organic 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 de-

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scribed 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.

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

By D. M. ROUNDHILL,* P. B. TRIPATHY, AND B. W. RENOE

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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tained but in the former case there is also present some of the zerovalent complex formed by the ligand coordinating by a donor bond from the sulfur atom. We have now found that both CF_3COOH and HBr will oxidatively add to $(P(C_6H_5)_3)_4Pt$ to give the hydride but that nitromethane ($pK_a = 10.2$) and phenol ($pK_a = 9.9$) resemble acetylacetone in not undergoing reaction to form the hydride. Although the former pair are strong acids and the latter pair weak acids,[12] the acidity cannot be the sole factor responsible for hydride formation or hydrides would not be obtained with HCN or imides. Although $(P(C_6H_5)_3)_4Pt$ readily reacts with formic and acetic acids,[13] the complexes formed are very unstable and can readily be decomposed by ether to give a yellow complex which is probably $(P(C_6H_5)_3)_3Pt$. With trifluoroacetic acid, a strong acid, a stable hydride is obtained however which contains a coordinated trifluoroacetate group.[13] An interesting trend occurs with phenols; in addition to the reaction with phenol itself, we have been unable to obtain a hydride under mild conditions with p-nitrophenol ($pK_a = 9.9$) or 2,4-dinitrophenol ($pK_a = 4.0$) but with picric acid, which is a strong acid, a hydride is readily formed.[14] This trend resembles that with carboxylic acids and indicates that the strength of the acid is an important factor upon the ease of the oxidative addition reaction for hydride formation, even though it may not be solely responsible.

The failure of the correlation with acidity is shown by the reactions with formic acid ($pK_a = 3.75$) and thioacetic acid ($pK_a = 3.33$). The former gives this very unstable system, but from the reaction with thioacetic acid which has a very similar acidity, a hydride can be readily obtained which is quite stable to ether. The ir spectrum shows sharp bands at 2140 cm^{-1} (ν_{Pt-H}) and 1625 cm^{-1} ($\nu_{C=O}$), but no band in the 1050–1200-cm^{-1} region which can be assigned to the C=S stretch. The nmr spectrum in $CDCl_3$ shows two bands, one due to the phenyl protons at τ 2.70 (10) and the other due to the methyl proton at τ 8.40 (1); this methyl peak is split into a triplet (1:4:1) which must be due to a long-range coupling with the ^{195}Pt isotope ($J^{195}_{Pt-CH_3} = 6$ cps). This nmr spectrum confirms that the complex is a platinum(II) hydride formed by oxidative addition of one molecule of the acid, and the ir spectrum confirms that the structure is the one shown in Figure 1, with the
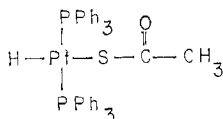

Figure 1.—Hydridothioacetatobis(triphenylphosphine)platinum-(II).

(12) Although pK_a values are measured in aqueous solution and we are working in nonaqueous solvents, we feel that discussion based on reported acid strengths is still valid since we shall be making comparisons between acids of greatly differing strength and not attempting to infer any change due to slight differences in pK_a values.

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thioacetic acid coordinated through the sulfur atom. This difference with formic and thioacetic acids cannot be due to their relative acidities, which are very slight, but is due to the different coordinating ability of the conjugate base for platinum, since sulfur is a better ligand for this metal than is oxygen. This strong coordination of platinum to sulfur ligands is further shown by the isolation of stable hydrides of thiobenzoic acid and 2-mercaptobenzothiazole (Figure 2). Although a
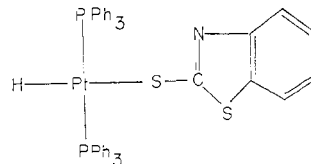

Figure 2.—Hydrido-2-mercaptobenzothiazolatobis(triphenylphosphine)platinum(II).

