several points can be made here. First the results of 1.02+ charge on the metal and 0.50− on the hydrogens are more in accord with the qualitative notion of the molecule as an oxidized metal atom with hydride ligands. Obviously one would not expect to see quite the demarcation of charge given by the formal description of +2 metal ion and 1− ligands. However, when compared with the description as virtually neutral hydrogens and a negatively charged metal in the standard analysis, the above picture appears more consistent with the chemical properties of the complex.

As a further check of the preceding analysis, a three-dimensional quadrature of the charge was performed within the sphere defining the metal region.[15] For *trans*-$Pt(PH_3)_2H_2$ the value is obtained as 8.96 e compared with the 8.98 e given by the modified population analysis and 10.46 e by the Mulliken analysis. (The excellent quantitative agreement we have is partly fortuitous since in the population analysis we are also appropriating density to the metal that is outside its sphere but not within one of the ligand cones.) This additional evidence still provides a clear indication that the modified analysis is giving a more faithful representation of the wave function than a standard analysis.

IV. Conclusions

The proposed modifications to a Mulliken analysis were found to resolve satisfactorily the interpretative difficulties resultant from the use of diffuse valence s and p basis functions, which are required to give reasonable theoretical descriptions of transition-metal systems. The method has two parameters that must be defined externally, the covalent radius of the metal atom and the solid angles defining the ligand space, and is currently limited to complexes having a single metal center. It requires very little additional computational effort to carry out such an analysis compared with that of traditional Mulliken population analysis. The results obtained thus far indicate the method yields an improved description of molecular charge densities, which should prove useful both in analyzing the results of theoretical calculations and in correlating with experimental probes of electron density in molecules.

Acknowledgment. The aid of S. Woodruff in implementing the three-dimensional quadrature is thankfully acknowledged. Thanks are also due to J. Hay for many helpful comments as well as a critical reading of the manuscript. This work was performed under the auspices of the U.S. Department of Energy.

Registry No. *trans*-$Pt(PH_3)_2H_2$, 76830-84-7.

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[15] The integration scheme is outlined in: S. B. Woodruff and M. Wolfsberg, *J. Chem. Phys.*, **65**, 3687 (1976); *Chem. Phys. Lett.*, **56**, 125 (1978); H. Conroy, *J. Chem. Phys.*, **47**, 5307 (1967).

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Ab Initio Treatment of the Structures of Square-Planar $Pt(PH_3)_2XY$ Species (X, Y = H, Cl) Using Relativistic Effective Core Potentials

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The structures and relative energies of $Pt(PH_3)XY$ isomers are investigated with use of ab initio molecular orbital theory and effective potentials. In particular, the cis and trans isomers of the dihydride, dichloride, and hydrochloride are studied. In all cases, the trans isomer is the more stable. Available experimental information is in good agreement with calculated bond lengths, bond angles, and vibrational frequencies.

I. Introduction

The intent of this work is to demonstrate that ab initio molecular orbital theory can provide useful geometric and energetic information for complexes involving third-row transition metals. The systems considered are the Pt(II) square-planar adducts $Pt(PH_3)_2XY$ (where X, Y = H, Cl) and the product of their reductive elimination $Pt(PH_3)_2$. Since a subset of these have been well characterized both structurally and spectroscopically, these data may be used to evaluate the success of the technique (if we assume that we are afforded the liberty of replacing the substituted phosphine PR_3 by its parent hydride).

The question of the structures of platinum–hydride complexes deserves special consideration. The hydrogen is often not easily located through X-ray diffractometry, and as a result there is comparatively less data on platinum–hydrogen bond lengths. In addition, since very few *cis*-dihydride complexes of any kind have been observed experimentally, any suggestions calculations can offer regarding their structure and bonding should aid in their experimental characterization.

