Table II of part I and the Rh(VI)$^{3+}$ radius of 0.665 Å, oxygen z parameters of 0.1076, 0.1072, and 0.1117 are found. This results in 1.95 Å for Pd–O, 1.83 Å for Cu–O, and 2.08 Å for Ag–O which compare well with the equivalent distances in Table IV.

Radii are also effective in comparing the delafossite structure types with those of other ABO_2 phases. Figure 2 shows a plot of r_A *vs.* r_B for the various known ABO_2's. With few exceptions, this plot gives a good idea of the structure to be expected for a particular composition. It also suggests new compositions which might be synthesized.

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Chemistry of Noble Metal Oxides. III. Electrical Transport Properties and Crystal Chemistry of ABO_2 Compounds with the Delafossite Structure

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A schematic model of chemical bonding for the ternary oxides ABO_2 (where A is Cu, Ag, Pd, or Pt and B is a trivalent ion such as Cr^{3+}, Fe^{3+}, Co^{3+}, or Rh^{3+}) is described. This model is shown to rationalize several features of the crystal chemistry of these compositions, including their common adoption of the delafossite-type structure. Electrical conductivity measurements as functions of temperature and crystallographic orientation are described and the results are shown to be qualitatively explainable on the basis of the proposed bonding scheme. All of the subject oxides exhibit anisotropic electrical conductivity that is metallic when A is Pt or Pd but semiconducting when A is Cu or Ag.

Introduction

Recent applications of low-temperature or high-pressure synthesis techniques have led to the discovery of several new polynary oxides containing elements of the platinum and coinage groups. In part I of this series some aspects of the general chemistry of such oxides were considered, and synthesis of ternary compositions having the general formula ABO_2 (where A is Pd, Pt, Cu, or Ag and B is one of the other transition elements) were described. Structural refinements of several of these ABO_2 compounds, which are isotypic with the mineral delafossite ($CuFeO_2$), were reported in part II. As discussed in that paper, the A ions in delafossite have only two anion near neighbors, while the B ions occur in regular octahedral interstices. Each oxygen is coordinated by four cations, one A and three B, at the corners of a tetrahedron.

The platinum and palladium analogs ($PtCoO_2$, $PdCoO_2$, $PdCrO_2$, and $PdRhO_2$) were the first of the delafossite type to be investigated by us. In addition to being among the first well-characterized oxides in which Pt or Pd occurs in combination with other transition metals, the structure and properties of these compositions presented several other unusual features. (1) Twofold, linear coordination by anions had not previously been observed for platinum or palladium. (2) Magnetic susceptibility measurements and Co–O distances indicated that cobalt in $PtCoO_2$ and in $PdCoO_2$ was in a trivalent, low-spin state. This conclusion was supported by the fact that chromium and rhodium could be wholly substituted for cobalt in the palladium analog. Since a trivalent oxidation state is the most stable for both Cr and Rh, there was little doubt that palladium in these compounds was formally present in the highly unusual monovalent state. (Similar reasoning would indicate Pt^+ in $PtCoO_2$; however, as pointed out in part I, the possibility of nonstoichiometry in the platinum composition, giving $Pt^{2+}{}_{0.8}Co^{3+}{}_{0.8}O_2$, cannot be excluded.) (3) Preliminary electrical resistivity measurements showed that single-crystal, hexagonal plates of the platinum composition exhibited exceptionally high electrical conductivity (10^6 ohm^{-1} cm^{-1}) in the plane of the plate (*i.e.*, perpendicular to the crystallographic c axis). Such a high metal-like conductivity is, in itself, quite uncommon for oxides, but even more unusual was an apparently large anisotropy of this property. Consideration of these features of the platinum and palladium delafossite phases has led to the development of a qualitative model for the chemical bonding in these oxides that appears to rationalize their crystal chemistry and electrical behavior. General application of this model suggests that $PdCoO_2$, $PdCrO_2$, and $PdRhO_2$ should have electrical properties analogous to those of $PtCoO_2$, but that copper and silver analogs should be semiconducting. In order to check this point, we made a careful study of the electrical conductivities of several of the delafossite-type oxides as functions of temperature and orientation. In this paper the results of that study are reported, the qualitative bonding model is described in terms of the crystal chemistry of the delafossite structure, and finally, the observed electrical properties are shown to be consistent with those expected on the basis of the model.

