained obscure until recently.[5] Tolman examined solutions of the ML_4 complexes by ^{31}P and ^1H NMR and uv–visible spectroscopy. All observations are consistent with complete dissociation of the ML_4 complexes to ML_3 and L [L = PPh_3, $P(p\text{-}CH_3C_6H_4)_3$]. Recent studies have reported a relationship between the steric requirements of the phosphine ligands and the degree of dissociation to $M(PR_3)_3$ (M = Ni,[6,7] Pd[8]). The Ni(0) complexes were categorized according to the degree of ligand dissociation and the rate of exchange, on the NMR time scale, between free and complexed ligands.

Unlike the triarylphosphine complexes, the zerovalent triarylstibine complexes of Ni, Pd, and Pt have not been extensively studied. $Ni(SbPh_3)_4$ was reported by Wilke.[9] $Pd(SbPh_3)_4$, the only reported palladium complex, was prepared by the reaction of (acetylacetonato)[8-(acetylacetonyl)cyclooct-4-enyl]palladium with Ph_3Sb.[10] There are no literature references to $Pt(SbR_3)_4$. The mixed-ligand complexes $Pd(PPh_3)_2(SbPh_3)_2$ and $Pt(PPh_3)_3(SbPh_3)$ were formed from the reaction of excess $SbPh_3$ with $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$.[11] All of the reported triarylstibine complexes are insoluble and thus do not lend themselves to solution studies. We therefore undertook the study of soluble zerovalent triarylstibine complexes in order to compare preparations, stabilities, and solution properties with those of the well-known phosphine analogues. This work is a continuation of our studies involving triarylstibine–transition metal complexes.[12,13]

Experimental Section

All reactions were carried out in Schlenk apparatus. Solvents were dried prior to use. Manipulations of the compounds were carried out in an inert-atmosphere box or in Schlenk apparatus under argon. The complexes $Ni(COD)_2$,[14] (COD = 1,5-cyclooctadiene), $Pd(PPh_3)_4$,[15] $Pt(PPh_3)_3$,[16] and $Pt(PPh_3)_2(C_2H_4)$[17] and the ligands $Sb(p\text{-}CH_3C_6H_4)_3$,[18] $Sb(p\text{-}CH_3OC_6H_4)_3$,[18] and $Sb(SPh)_3$[19] were prepared by literature methods. Analytical data are given in Table I. Preparations are shown in Figure 1.

(a) Preparation of $Ni(SbR_3)_4$ (R = Ph, $p\text{-}CH_3C_6H_4$, $p\text{-}CH_3OC_6H_4$), Method I. $(CH_3CH_2)_3Al$ (0.50 ml, 0.46 mmol) was added slowly in a Schlenk filtration apparatus to a dried and deaerated diethyl ether solution (30 ml) of $Ni(acac)_2$ (0.5 g, 0.19 mmol) and SbR_3 (0.80 mmol) at 0°C. A yellow crystalline material precipitated (R = Ph). For the more soluble complexes (R = $p\text{-}CH_3C_6H_4$, $p\text{-}CH_3OC_6H_4$), the solution was reduced in volume to ca. 15 ml and 10 ml of hexane was added, inducing the precipitation of an off-white solid. The complexes were collected by filtration, washed with hexane, and dried under vacuum; yield ca. 75%.

(b) Preparation of $Ni(SbR_3)_4$ (R = Ph, $p\text{-}CH_3C_6H_4$, $p\text{-}CH_3OC_6H_4$), Method II. A solution of SbR_3 (0.15 mmol) was added slowly to a benzene solution (20 ml) of $Ni(COD)_2$ (0.10 g, 0.036 mmol) in a Schlenk filtration apparatus. Further work-up was identical with that described in section a.

(c) Preparation of $Pd(SbR_3)_4$ (R = Ph, $p\text{-}CH_3C_6H_4$, $p\text{-}CH_3OC_6H_4$). $(CH_3CH_2)_3Al$ (0.21 ml, 0.20 mmol) was added slowly in a Schlenk filtration apparatus to a dried and deaerated diethyl ether solution (30 ml) of $Pd(acac)_2$ (acac = acetylacetonate) (0.25 g, 0.08 mmol) and SbR_3 (0.34 mmol) at 0°C. The yellow solution was stirred at 0°C for 1 hr. Further work-up was identical with that described in section a.