Finally these studies are to lay the ground work for an investigation of a prototype oxidative addition. Indeed the results of the present paper suggested the possibility of examining the $H_2 + Pt(PH_3)_2 \rightarrow cis\text{-}Pt(PH_3)_2H_2$ reaction. It is in the arena of potential surfaces that ab initio calculations should have their greatest impact. This topic will be addressed in a later paper.[1]

II. Method of Calculation

The calculations reported here were of the ab initio restricted Hartree–Fock (RHF) form. The $[Xe]4f^{14}$ core of the platinum atom was, in all cases, replaced by a relativistic potential[2] derived according to the scheme of Kahn, Hay, and Cowan.[3] The mass velocity and Darwin relativistic effects are included implicitly with the potential. As has been documented previously, these are critical in order to obtain the proper size and energy of the valence orbitals for metal atoms of the third transition series.[4] The [Ne] cores of the phosphorus and

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(3) L. R. Kahn, P. Jeffrey Hay, and R. D. Cowan, *J. Chem. Phys.*, **68**, 2386 (1978).
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0020-1669/82/1321-0014$01.25/0

Table I. Effective Core Potentials for P, Cl, and Pt Atoms[a]

n_k	α_k	d_k	n_k	α_k	d_k
Phosphorus Atom					
d Potential					
1	82.756 16	−10.000 000 0	2	8.497 23	−13.187 596 1
2	145.365 52	60.705 362 0	2	2.765 14	−2.329 759 9
2	26.501 98	−27.967 510 4			
s-d Potential					
0	24.392 35	3.000 000 0	2	8.886 48	70.447 681 0
1	8.746 18	−14.639 473 0	2	3.140 93	13.902 840 0
2	19.119 35	80.930 335 0	2	1.093 08	2.171 923 4
p-d Potential					
0	48.588 17	5.000 000 0	2	13.870 53	57.006 624 0
1	27.955 11	−7.499 233 2	2	4.377 41	16.056 945 0
2	35.773 54	150.086 110 0	2	1.305 61	2.921 705 1
Chlorine Atom					
d Potential					
2	3.530 77	−2.078 360 0	2	131.588 00	62.711 660 0
2	11.007 80	−14.516 710 0	1	80.236 70	−10.000 000 0
2	30.330 20	−24.588 400 0			
s-d Potential					
2	2.366 86	10.430 870 0	2	78.330 70	201.125 620 0
2	8.833 44	56.127 780 0	1	20.944 10	−16.463 020 0
2	27.400 70	188.362 240 0	0	112.359 00	3.000 000 0
p-d Potential					
2	2.951 16	11.938 900 0	2	133.161 00	568.743 870 0
2	13.157 10	65.060 380 0	1	41.035 30	−8.584 260 0
2	47.839 00	292.651 070 0	0	194.043 00	5.000 000 0
Platinum Atom					
g Potential					
2	1.315 47	−3.072 277 5	2	45.435 55	−249.960 990 0
2	3.744 84	−21.267 164 0	1	146.266 96	−46.122 446 0
2	12.328 35	−101.386 590 0	0	0.461 04	−0.161 926 8
s-g Potential					
2	0.584 21	3.053 200 0	2	25.744 04	207.675 910 0
2	1.898 02	23.711 864 0	1	77.540 53	54.937 659 0
2	5.884 87	76.291 136 0	0	266.376 37	0.911 140 6
p-g Potential					
2	0.500 03	2.870 493 0	2	11.222 72	90.298 018 0
2	1.663 67	21.158 990 0	1	43.334 58	61.974 311 0
2	4.714 71	68.957 532 0	0	174.635 18	1.887 856 8
d-g Potential					
2	0.529 65	−0.906 188 7	2	19.283 86	237.525 490 0
2	1.572 51	4.631 627 6	1	55.506 49	90.568 974 0
2	5.665 09	56.842 339 0	0	24.402 37	2.934 367 8
f-g Potential					
2	3.800 95	21.171 795 0	2	272.438 56	987.781 740 0
2	12.567 80	82.520 968 0	1	85.064 50	81.054 809 0
2	37.271 60	265.306 350 0	0	477.523 82	3.953 425 3

[a] See text for definitions of the symbols.

chlorine atoms were similarly replaced by nonrelativistic potentials.[5] The analytic forms for these potentials are given in Table I. The total potential is given in terms of its angular components:

$$V(r) = V_L(r) + \sum_{l=0}^{L-1}(V_l(r) - V_L(r))|l\rangle\langle l|$$

and each component is expressed as a linear combination of Gaussian terms $d_k r^{n_k} e^{-\alpha_k r^2}$.