Experimental Section. Electrical Transport Properties of Delafossite Phases

Crystals of ABO_2 compositions having the delafossite structure normally grow in the form of thin hexagonal plates in which the crystalline c axis is perpendicular to the plane of the plate. Resistivity measurements on several crystals were made in the plane of the plate ($\perp c$) by application of a standard, four-probe technique to regularly shaped bars cut from the crystals. The bars, after cutting, were of submillimeter size, and attachment of the probes, which utilized indium contacts soldered to the crystal, required the aid of a microscope and a micromanipulator. Measurements were routinely made over the temperature range 4.2–298°K and employed a Keithley electrometer (Model 600A or 610A) for high-resistance samples ($R > 100$ ohms) and a Keithley microvoltmeter (Model 150B) for lower resistance samples. In this way, resistivities perpendicular to the c axis were determined as a function of temperature for crystals of the compositions $PtCoO_2$, $PdCoO_2$, $CuCoO_2$, $AgCoO_2$, $CuFeO_2$, $AgFeO_2$, $AgInO_2$, and $AgGaO_2$. The platinum and palladium compositions exhibited a metallic temperature dependence with resistivity ratios ($\rho(298°K)/\rho(4.2°K)$) that varied between 10 and 100 for several crystals. All the copper and silver compositions were semiconductors. For the latter oxides, activation energies for semiconductivity were determined in the usual way from the slopes of log ρ *vs.* $1/T$ plots. The room-temperature resistivities for all compositions and activation energies for the semiconductors are reported in Table I.

TABLE I

ROOM-TEMPERATURE RESISTIVITIES (ρ) AND ACTIVATION ENERGIES (E_a) FOR SEMICONDUCTION MEASURED PARALLEL AND PERPENDICULAR TO THE c AXIS OF SEVERAL DELAFOSSITE-TYPE OXIDES

Compn	$\rho(\parallel c)$, ohm-cm	$E_a(\parallel c)$, eV	$\rho(\perp c)$, ohm-cm	$E_a(\perp c)$, eV
$PtCoO_2$	1×10^{-3}	. . .	3×10^{-6}	. . .
$PtCo_{0.97}Mn_{0.03}O_2$	1×10^{-3}	. . .	1.2×10^{-5}	. . .
$PtCo_{0.95}Mn_{0.05}O_2$	2×10^{-3}	. . .	6×10^{-6}	. . .
$PdCoO_2$	2.1×10^{-3}	. . .	2×10^{-6}	. . .
$CuCoO_2$	5×10^{7}	0.7	2×10^{5}	0.2
$CuFeO_2$	3×10^{3}	0.23	5×10^{-1}	0.05
$AgFeO_2$	2×10^{10}	0.8	3×10^{7}	0.7
$AgCoO_2$	. . .	. . .	1.5×10^{4}	0.11
$AgInO_2$	. . .	. . .	1×10^{4}	0.15
$AgGaO_2$	. . .	. . .	5×10^{7}	0.5