quantitative measure of the coordinating ability of these ligands for platinum is difficult to obtain, two criteria which have been used are the nephelauxetic series and the "hard–soft" concept developed by Pearson. A recent review[15] has considered the effect of ligand and metal hardness on the formation of hydrides by the β interaction, and it is apparent that a similar effect of ligand hardness controls the oxidative addition of protonic acids to $(P(C_6H_5)_3)_4Pt$ to form hydrides. This explains many of the results obtained from the reactions between protonic acids and $(P(C_6H_5)_3)_4Pt$. The reaction between HCN and $(P(C_6H_5)_3)_4Pt$ readily yields a hydride even though HCN is a weak acid, because cyanide is a very strong ligand with a high nephelauxetic effect[16] and, as thioacetic acid, is classed like platinum as a soft class b ligand.[17] Although HF is a considerably stronger acid than is HCN, the oxidative addition reaction gives $(P(C_6H_5)_3)_2PtF_2$[9] rather than the hydride. The nephelauxetic effect of fluoride is very low and is classed as a hard class a ligand and therefore resembles acetic and formic acids in not forming readily isolable stable hydrides; the stability of hydrides where the conjugate base is a poor ligand will probably be low because of the large trans influence of the hydride causing a weakening of the bond between the conjugate base and the metal. Hydrogen sulfide seems to represent intermediate cases where a hydride can be isolated but is a mixture with the sulfur donor–platinum(0) complex; with water and phenol, however, where the oxygen atom is a "hard" ligand, no reaction takes place. This also explains why hydrides are not obtained with nitromethane and acetylacetone since although they have comparable acidity to HCN, metal–carbon bonds are usually rather weak and hence would preclude hydride formation.

Finally we have been unable to obtain a reaction between fluoroform and $(P(C_6H_5)_3)_4Pt$; even though a transition metal–fluorocarbon bond is usually quite

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TABLE I

SPECTRAL DATA FOR THE COMPLEXES *trans*-$(P(C_6H_5)_3)_2Pt(H)X$

	X^a						
	COOCF₃	Cl	Br	$(CH_2)_2(CO)_2N$	SCOCH₃	NCS	CN
ν_{Pt-H}, cm^{-1}	2280	2220	2215[b]	2190	2140	2250	2080
τ_{Pt-H}	31.3	26.2	26.4	24.1	19.8	26.9	17.5

[a] The ligand X must be trans to the hydride since no ³¹P–H trans-coupling constant of the order of 160 Hz is observed. [b] In ref 18 this band is reported to be at 2280 cm^{-1} and a comment is made that such a value is out of order; however in our complex the band is found at 2215 cm^{-1} which is closer to the expected value.

strong,[18] the acidity of fluoroform is insufficient for the formation of a hydride by oxidative addition. From these results we believe that both the acidity of the protonic acid and the nephelauxetic effect of the conjugate base are responsible for the formation of stable hydrides. The reactions with trifluoroacetic acid and picric acid show that with very strong acids a stable hydride can be obtained even when the conjugate base is classed as a "hard" ligand, but the reactions with HCN and thioacetic acid show that a "soft" conjugate base ligand must usually be present for a stable hydride to be formed with a weak acid.

The trans influence of a series of ligands X has been compared to their effect on the ¹H chemical shift and infrared stretching frequency of the hydrides in the triethylphosphine complexes *trans*-$(P(C_6H_5)_3)_2Pt(H)X$.[19] It was found that if the ligands were arranged in order of decreasing trans influence, these complexes showed a corresponding increasing order for ν_{Pt-H} and τ_{Pt-H}. If there is a similar correlation with the triphenylphosphine hydrides, we will have a useful method of estimating the trans influence of the ligands X in the new complexes *trans*-$(P(C_6H_5)_3)_2Pt(H)X$. In order to verify this correlation we have prepared the short series of triphenylphosphineplatinum hydrides of general formula *trans*-$(P(C_6H_5)_3)_2Pt(H)X$ where X = Cl,[7] Br, CN,[7] NCS,[20] or COOCF₃, the known complexes being prepared because their nmr spectra had not been reported.[21] This series represents a useful group for correlation since the groups X cover quite a wide range in the trans-influence series.

The bromo complex *trans*-$(P(C_6H_5)_3)_2Pt(H)Br$ has been prepared by the oxidative addition reaction rather than by anion displacement as previously published.[19] This can be carried out using HBr and $(P(C_6H_5)_3)_4Pt$, but it is preferable however to use the acid and $(P(C_6H_5)_3)_2Pt(C_2H_4)$ because HBr readily reacts with the 2 mol of triphenylphosphine which dissociates from $(P(C_6H_5)_3)_4Pt$ to form a large amount of the salt $(P(C_6H_5)_3{}^+H)(Br^-)$[22] thereby making isolation of the platinum hydride rather difficult. The salt was characterized by microanalysis and by its ir spectrum which

shows strong bands at 1118, 940, and 890 cm^{-1}.[23] *Anal.* Calcd for $C_{18}H_{16}BrP$: Br, 23.00. Found: Br, 22.85.

The initial product from the oxidative addition of HBr shows two bands in the ir spectrum at 2245 and 2295 cm^{-1} (which is similar to the suggested formation of $(P(C_6H_5)_3)_2PtH_2Cl_2$ by the oxidative addition of HCl[7]), but on repeated recrystallization these bands disappear and are replaced by a single band at 2215 cm^{-1} for *trans*-$(P(C_6H_5)_3)_2Pt(H)Br$.