All atomic bases were of at least double-ζ quality (i.e., two contracted Gaussian orbitals to represent each atomic orbital) for the valence electrons. The platinum (4s4p5d)→[3s3p2d] basis and the chlorine and phosphorus (3s4p)→[2s2p] bases were all optimized for neutral atomic states and are listed in Table II. Two separate sets[6] were deployed for hydrogen atoms. As a hydride ligand a triple-ζ (5s)→[3s] expansion was used in anticipation of the considerable negative charge expected on the ligand. The hydrogens of the phosphine ligands were represented by a double-ζ (4s)→[2s] contraction. The most notable aspect of the basis is the use of diffuse functions used to describe the valence 4s and 4p orbitals of the platinum atom (see also Figure 1 of the previous paper[7]). Although using such diffuse functions leads to wave functions that are more difficult to interpret, omitting them was found

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(7) J. O. Noell, *Inorg. Chem.*, preceding paper in this issue.

Table II. Gaussian Exponents and Contraction Coefficients for the s, p, and d Valence Orbitals of Pt, Cl, P, and H

α_s	C_s	α_p	C_p	α_d	C_d
			Pt		
0.9521	−0.40432	1.274	−0.06034	18.10	−0.01050
0.1339	1.15527	0.1854	0.20350	2.943	0.10152
0.08208	1.0	0.1006	0.82671	1.636	0.36945
0.04247	1.0	0.03765	1.0	0.6596	0.63704
				0.2103	1.0
			Cl		
3.465	−0.28384	11.38	−0.01926		
0.4479	1.11388	0.8660	0.43690		
0.1656	1.0	0.3206	0.63382		
		0.1145	1.0		
			P		
2.401	−0.27712	7.272	−0.01887		
0.2936	1.10678	0.5913	0.35206		
0.1085	1.0	0.2316	0.70624		
		0.08474	1.0		

H (PH_3)		H (H_2)	
α_s	C_s	α_s	C_s
19.2384	0.03283	33.6444	0.02537
2.89872	0.23120	5.05796	0.18968
0.653472	0.81723	1.14680	0.85293
0.177552	1.0	0.321144	1.0
		0.101309	1.0

to require an unacceptably large sacrifice in the energy. The charge analysis outlined in the preceding paper[7] was developed to circumvent difficulties in interpretation with these bases.

The geometries of these systems were optimized subject to the following constraints. In all calculations reported here, the ligand framework was kept planar. Reported X-ray structures show very little deviation from planarity, and cursory calculations for *trans*-$Pt(PH_3)_2HCl$ also indicated a clear preference for a planar configuration. The phosphine ligand was always assumed to have P–H bond lengths of 1.0124 Å[8] (the equilibrium separation in the gas-phase molecule) with tetrahedral angles between the bonds. The phosphines were oriented in each molecule such that the maximum possible symmetry was attained (C_{2v} for all species except *cis*-$Pt(PH_3)_2HCl$, which has C_s symmetry). The closest interligand approach of two phosphine hydrogens in any of the complexes is about 2.9 Å, and hence the orientation of the phosphines would not be expected to play a significant role. Typically the metal–hydrogen and metal–chlorine bond lengths were optimized with 90° bond angles. Bond angles were subsequently optimized with use of these bond lengths. The slight distortions (10° or less) obsered from idealized bond angles suggest little change would be evident in the bond lengths at the optimum bond angles.

III. Structural Characteristics

The calculated structure for the platinum diphosphine dihydride, dichloride, and hydrochloride complexes are summarized in Figure 1. Detailed discussion and comparison with experiment are given below.