(d) Preparation of $Pd(PPh_3)_2(SbR_3)_2$ (R = Ph, $p\text{-}CH_3C_6H_4$), Method I. A benzene solution (10 ml) of SbR_3 (0.086 mmol) was added dropwise to a suspension of $Pd(PPh_3)_4$ (0.25 g, 0.022 mmol)

Table I. Analytical Data for Zerovalent Ni, Pd, and Pt Complexes of Triarylstibines[a]

Compd	C	H	M	S
$Ni[Sb(p\text{-}CH_3C_6H_4)_3]_4$	61.56 (60.75)	5.13 (4.93)	3.69 (3.27)	
$Pd[SbPh_3]_4$	56.94 (56.75)	4.97 (4.83)	7.01 (6.71)	
$Pd[Sb(p\text{-}CH_3C_6H_4)_3]_4$	59.91 (59.61)	5.03 (4.95)	6.12 (5.80)	
$Pd[Sb(p\text{-}CH_3OC_6H_4)_3]_4$	57.71 (58.02)	4.85 (4.90)		
$Pd(PPh_3)_2[Sb(p\text{-}CH_3C_6H_4)_3]_2$	64.52 (64.06)	4.54 (4.55)	8.01 (7.67)	
$Pd(PPh_3)_2(SbPh_3)_2$	66.08 (65.78)	5.08 (4.76)	7.27 (7.01)	
$Pt(PPh_3)_2(SbPh_3)_2$	60.88 (59.94)	4.23 (4.01)		
$Pt(PPh_3)_2[Sb(p\text{-}CH_3C_6H_4)_3]_2$	62.05 (61.61)	4.75 (4.95)	12.87 (12.83)	
$Pt(PPh_3)_2[Sb(SPh)_3]_2$	53.35 (52.84)	3.70 (3.76)		11.85 (11.42)

[a] Calculated (found).

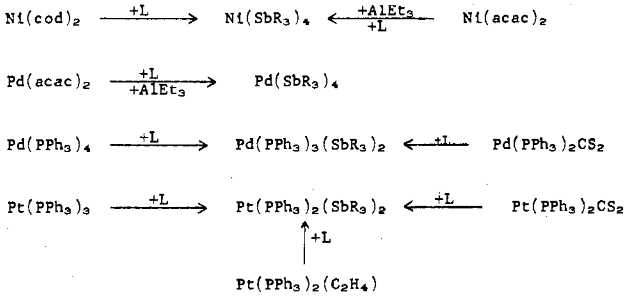

Figure 1. Preparation of zerovalent nickel, palladium, and platinum complexes of triarylstibines.

in benzene (20 ml) at room temperature. The resulting white powder (R = Ph) was collected by filtration, washed with hexane, and dried under vacuum. For the more soluble complex (R = p-$CH_3C_6H_4$) the solvent was removed under vacuum to give a yellow oil. Washing the oil with acetone–hexane gave a yellow powder which was collected by filtration, washed with hexane, and vacuum dried; yield ca. 70%.

(e) Preparation of $Pd(PPh_3)_2[Sb(p\text{-}CH_3C_6H_4)_3]_2$, Method II. A suspension of $Pd(CS_2)(PPh_3)_2$ (0.10 g, 0.015 mmol) and $Sb(p\text{-}CH_3C_6H_4)_3$ (0.12 g, 0.30 mmol) in benzene (25 ml) was stirred overnight under argon. Unreacted $Pd(CS_2)(PPh_3)_2$ was removed by filtration and the solvent was removed under vacuum to give a yellow oil. The complex was further worked up as described in section d; yield ca. 50–60%.

(f) Preparation of $Pt(PPh_3)_2(SbR_3)_2$ (R = Ph, p-$CH_3C_6H_4$), Method I. A benzene solution (10 ml) of SbR_3 (0.114 mmol) was added dropwise to a suspension of $Pt(PPh_3)_3$ (0.25 g, 0.025 mmol) in benzene (20 ml) at room temperature. The resulting yellow powder (R = Ph) was collected by filtration, washed with hexane, and dried under vacuum.

For R = p-$CH_3C_6H_4$, after 3.5 h the solvent was removed under vacuum to give a yellow oil. Further work-up was as described in section d. The yield of $Pt(PPh_3)_2[Sb(p\text{-}CH_3C_6H_4)_3]_2$ was 60–70% and that of $Pt(PPh_3)_2(SbPh_3)_2$ was 90–95%.