Standard, four-probe measurements along the c axis of the delafossite-type oxide crystals were impossible in most cases since the crystalline plates were too thin to attach voltage probes to the edges in the normal way. For these measurements a novel electrode configuration was used as illustrated in Figure 1. Such a configuration gives best results when resistivity in the plane of the plate is small relative to that perpendicular to the plane, as is the case for the delafossite oxides (see below). This condition provides little distortion of the equipotential planes that are established perpendicular to the current direction. Both current and voltage contacts consisted of gold, vacuum-deposited through appropriate masks. Lead wires to these contacts were attached with silver paste. Using this technique, measurements of resistivity as a function of temperature were made parallel to the c axis on crystal plates of $PtCoO_2$, $PdCoO_2$, $CuCoO_2$, $CuFeO_2$, and $AgFeO_2$. All measurements were reproducible on various samples of the same composition and indicated a high anisotropy in electrical conductivity for each oxide. In order to check the validity of measurements using the probe configuration of Figure 1, measurements were made both parallel and perpendicular to the c axis on a few crystals that were sufficiently thick in the c direction to permit measurements by the standard method. One of these crystals was a sample of $PtCoO_2$ that fortuitously grew as a thick plate; the other crystals were samples of $PtCo_{0.97}Mn_{0.03}O_2$ and $PtCo_{0.95}Mn_{0.05}O_2$, which grew as small rhombohedra. (As mentioned in part I of this series, small substitutions of Mn for Co in $PtCoO_2$ stabilize a rhombohedral crystal habit.) Resistivities measured by the normal method on these materials were of the same order of magnitude as those measured by the configuration of Figure 1, and the anisotropies were comparably large. In all cases, higher resistivities were observed in the c direction of the delafossite oxides. For $PdCoO_2$, $PtCoO_2$, $PtCo_{0.97}Mn_{0.03}O_2$, and $PtCo_{0.95}Mn_{0.05}O_2$, a metal-like temperature dependence was observed ($\rho(298°K)/\rho(4.2°K) > 10$); for $CuCoO_2$, $CuFeO_2$, and $AgFeO_2$, semiconductivity was found. Room-temperature resistivities for each composition and activation energies for the semiconductors parallel to c are also given in Table I.

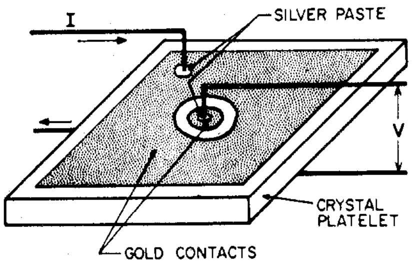

Figure 1.—Electrode configuration used in making four-probe resistivity measurements perpendicular to the plane of very thin crystal platelets. Opposite-face configuration is identical with the one shown.

Discussion

A. Crystal Chemistry of Delafossite Phases.—As pointed out in part II of this series, several structural types are found for oxides having general compositions ABO_2 in which A and B are cations of different oxidation states. For the majority of these structures, the coordination numbers of the ions A^+, B^{3+}, O^{2-} by ions of opposite charge fall into one of the classes 6:6:6, 4:4:4, or 8:4:6. For these, variations in structure can be partially rationalized by simple considerations of ionic radii and electrostatic forces. For example, the "ordered NaCl" structures (6:6:6), which are the most prevalent, achieve a reduction in electrostatic potential energy by ordering cations of different charge into separate sublattices. For most compositions of this type, the cations A and B are ordered into separate layers along the (111) direction of the cubic NaCl-type pseudocell, and a hexagonal structure is obtained, as exemplified by α-$NaFeO_2$. In a few cases, a different type of superstructure results in tetragonal symmetry, as found for the ordered form of $LiFeO_2$ (α) and for $LiInO_2$. For smaller B-site ions and particularly for those with strong preferences for tetrahedral sites such as Ga^{3+}, a fourfold coordination for the B ions becomes competitive among the ABO_2 structures. Provided that the A ion can also adopt a fourfold coordination, the most predominant structure for these compositions is orthorhombic and is related to wurtzite in much the same way as the tetragonal and hexagonal 6:6:6 compositions are related to rock salt. However, for large A-site ions, such as K, Rb, and Cs, a larger coordination number is more stable and the 8:4:6 compositions with orthorhombic symmetry are favored. For the relatively few compositions with delafossite structure, the coordination numbers are 2:6:4. In addition to the twofold coordination of the A-site ion by oxygen, this cation has six other A ion near neighbors hexagonally arranged in the basal plane, perpendicular to the O–A–O axis. Clearly, the adoption of this structure by certain compositions is not readily rationalized by simple ionic considerations such as those applied in the above examples.