In Table I are shown the ir and nmr data for the complexes we have obtained for the series of ligands (X). These ligands are arranged in order of increasing trans influence across the table, and the spectral data on the hydride are shown below. Although there is a paucity of kinetic data on the trans influence of trifluoroacetate, it can be estimated from the spectrum of the triethylphosphineplatinum hydride. This complex, *trans*-$(P(C_2H_5)_3)_2Pt(H)COOCF_3$, shows a high-field resonance at τ 33.0[24] which is similar to that of *trans*-$(P(C_2H_5)_3)_2Pt(H)NO_3$, thereby placing COOCF₃ low in the trans-influence series like NO₃.

The table shows that a reasonable correlation exists between the spectral data of the hydride and the trans influence of the ligand. The isothiocyanate complex has been reported to show an anomalously high-energy band in the ir spectrum for the platinum–hydride stretch,[7,20] and this deviation is confirmed in the nmr spectrum. The nmr spectrum does show only one central peak however for the hydride and not two well-spaced resonances as was found for the triethylphosphine complex.[19] This deviation from the trans-influence series is surprising and no real explanation seems available. From the table it is possible to obtain an approximate value of the trans influence of imides from the spectral data obtained from the previously prepared triphenylphosphineplatinum hydrides.[8] From these data succinimide will have a trans influence somewhat larger than the halogens but appreciably smaller than is found for CN. The analogous phthalimide complex (τ_{Pt-H} 24.0) will be expected to have a very similar trans influence whereas saccharin[8] (τ_{Pt-H} 25.7) will have a rather lower influence, being more closely that of the halogens. Thioacetate resembles other sulfur ligands in having a high trans influence although it is somewhat less than that for cyanide.

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Experimental Section

All preparations were carried out under nitrogen, and the benzene used was dried over sodium and calcium hydride. Microanalyses were performed by Chemalytics Inc., Tempe, Ariz. Nuclear magnetic resonance spectra were obtained on Varian A-60, T-60, and modified HA-60 spectrometers as saturated solutions in $CDCl_3$. Infrared spectra were obtained as Nujol mulls on a Perkin–Elmer Model 700 or a Beckman IR 8 spectrometer. Melting points were obtained on a Fischer-Johns apparatus and are uncorrected. The complexes $(P(C_6H_5)_3)_2Pt(H)Cl$, $(P(C_6H_5)_3)_2Pt(H)CN$, and $(P(C_6H_5)_3)_2Pt(H)NCS$ (ν_{CN} 2100, ν_{CS} 872 cm^{-1}) were prepared as described in the literature. The protonic acids used were commercial samples and used without purification except for HCN which was prepared from KCN and H_2SO_4. $(P(C_6H_5)_3)_4Pt^{25}$ was prepared by the hydrazine reduction method, and $(P(C_6H_5)_3)_2Pt(C_2H_4)^{26}$ was prepared by the reduction of the oxygen compound with $NaBH_4$. Potassium tetrachloroplatinite was obtained from Engelhard Industries, Inc. The yields of the complexes were essentially quantitative.

Hydridothioacetatobis(triphenylphosphine)platinum(II).—To a filtered solution of $(P(C_6H_5)_3)_4Pt$ in benzene was added thioacetic acid when immediate decolorization of the yellow solution occurred. The solvent was removed at room temperature and ether was added to give a colorless precipitate which was recrystallized from a benzene–hexane mixture to give the pure *complex* which was dried *in vacuo;* mp 122° dec. *Anal.* Calcd for $C_{38}H_{34}OP_2PtS$: C, 57.4; H, 4.31; S, 4.03. Found: C, 57.1; H, 4.04; S, 4.25. $\nu_{C=O}$ 1625 cm^{-1}, ν_{Pt-H} 2140 cm^{-1}, τ_{CH_3} 8.40, J_{Pt-CH_3} = 6 Hz, τ_{Pt-H} 19.8, J_{Pt-H} = 998 Hz.

Hydridothiobenzoatobis(triphenylphosphine)platinum(II).—To a filtered solution of $(P(C_6H_5)_3)_4Pt$ in benzene was added thiobenzoic acid dropwise until the yellow color of the solution disappeared. The solvent was removed and C_2H_5OH added to give the pure *complex* which was dried *in vacuo;* mp 160° dec. *Anal.* Calcd for $C_{43}H_{36}OP_2PtS$: C, 60.2; H, 4.23. Found: C, 60.0; H, 4.09. $\nu_{C=O}$ 1595 cm^{-1}, ν_{Pt-H} 2125 cm^{-1}. This complex is too insoluble to obtain a high-field nmr spectrum.