A. $Pt(PH_3)_2$. Before examining complexes that may be regarded as the result of oxidative addition of H_2, HCl, and Cl_2 to $Pt(PH_3)_2$, we first considered the bis(phosphine)platinum(0) complex itself. Of necessity throughout the paper we will be comparing our results for the model compound with PH_3 ligands with experimental measurements on triply substituted phosphines. Phosphines coordinated to platinum have been found to have very similar M–P separations regardless of the oxidation state of the metal. For example, Otsuka et al. found a separation of 2.252 Å with the Pt(0) complex $Pt[PPh(t\text{-}Bu)_2]_2$.[9] This is little different from observed values in four-coordinate Pt(II) complexes. Typical values for phosphine complexes of interest here include 2.268 Å in *trans*-$PtHCl[PPh_2Et]_2$,[10] 2.300 Å in *trans*-$PtCl_2[PEt_3]_2$,[11] and 2.239 and 2.256 Å in *cis*-$PtCl_2[PMe_3]_2$[12] with standard deviations of ~0.02 Å or less. For $Pt(PH_3)_2$ at the RHF level, our calculated value is 2.36 Å, approximately 0.1 Å too long. This trend toward longer theoretical bond lengths is also observed, though to a lesser extent, for the platinum–chloride linkages. Unsubstituted phosphine, a poorer π acceptor, would be expected to have a somewhat longer bond, however, than trialkylphosphines. Still we consider the agreement between our calculated value and the experimental estimates to be adequate, especially since these linkages are not those of primary interest in the remaining molecules that we studied. In fact, in the remaining computations we considered this parameter not to be significant and rather than optimize it independently for each molecule, a constant value of 2.268 Å

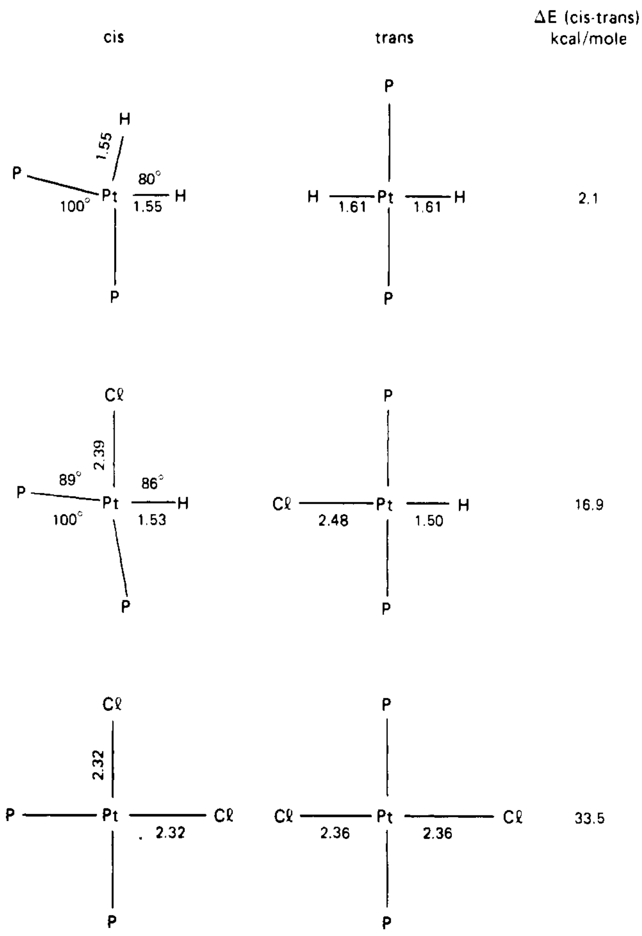

Figure 1. Calculated structures and relative energies for $(PH_3)_2PtXY$ isomers.

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(12) G. G. Messmer and E. L. Amma, *Inorg. Chem.*, **6**, 1725 (1967).

(13) Though a significant number of metal–hydrogen bond lengths have been determined more recently, they fall within the 1.5–1.7 Å range defined in B. A. Frenz and J. A. Ibers, "Transition Metal Hydrides", E. L. Muetterties, Ed., Marcel Dekker, New York, 1971.