The delafossite structure is most frequently found when the A-site ion is H^+ ($HCrO_2$), Cu^+ ($CuFeO_2$), or Ag^+ ($AgFeO_2$). For these ions, twofold coordination by anions is well known. However, this coordination for palladium and platinum is unusual and the occurrence of these elements in compositions with a delafossite structure was unexpected. Normally, the stereochemistry of divalent palladium and platinum is dominated by fourfold coordination with a square-planar arrangement of ligands and the ions are diamagnetic. This coordination and diamagnetism for d^8 ions are well accounted for by ligand field theory. Similarly, ligand field theory provides an explanation for the square-planar coordination frequently observed for the Jahn–Teller ion Cu^{2+} with a d^9 electronic configuration. In both cases energy is gained by stabilizing the d_{z^2} orbital at the expense of the $d_{x^2-y^2}$ orbital so that the electronic degeneracy of the e_g electrons is removed. In the case of a d^8 ion the energy must exceed the intraatomic exchange energy in order for the square-planar arrangement to be more stable than an octahedral one. Thus, the d^8 ion Ni^{2+} frequently occurs in a regularly octahedral site, as in NiO, while Pd^{2+} and Pt^{2+} commonly prefer four ligands in a planar array, as in PdO and PtS. Monovalent palladium and platinum have not previously been observed in well-characterized compounds. By analogy with Cu^{2+}, a distorted octahedral environment or a planar arrangement of four ligands might be anticipated; however, since ligand field theory only predicts that a distortion from cubic symmetry should occur for these d^9 ions without indicating the sign of the distortion, a linear coordination by two anions is also consistent with the theory. In the latter environment the order of e_g orbital splitting is simply reversed, the $d_{x^2-y^2}$ orbital becoming the more stable of the two. To our knowledge, $PdCoO_2$, $PdCrO_2$, $PdRhO_2$, and $PtCoO_2$ are the only examples of such linear coordination for ions of palladium and platinum.

Since the structures of the palladium and platinum compounds are isotypic with those in which the A-site ions are Cu^+ and Ag^+, it seems reasonable to suppose that the bonding of d^9 ions in this structure is similar to that for ions with filled d levels. Orgel[1] has suggested that linear bonding for d^{10} ions, such as Cu^+, Ag^+, and Hg^{2+}, involves hybrid wave functions derived from the s and d_{z^2} atomic orbitals. Following Jørgensen,[2] who had first noted that the occurrence of linear complexes with d^{10} ions is strongly correlated with the energies of the excited states $(n-1)d^9ns$ and $(n-1)d^9np$ above the $(n-1)d^{10}$ ground states, Orgel pointed out that, if the d_{z^2} and s orbitals are initially degenerate, or nearly so, then the stable configuration must be distorted from purely cubic symmetry. This reasoning follows from the fact that initial degeneracy requires no expenditure of energy to produce d–s mixing with the formation of the hybrid orbitals $1/\sqrt{2}(d_{z^2} + s)$ and $1/\sqrt{2}(d_{z^2} - s)$. Electronic charge placed in the $(d_{z^2} - s)$ orbital is concentrated in the xy plane, and in a linear crystalline field this results in a considerable gain of electrostatic energy. If the d_{z^2} and s orbitals are not degenerate, the expenditure of energy required to produce d–s mixing is proportional to the d–s separation. Presumably, it is this correlation that Jørgensen had observed between those d^{10} ions that form linear bonds and those that do not. Assuming that similar arguments are applicable to the formation of linear bonds in delafossite phases, a qualitative molecular orbital model can be constructed for the A sublattice of these compounds that is consistent with their crystal chemistry and observed electrical-transport properties. Such a model is illustrated schematically by the diagram shown in Figure 2 for the Ag sublattice of an $Ag^+B^{3+}O_2$ ($B^{3+} = Co^{3+}, Fe^{3+}, Rh^{3+}$, etc.) compound.