Hydridobromobis(triphenylphosphine)platinum(II).—Through a solution of $(P(C_6H_5)_3)_2Pt(C_2H_4)$ in benzene was bubbled HBr.

The solvent was removed and ether was added to obtain the crude product. Recrystallization from a benzene–ether mixture gave the pure complex which was dried *in vacuo. Anal.* Calcd for $C_{36}H_{31}BrP_2Pt$: C, 54.0; H, 3.88; Br, 10.0. Found: C, 53.9; H, 3.71; Br, 10.2. ν_{Pt-H} 2215 cm^{-1}, τ_{Pt-H} 26.4.

Bis(thioacetato)bis(triphenylphosphine)platinum(II).—To a solution of $(P(C_6H_5)_3)_2Pt(butyne-2)$ or $(P(C_6H_5)_3)_2Pt(C_6H_5C\equiv CC_6H_5)$ in benzene was added thioacetic acid and the mixture was stirred. After 1 hr the colorless precipitate was filtered, washed well with solvent, and dried *in vacuo. Anal.* Calcd for $C_{40}H_{36}O_2P_2PtS_2$: C, 55.2; H, 4.17; S, 7.37. Found: C, 55.3; H, 4.12; S, 8.29. $\nu_{C=O}$ 1630 cm^{-1}. The ^1H nmr spectrum in CF_3COOH shows a phenyl resonance at τ 2.92 (5) and a methyl resonance at τ 8.92 (1), the area ratio confirming the stoichiometry.

Bromochloroallenylcarbonylbis(triphenylphosphine)rhodium(III).—To a solution of $(P(C_6H_5)_3)_2Rh(CO)Cl$ in CH_2Cl_2 was added excess propargyl bromide, and the solution was allowed to stand for several hours. The solvent was removed and C_2H_5OH was added to give a dark yellow precipitate. The product was recrystallized from CH_2Cl_2–C_2H_5OH to give mustard yellow crystals of the *complex* which were dried *in vacuo;* mp 180°. *Anal.* Calcd for $C_{40}H_{33}BrClO_2P_2Rh$: C, 59.3; H, 4.1; halogen, 14.25. Found: C, 58.0; H, 3.8; halogen, 14.67. $\nu_{C=C=C}$ 1920 cm^{-1}, $\nu_{C=O}$ 2080 cm^{-1}, $\tau_{=CH_2}$ 6.1, $\tau_{=CH}$ 8.2.

Hydrido-2-mercaptobenzothiazolatobis(triphenylphosphine)-platinum(II).—To a filtered solution of $(P(C_6H_5)_3)_4Pt$ in benzene was added 2-mercaptobenzothiazole. The solution became pale yellow and the solvent was reduced to low volume on a rotary evaporator. Addition of C_2H_5OH gave a yellow crystalline *complex* which was dried *in vacuo;* mp 147° dec. *Anal.* Calcd for $C_{43}H_{36}NP_2PtS_2$: C, 58.2; H, 4.09. Found: C, 58.2; H, 3.80. ν_{Pt-H} 2170 cm^{-1}. This complex is rather unstable, decomposing slowly in solution in the absence of excess ligand.

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Reactions of Gaseous Inorganic Negative Ions. II. SF6- and Nonmetal Fluorides[1,2]

BY THOMAS C. RHYNE AND JOHN G. DILLARD*

The reactions of negative ions produced *via* electron capture in SF_6 at low electron energies with nonmetal fluorides have been studied. It is observed that the radical ion SF_6^- reacts with nonmetal fluorides AF_n ($AF_n = BF_3$, SiF_4, PF_5, PF_3) *via* fluoride ion transfer. Rate constants and reaction cross sections are presented and discussed.

Introduction

Gas-phase ion–molecule reactions have been known since the beginning of mass spectrometry[3] but only in the past decade have these processes been the subject of

intensive study. Investigations of ion–molecule reactions have in general been directed toward positive ion systems, and outside the area of atmospheric studies little emphasis has been placed on studies of the reactions of gaseous negative ions in simple inorganic systems. Since it is likely that negative ions may be important constituents in gaseous discharges,[4] in flames,[5]

(1) Presented in part at the 21st Southeastern Regional Meeting, American Chemical Society, Richmond, Va., Nov 1969.

(2) This study is a portion of a dissertation to be presented by T. C. Rhyne to the Graduate School of Virginia Polytechnic Institute in partial fulfillment of the requirements for the degree Doctor of Philosophy.

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