Table III. Structural Parameters For *trans*-$PtHCl(phosphine)_2$

	calcd[a]	exptl
R_{Pt-Cl}, Å	2.48	2.422[b]
ω_e(Pt–Cl), cm^{-1}	268	270[c]
R_{Pt-H}, Å	1.50	1.50–1.70[d]
ω_e(Pt–H), cm^{-1}	2159	2201,[c] 2235,[e] 2183,[f] 21830,[g] 2199,[h] 2210,[i] 2248[j]

[a] phosphine = PH_3. [b] phosphine = $[P(C_6H_5)_2(C_2H_5)]$.[13] [c] phosphine = $[P(C_2H_5)_3]$.[17] [d] This represents the range of well-characterized metal–hydrogen bond lengths;[18] some shorter linkages have been found recently for Rh(III) compounds.[17] [e] phosphine = $[P(C_2H_5)_3]$.[18] [f] phosphine = $[P(C_2H_5)_3]$.[19] [g] phosphine = $[P(i\text{-}C_3H_7)_3]$.[19] [h] phosphine = $[P(C_6H_5)(C_2H_5)_2]$.[19] [i] phosphine = $[P(C_6H_5)_2(C_2H_5)]$.[19] [j] phosphine = $[P(C_6H_5)_3]$.[19]

(that found in *trans*-$PtHCl[P(C_6H_5)_2C_2H_5)_2]$[10] was assumed.

B. *trans*-$PtHCl(PH_3)_2$. The X-ray characterization of *trans*-$PtHCl[P(C_6H_5)_2(C_2H_5)]$, the analogue of our model compound, was performed by Eisenberg and Ibers.[10] Though the hydride ligand could not be located, it was nonetheless evident that the molecule was square planar, since the P–Pt–Cl angles were within 5° of the 90° expected of an idealized square-planar compound. In Table III the calculated values for the Pt–H and Pt–Cl bond distances as well as for the vibrational stretching frequencies (the Pt–H and Pt–Cl were assumed to stretch independently in the calculations) are compared with the experimental determinations. Though the metal–hydrogen separation was not determined in the X-ray analysis, the calculated value of 1.50 Å is within the range (1.5–1.7 Å) one would expect for a hydride of the third transition series upon the basis of those metal–hydrogen bonds that have been well characterized. In addition, excellent agreement is obtained between the calculated ω for the metal–hydrogen linkage and the observed values for a variety of phosphine complexes.[14-16] While the close agreement must be partly fortuitous, it serves as another indication that a reasonable description of the metal–hydrogen bond has been achieved.

The anomalously long metal–chloride linkage—generally ascribed as a result of the trans-labilizing influence of the hydride ligand—is also well modeled by the calculations, although the bond length is overestimated slightly, in this case by about 0.06 Å. Again, the calculated vibrational frequency is in good agreement with the experimentally determined value.[14] This frequency is approximately 50–80 cm^{-1} less than that found for most Pt–Cl linkages not having a labilizing ligand trans to the Cl.[17] It is encouraging that the hydrogen influence on both the metal–chlorine bond length and stretching frequency is well treated here. When the two P–M–H angles were compressed from 90 to 85°, the energy of this configuration was 1.4 kcal/mol higher, confirming that the assumed 90° bond angles are nearly optimum. As will be discussed shortly, deviations from the ideal square plane were calculated for some of the other systems studied.

C. *cis*-$PtHCl(PH_3)_2$. Though a direct analogue of the cis HCl adduct is not known experimentally, its theoretical consideration is germane to the question of the trans-labilizing influence of the hydride ligand. The calculated structural parameters are as follws: $R_{Pt-H} = 1.53$ Å, $\omega_e(\text{Pt-H}) = 2076$ cm^{-1}, $R_{Pt-Cl} = 2.39$ Å, $\omega(\text{Pt-Cl}) = 299$ cm^{-1}, $\angle\text{P-Pt-P} = \angle\text{P-Pt-H} - 85°$, and $\angle\text{H-Pt-Cl} = 86°$. The key point is that we do attain the anticipated changes in the Pt–Cl bond. We calculate it to be 0.09 Å shorter with a vibrational frequency 31 cm^{-1} higher than the Pt–Cl bond in the trans isomer. It is difficult to assess the accuracy of these predictions quantitatively, but the Pt–Cl distance in $PtCl_4^{-2}$ is 2.33 Å, or 0.092 Å shorter than the 2.422 Å noted earlier for the Cl trans to a hydride ligand. The Pt–Cl bond lengths in the dichloro complexes (see below) are also comparable to the Pt–Cl value in the cis HCl adduct. On this basis of this, it appears that a reasonable description of the trans-labilizing influence of the hydride ligand has been obtained. The metal–hydrogen bond is found to be slightly longer (0.03 Å) than is the bond in the trans compound. We do not assign significance to this rather minor change since the difference between a substituted phosphine and phosphine itself could be of importance. There is nothing of special import in thecalculated angles save that the hydride ligand expectably requires only a little less room than the other ligands.