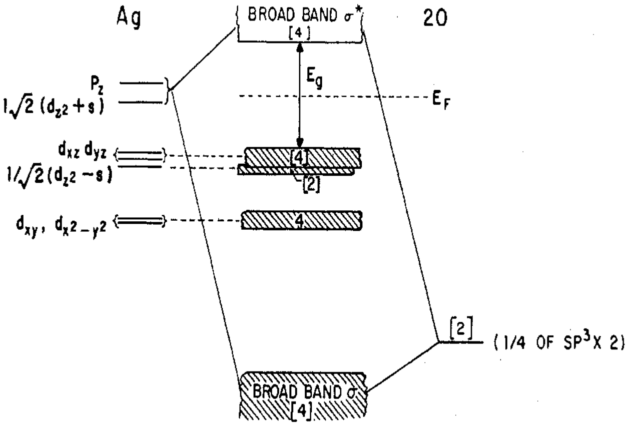

Figure 2.—Schematic, one-electron energy diagram for the Ag–O sublattice of an $Ag^+B^{3+}O_2$ ($B^{3+} = Co^{3+}, Fe^{3+}, Rh^{3+}$, etc.) compound.

In the diagram of Figure 2, the energy levels for the cation are shown in the left-hand column as perturbed by the linear crystalline field and with d–s hybridization as proposed by Orgel and described above. The orbitals of oxygen, which is tetrahedrally coordinated by three B cations and by one of silver, are assumed to be in an sp^3-hybridized state. Three of the hybrid orbitals are used in bonding with B-sublattice cations

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(1) L. E. Orgel, *J. Chem. Soc.*, 4186 (1958).

(2) C. K. Jørgenson, Thesis, Copenhagen, 1957.

and the fourth is of proper symmetry for the formation of a σ bond with the p_z and $1/\sqrt{2}(d_{z^2} + s)$ orbitals of the neighboring Ag^+. It is this fourth orbital of oxygen that is shown in the right-hand column, and it must be weighted by a factor of 2 because of the chemical formula. Since the oxides are crystalline, the interaction between the oxygen wave function and the p_z and $1/\sqrt{2}(d_{z^2} + s)$ wave functions of Ag^+ produce a bonding valence band (σ) and an antibonding conduction band (σ^*). Each of these bands has four states per formula unit, including both orbital and spin degeneracy. The four cation wave functions of purely d character and the $1/\sqrt{2}(d_{z^2} - s)$ wave functions are nonbonding with respect to the anion sublattice but are strongly oriented in the direction of near-neighbor silver ions in the basal plane of the structure. In view of the close proximity of these neighboring cations, considerable mixing of their wave functions is expected and the formation of metallic bands in the basal plane can occur as shown in the figure.

For ABO_2 compounds where A is a d^{10} ion, any metallic bands formed by direct interactions between cations are filled as shown in the figure for $A = Ag^+$. In this case the Fermi level, E_F, occurs in the energy gap between the filled metallic bands and the empty σ^* conduction band so that semiconducting or insulating electrical behavior is expected for such oxides. For A ions with less than 10 d electrons (*e.g.*, Pd^+ in $PdCoO_2$ or Pt^+ in $PtCoO_2$) the metallic bands are only partially filled and metallic conductivity is clearly possible. These metallic interactions impart an additional stabilization to the overall bonding and render any assignment of oxidation state for the A-site ion only formal. Thus, the occurrence of palladium and platinum in formally monovalent states with twofold coordination by anions seems quite plausible. In reality, of course, the first coordination sphere of the A-site ions contains not only two anions, but also six cations. On this basis, the structure can be alternatively viewed as consisting of layers of cations, one atomic dimension in thickness, that are essentially metallic in nature and that are sandwiched by and covalently bound to layers of octahedrally coordinated B ions. It is perhaps significant that the palladium and platinum analogs have been found to occur only when the companion B-site cation has empty e_g orbitals, *i.e.*, when B is Cr^{3+} or low-spin Co^{III} or Rh^{III}. For these ions covalent bonding to oxygen *via* d^2sp^3 hybrid orbitals is maximum. Curiously, the platinum phase appears to be stable only in combination with low-spin Co^{III} as the B ion.