(g) Preparation of $Pt(PPh_3)_2(SbR_3)_2$ (R = Ph, p-$CH_3C_6H_4$), Method II. A benzene solution (10 ml) of SbR_3 (0.04 mmol) was added dropwise to a benzene solution (10 ml) of $Pt(PPh_3)_2(C_2H_4)$ (0.15 g, 0.02 mmol). After 1 h of stirring at room temperature, the solvent was removed under vacuum to give an oil. Further work-up was as in section d; yield ca. 80–85%.

(h) Preparation of $Pt(PPh_3)_2[Sb(p\text{-}CH_3C_6H_4)_3]_2$, Method III. A suspension of $Pt(CS_2)(PPh_3)_2$ (0.3 g, 0.025 mmol) and $Sb(p\text{-}CH_3C_6H_4)_3$ (0.2 g, 0.05 mmol) in benzene (25 ml) was stirred overnight under argon. Further work-up was as in section d; yield 60–65%.

(i) Preparation of $Pt(PPh_3)_2[Sb(SPh)_3]_2$. A benzene solution (10 ml) of $Sb(SPh)_3$ (0.18 g, 0.04 mmol) was added dropwise to a benzene solution (10 ml) of $Pt(PPh_3)_2(C_2H_4)$ (0.15 g, 0.02 mmol). After 1.5 h of stirring at room temperature, the lime green solution was reduced in volume to ca. 5 ml and 10 ml of hexane was added to induce precipitation. The yellow complex was collected by filtration, washed with Et_2O, and dried under vacuum; yield ca. 75%.

Discussion

$Ni(PPh_3)_4$ is easily prepared by the zinc dust reduction of $NiCl_2$, in the presence of PPh_3.[5] When the reaction was attempted with SbR_3, a black metallic precipitate was observed and no triarylstibinenickel complex was obtained. $Ni(SbR_3)_4$, was, however, prepared by the $(CH_3CH_2)_3Al$ reduction of $Ni(acac)_2$ in the presence of SbR_3 (R = Ph, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$) or by the replacement of cyclooctadiene from $Ni(COD)_2$.

Table II. 220-MHz ^1H NMR[a] Data for Zerovalent Ni, Pd and Pt Complexes of Triarylstibines

Compd	Aromatic	CH_3 or OCH_3
$Sb(p\text{-}CH_3C_6H_4)_3$	1.80, 2.00	7.69
$Sb(p\text{-}CH_3OC_6H_4)_3$	2.75, 3.20	6.27
$Pd[Sb(p\text{-}CH_3C_6H_4)_3]_4$	3.00, 3.32	7.74
$Pd[Sb(p\text{-}CH_3OC_6H_4)_3]_4$	3.05, 3.64	6.39
$Ni[Sb(p\text{-}CH_3C_6H_4)_3]_4$	3.10, 3.36	7.77
$Ni[Sb(p\text{-}CH_3OC_6H_4)_3]_4$	3.12, 3.72	6.42
$Pd(PPh_3)_2[Sb(p\text{-}CH_3C_6H_4)_3]_2$	2.27–3.40[b]	7.75
$Pt(PPh_3)_2[Sb(p\text{-}CH_3C_6H_4)_3]_2$	2.27–3.41[b]	7.73, 7.77

[a] τ scale, $CDCl_3$. [b] Multiplets due to several species present in solution.

$Pd(PPh_3)_4$ is easily prepared by the hydrazine hydrate reduction of $PdCl_2$ in the presence of PPh_3 or by $NaBH_4$ reduction of K_2PdCl_4 in the presence of PPh_3.[20] When either of these standard methods was attempted with SbR_3, a black metallic precipitate was obtained. The palladium complexes $Pd(SbR_3)_4$ (R = Ph, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$) were obtained by the $(CH_3CH_2)_3Al$ reduction of $Pd(acac)_2$ in the presence of SbR_3.

Attempted preparation of $Pt(SbR_3)_4$ by standard procedures for preparing $Pt(PPh_3)_4$[20] also failed. When the preparation was attempted by the $(CH_3CH_2)Al$ reduction of $Pt(acac)_2$, a very air-sensitive red oil was obtained in addition to a large amount of black metallic material. No triarylstibineplatinum complex could be isolated.