Table IV. Structural Parameters for *cis*- and *trans*-$PtCl_2(phosphine)_2$

	trans		cis	
	calcd[a]	exptl	calcd[a]	exptl
R_{Pt-Cl}, Å	2.36	2.294 (90)[b]	2.32	2.364 (6), 2.388 (8)[e]
ω(Pt–Cl), cm^{-1}	306	326[c] 329[c] 343[d]	345	

[a] phosphine = PH_3. [b] phosphine = $P(C_2H_5)_3$.[11] [c] phosphine = $P(C_2H_5)_3$. This is the asymmetric, IR-active stretch. The symmetric stretch would be expected to be at a somewhat lower frequency.[20,21] [d] Average for three trialkylphosphines.[21] [e] phosphine = $P(CH_3)_3$.[12]

D. *cis*- and *trans*-$PtCl_2(PH_3)_2$. Analogues of both of these molecules have been structurally characterized, allowing direct comparisons with which to test our results. Both *trans*-$PtCl_2[P(C_2H_5)_3]_2$[11] and *cis*-$PtCl_2[P(CH_3)_3]$[12] exhibit structures with bond angles deviating only slightly from a square plane. In view of this, we examined only the Pt–Cl bond lengths in our studies. The optimal values along with symmetric stretch vibrational frequencies are collected in Table IV. Though the general description is again very reasonable some difficulties arise in comparing the cis and trans isomers. While we calculate the Pt–Cl bond to be very slightly longer in the trans isomer, the experimental values exhibit an opposite trend. Unfortunately, the trans crystal had considerable disorder, resulting in an unusually large error in the Pt–Cl distance, thus clouding the experimental situation. Still, the discrepancy is probably real and the most reasonable rationale for it is that a naked phosphine is not an adequate model for the trialkylphosphines deployed in the experimental studies. Most critically it would not possess as strong a trans-labilizing effect as the molecules we are hoping it will model.[19] This would result in calculated metal–chloride distances in the cis isomer that were too short.

Consistent with having a shorter bond length, the calculations predict a higher vibrational frequency for the cis isomer compared with the *trans* isomers. Experimentally, the asymmetric stretch for a trans adduct is ~330 cm^{-1}[20,21] in reasonable accord with the calculated value.

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(19) Though most trans effects are kinetic in origin, the large effect of a trialkylphosphine (F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, 1972, p 608) should also be evident as a geometrical effect. As evidence for this suggestion, replacement of the phosphine ligands with the weakly directing ligand NH_3 results in complexes in which the cis and trans isomers have nearly identical bond lengths (G. H. W. Milburn and M. R. Truter, *J. Chem. Soc. A*, 1609 (1966).

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Table V. Structural Parameters for *cis*- and *trans*-Dihydrides

	calcd[a]	exptl
	trans	
RPt-H, Å	1.61	
ω_e(Pt-H)$_{sym}$, cm^{-1}	2015	
ω(Pt-H)$_{asym}$, cm^{-1}	2088	1736[b]
	cis	
R_{Pt-H}, Å	1.55	
ω_e(Pt-H), cm^{-1}	2037	1984[c]
∠HPtH, deg	80	[81.2][d]
∠PPtP, deg	100	103[e]