B. Electrical Transport Properties.—The results of our determination of electrical conductivity of delafossite phases as functions of temperature and crystal orientation are consistent with the properties expected on the basis of the qualitative molecular orbital model schematically illustrated in Figure 2. $PtCoO_2$ and $PdCoO_2$ are metallic conductors, as expected, since the A-site ions in these compositions have an insufficient number of d electrons to fill the metallic bands completely. The electrical conductivity in the plane of the single-crystal platelets (*i.e.*, in a direction perpendicular to the *c* axis) is remarkably high for oxidic materials, indicating that the metal–metal interactions in the basal plane are strong and give rise to a relatively broad band. On the other hand, conductivity in the *c* direction is three orders of magnitude lower. This high anisotopy is also consistent with the model since the metallic bands are primarily confined to the A sublattice.

Semiconductivity observed for $CuFeO_2$, $CuCoO_2$, $AgFeO_2$, and $AgCoO_2$ is also explainable on the basis of the qualitative model. For these compositions with d^{10} ions on the A site, any d bands are filled and energy is required to create separated hole–electron pairs as charge carriers. The large anisotropies observed for the conductivities and for the activation energies for semiconduction in these compositions are, at first glance, somewhat surprising since the energy required for carrier activation in semiconductors is normally independent of direction. However, it is important to remember that measured activation energies, E_a, are empirical parameters and give little direct information as to the nature of the activation process. The conductivity, σ, is given by the relation $\sigma = ne\mu$, where n is the number and μ the mobility of carriers of charge e. For semiconductors, $\sigma = ne\mu \approx \sigma_0 \exp(-E_a/kT)$, where σ_0 is assumed to be a constant and where E_a is the measured activation energy. (Actually, σ_0 varies with the temperature in many materials approximately as $T^{-3/2}$ but this temperature dependence can normally be neglected relative to that of the exponential term.) For broad-band semiconductors the mobility term is relatively independent of temperature and the measured activation energy is simply the energy required to create a charge carrier. However, in many systems, particularly in those that contain localized d electrons, the mobility of charge carriers is also an activated process. Ideally in such systems, the measured activation energy is a sum of the energies required both for carrier creation and for mobility; in an extrinsic system, containing nonintegral numbers of electrons, no energy may be required for carrier creation and the measured value may simply be that for carrier mobility (or "hopping"). It seems reasonable to suppose that the observation of anisotropy in the measured activation energies of $CuFeO_2$, $CuCoO_2$, and $AgFeO_2$ means that, while the energy required for carrier creation should be independent of direction, the mobility of carriers in these systems is not. A nonactivated mobility in the basal plane and an activated mobility in the *c* direction would account for the properties observed. Such an explanation is consistent with the model proposed in this paper.

Summary

One-electron molecular orbital models of the type developed in the present paper for ABO_2 compounds with delafossite-type structures have recently been proposed by several authors in attempting to account for the physical properties of various crystalline inorganic solids.[3-6] In spite of the very qualitative nature of such models, they have been remarkably successful in providing not only a rationale for the observed properties of a given compound, but also in predicting or accounting for property trends within a series of isostructural compounds. The work described in this paper appears to provide another example in which such a model is useful. Several unusual features of ABO_2 compounds with delafossite structure have been discussed in terms of the crystal chemistry of the compositions, and a qualitative bonding scheme has been proposed that appears to rationalize their physical characteristics. In particular, measurements of electrical transport parameters for some of these oxides revealed several anomalies, each of which is explainable on the basis of the proposed bonding scheme.