Reaction of $Pd(PPh_3)_4$ with excess SbR_3 (R = Ph, p-$CH_3C_6H_4$) resulted in a white powder which analyzed as $Pd(PPh_3)_2(SbR_3)_2$, in agreement with the formulation proposed in a previous study for R = Ph.[11] $Pd(PPh_3)_2(SbR_3)_2$ was also isolated from the reaction of $Pd(PPh_3)_2(CS_2)$ with SbR_3.

Reaction of $Pt(PPh_3)_3$ with excess SbR_3 (R = Ph, p-$CH_3C_6H_4$) resulted in a yellow powder which analyzed as $Pt(PPh_3)_2(SbR_3)_2$—which is not in agreement with the previous formulation, $Pt(PPh_3)_3(SbPh_3)$, obtained from $Pt(PPh_3)_4$.[11] $Pt(PPh_3)_2(SbR_3)_2$ was also isolated from the reaction of $Pt(PPh_3)_2(C_2H_4)$ or $Pt(CS_2)(PPh_3)_2$ with SbR_3.

The reaction of $Pt(PPh_3)_2(C_2H_4)$ with $Sb(SPh)_3$ resulted in the isolation of $Pt(PPh_3)_2[Sb(SPh)_3]_2$ the first reported thioantimonite–transition metal complex. The complex is insoluble in all common organic solvents and thus its ^1H NMR spectrum could not be obtained.

The zerovalent triarylstibine complexes of nickel, platinum, and palladium were found to have air stability similar to that of the platinum– and palladium–phosphine analogues whereas the nickel–triarylphosphine complexes are more reactive.

^1H NMR Data. ^1H NMR data for solutions of the free ligands and isolated complexes are given in Table II. Examination of the chemical shifts of the $M(SbR_3)_4$ complexes shows an upfield shift of the aromatic protons and a corresponding though smaller upfield shift in the methyl or methoxy resonances vs. the free ligands.

Addition of free ligand to a solution of any of the $M(SbR_3)_4$ (M = Pd, Ni) complexes simply added the resonances of the ligands to the spectra, indicating little dissociation and slow exchange or type I behavior as discussed by Tolman.[7] Analogous $P(p\text{-}CH_3C_6H_4)_3$ complexes exhibit extensive dissociation and fast exchange,[5] i.e., type IV behavior.[7]

The steric bulk of the triarylphosphine and stibine ligands can be compared by methods previously outlined.[6,7] The covalent radius of the coordinated antimony is about 0.3 Å larger than for phosphorus[31] and results in a lengthening of the M–Sb and Sb–C bonds such that the cone angle for the $SbPh_3$ is <132° vs. that for PPh_3, 145°. The steric bulk is more similar to that of $P(p\text{-}CH_3C_6H_4O)_3$, 128°, which also exhibits type I behavior.[22]

The ^{1}H NMR spectrum of $Pd(PPh_3)_2(SbR_3)_2$, R = $p\text{-}CH_3C_6H_4$, exhibited a single methyl resonance (peak width at half-height 7 Hz) and a very complex phenyl region. Examination of the phenyl region indicated the presence of several species, consistent with the redistribution of $Pd(PPh_3)(SbR_3)_2$ in solution

$$2Pd(PPh_3)_2(SbR_3)_2 \rightleftharpoons Pd(PPh_3)_3(SbR_3) + Pd(PPh_3)(SbR_3)_3$$

The observation of a single broadened methyl resonance is consistent with nearly identical methyl chemical shifts for the species present. The material obtained from solution analyzing as $Pd(PPh_3)_2(SbR_3)_2$ could be either a single product or a complex mixture, $Pd(PPh_3)_n(SbR_3)_{4-n}$ (n = 4–0), in appropriate ratios.

The ^{1}H NMR spectrum of $Pt(PPh_3)_2(SbR_3)_2$ showed methyl resonances at τ 7.73 and 7.77. The aromatic region was again more complex than expected for a single species. ^{1}H NMR spectra of the complexes obtained from $Pt(PPh_3)_3$, $Pt(CS_2)(PPh_3)_2$, or $Pt(PPh_3)_2(C_2H_4)$ were identical. An equilibrium similar to that for $Pd(PPh_3)_2(SbR_3)_2$ must again be proposed.