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Preparative and Spectral Aspects of Hydrides Derived from Tetrakis(triphenylphosphine)platinum[1]

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New complexes of stoichiometry $(P(C_6H_5)_3)_2Pt(H)X$ (X = $SCOCH_3$, $SCOC_6H_5$, and $C_7H_5S_2N$) are described. The formation of hydrides by the oxidative addition of both weak and strong protonic acids to $(P(C_6H_5)_3)_4Pt$ is discussed, evidence being presented that stable hydrides are expected to be formed when the acid is strong or when the conjugate base is a good ligand for platinum. The high-field nmr spectra and the position of the metal hydride in the ir spectrum for the complexes *trans*-$(P(C_6H_5)_3)_2Pt(H)X$ (X = $COOCF_3$, Cl, Br, NCS, CN) are discussed in relation to the trans influence of the ligand X and used to obtain an approximate estimation of the trans influence of succinimide and thioacetate.

Results and Discussion

The oxidative addition reaction of protonic acids to low-valent transition metal complexes to form hydrides has been the subject of much recent work.[2,3] One of the most reactive compounds which undergoes the oxidative addition reaction is $(P(C_6H_5)_3)_4Pt$ which has been found to add oxidatively a large number of small molecules such as alkyl halides,[4] acyl halides,[4] carbon disulfide,[4] diketene,[5] and propargyl bromide.[6] We have found that propargyl bromide will also oxidatively add to $(P(C_6H_5)_3)_2Rh(CO)Cl$ to give the σ-allene complex $(P(C_6H_5)_3)_2Rh(CO)ClBr(CH{=}C{=}CH_2)$; with this complex however the long-range couplings (J_{H-H} = 7 Hz and J_{P-H} Hz) which are found for the complex from $(P(C_6H_5)_3)_4Pt$ cannot be readily identified because of the overlapping coupling found in this new complex from ^{103}Rh. The complex $(P(C_6H_5)_3)_2PtBr(HC{=}C{=}CH_2)$ can also be obtained from $(P(C_6H_5)_3)_2Pt$(alkyne) and propargyl bromide. With $(P(C_6H_5)_3)_4Pt$ and 1,4-dichlorobut-2-yne a similar complex is obtained with a band in the ir at 1920 cm^{-1} for the allene; the structure of this new complex is probably $(P(C_6H_5)_3)_2PtCl[C(CH_2Cl){=}C{=}CH_2]$ although this could not be confirmed by microanalysis because of its ready decomposition to *cis*-$(P(C_6H_5)_3)_2PtCl_2$ even in the solid state. Although we cannot discount the possibility of the formation of a coordinated butatriene the allenic structure is considered more likely. The addition of strong protonic acids has also been carried out, the product being the hydrides $(P(C_6H_5)_3)_2Pt(H)X$ or $[(P(C_6H_5)_3)_3PtH]^+X^-$,[7] and recently we have reported complexes of similar stoichiometry from imides.[8] Many of these oxidative addition reactions have been carried out as a means of preparing new compounds, but in this work we have considered the oxidative addition reaction of protonic acids of varying strength to $(P(C_6H_5)_3)_4Pt$ in order to try to understand some of the factors which control hydride formation, especially for the case of the addition of weak acids.

In considering the scope of the oxidative addition of protonic acids, the reaction with HCN, which is a weak acid, resembles imides (pK_a = 8–12) in oxidatively adding to $(P(C_6H_5)_3)_4Pt$ to form the hydride, but it has been found that HF[9] (pK_a = 3.5) and acetylacetone[10] (pK_a = 9.0) will not react to give hydrides. In the case of hydrogen sulfide and thiophenol[11] hydrides have been ob-

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