Triarylstibinerhodium(I) complexes favor five-coordination in the solid state whereas analogous phosphine complexes are four-coordinate.[12] We now find that $M(SbR_3)_4$ (M = Pd, Ni) are not extensively dissociated in solution, unlike the analogous phosphine complexes. These observations can be rationalized on the basis of steric considerations. Measurements of cone angles indicate the steric nature of SbR_3 is closer to that of $P(OR)_3$ than of PR_3. It appears that, compared with triarylphosphine ligands, the lower steric requirements of the triarylstibine ligands allow higher coordination and do not force dissociation in such systems.

Registry No. $Ni[Sb(p\text{-}CH_3C_6H_4)_3]_4$, 57527-33-0; $Ni[Sb(p\text{-}CH_3OC_6H_4)_3]_4$, 57527-34-1; $Pd[SbPh_3]_4$, 23854-68-4; $Pd[Sb(p\text{-}CH_3C_6H_4)_3]_4$, 57527-39-6; $Pd[Sb(p\text{-}CH_3OC_6H_4)_3]_4$, 57527-40-9; $Pd(PPh_3)_2[Sb(p\text{-}CH_3C_6H_4)_3]_2$, 57527-35-2; $Pd(PPh_3)_2(SbPh_3)_2$, 14263-83-3; $Pt(PPh_3)_2(SbPh_3)_2$, 57527-36-3; $Pt(PPh_3)_2[Sb(p\text{-}CH_3C_6H_4)_3]_2$, 57527-37-4; $Pt(PPh_3)_2[Sb(SPh)_3]_2$, 57527-38-5; $Ni(acac)_2$, 3264-82-2; $Ni(COD)_2$, 1295-35-8; $Pd(acac)_2$, 14024-61-4; $Pd(PPh_3)_4$, 14221-01-3; $Pd(PPh_3)_2CS_2$, 57527-52-3; $Pt(PPh_3)_3$, 13517-35-6; $Pt(PPh_3)_2CS_2$, 50588-64-2; $Pt(PPh_3)_2(C_2H_4)$, 12120-15-9; $AlEt_3$, 97-93-8.

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Investigation of the Utility of "Virtual Coupling" in the $^{13}C\{^1H\}$ Nuclear Magnetic Resonance Spectra of Bis-Phosphite Complexes of Palladium and Platinum. Algebraic Cancelation of Spin–Spin Coupling

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Following the early observation of "virtual coupling" in the ^{1}H NMR spectra of bis-organophosphorus compounds by King[2] and by Jenkins and Shaw,[3] this phenomenon has become a fundamental tool for geometry assignment. Several hundred articles have appeared in which it has been utilized to assign the geometry of transition metal–phosphine complexes. Unfortunately, there are a large number of compounds for which ^{1}H NMR virtual coupling is not applicable. The method generally cannot be applied unless the phosphorus ligand bears an α-methyl, α-methoxy, α-methylene, or ortho methylene group which is not coupled to other protons. This excludes such commonly utilized ligands[4] as triphenylphosphine, triethylphosphine, and triethyl phosphite for which the method is applicable only in fortuitous circumstances.[5] Because of this limitation as well as the increasing availability of Fourier transform spectrometers $^{13}C\{^1H\}$ NMR has been briefly investigated for similar use.[6] In several instances it has been shown that ^{13}C NMR can provide structural information where ^{1}H NMR cannot.[7] Yet few systematic investigations have appeared. In the course of our studies, we noted that the $^{13}C\{^1H\}$ NMR spectrum of *cis*-$[(MeO)_3P]_2PdCl_2$ was a singlet instead of the anticipated multiplet.[6] We had also observed other instances of the apparent lack of phosphorus–carbon coupling, e.g., in the aryl groups of arylphosphine complexes.[8] In order to seek an explanation for this phenomenon and to investigate the general utility of $^{13}C\{^1H\}$ NMR for geometry assignments we undertook an investigation of the $^{13}C\{^1H\}$ NMR spectra of complexes of the type L_2MCl_2, where L is a phosphite or phosphine and M is Pd(II) or Pt(II). The chosen ligands are ones for which ^{1}H virtual coupling for the most part is not applicable. Furthermore, no previous $^{13}C\{^1H\}$ studies of phosphite complexes have been reported. For comparison, a few compounds of the type *cis*-LL′$PdCl_2$ were also investigated.[9] While this work was being completed, a similar study of phosphine complexes appeared.[7b] Our results on the