[a] Calculations were for *cis*- and *trans*-$PtH_2(PH_3)_2$. [b] Average of three separate *trans*-$PtH_2(PR_2)_2$ compounds.[24] [c] Average of eight molecules of the form *cis*-PtH_2(diphos).[27] [d] ∠HRhH in the distorted octahedral compound $RhH_2(P(i\text{-}Pr)_3)_2O_2COH$.[32] [e] PPtP angle in [Pt^{II}(diphos)]$_2$.[27]

E. *cis*- and *trans*-$PtH_2(PH_3)_2$. While no alkylphosphines analogous of these species have been structurally characterized, they nonetheless have attracted great interest. Their synthesis in itself presented quite a challenge, and hence considerable spectroscopic data is available, particularly for the more easily isolated trans adducts.[22-26] While four-coordinate *cis*-dihydrides proved more obdurate, several examples have now been prepared and characterized spectroscopically.[27,28] In addition, numerous five- and six-coordinate rhodium and iridium dihydrides have been examined.[26-29]

As these molecules were our primary candidates for treating a model oxidative-addition reaction, it was especially critical that they be well characterized theoretically. The optimum bond lengths and bond angles are shown in Table V. Direct comparison with experiment is ruled out since analogues to the calculated species have not been structurally characterized. Still what evidence there is does seem to imply that the Hartree–Fock level offers a credible treatment of the dihydrides. The calculated bond lengths—1.55 (cis) and 1.61 Å (trans)—lie within the range (1.5–1.7 Å) commonly observed for metal hydrides.[13] As expected, the *trans*-dihydride has an 0.06 Å longer bond length than the cis isomer. Though this differential might be expected to be partially reduced had we used an alkylphosphine rather than phosphine itself, one would still expect a longer bond length in the trans isomer since the hydride ligand should be a stronger trans labilizer than even a trialkylphosphine.[30] Perhaps a better measure of the description of the platinum–hydrogen linkage is the excellent agreement between the calculated vibrational frequencies and the observed IR frequencies.

An appreciable narrowing of the H–Pt–H angle from an ideal square-planar value of 90° to around 80° is observed.[31] The only *cis*-dihydride of which we are aware in which the hydrogens have been crystallographically located had a H–M–H angle of 81.2°.[32] The comparison, however, is not altogether fair since the experimentally characterized molecule ($RhH_2[P(i\text{-}Pr)_3]_2O_2COH$) was a d^6 Rh(III) octahedral complex with very short (1.41 Å) M–H bonds. It is also interesting to note the similarity between the bite size of ~102° for bidentate phoshpine ($PCH_2C_6H_4CH_2P$) capable of stabilizing a Pt(II) *cis*-dihydride[27] and the calculated value of 100° for the P–M–P angle.

Table VI. Energetics of the Platinum–Phosphine Bond

process	energy, kcal/mol
Pt(^{3}D) → Pt(^{1}S)	31.2 (16.4 exptl)[a]
Pt(^{3}D) + PH_3 → Pt(PH_3)	9.2
Pt(^{1}S) + PH_3 → Pt(PH_3)	−22.0
Pt(^{3}D) + 2PH_3 → Pt$(PH_3)_2$	−14.6
Pt(^{1}S) + 2PH_3 → Pt$(PH_3)_2$	−45.9
Pt(PH_3) + PH_3 → Pt$(PH_3)_2$	−23.9

[a] C. E. Moore, *Natl. Buk. Stand.* (*U.S.*), *Circ.*, 3, No. 467 (1949). ^{3}D energy averaged over J states.

Table VII. Energetics of Model Oxidative Additions[a]

reactants X	reactants Y	product $Pt(PH_3)_2XY$	calcd energy, kcal/mol
X	H	*cis*-PtH_2	−8.2
H	H	*trans*-PtH_2	−10.3
Cl	H	*cis*-PtHCl	−21.3
Cl	H	*trans*-PtHCl	−38.2
Cl	Cl	*cis*-$PtCl_2$	−99.0
Cl	Cl	*trans*-$PtCl_2$	−132.5

[a] Results are given with the basis used throughout the paper.

We have most recently become aware that these dihydrides have been investigated with use of a gradient technique, which allowed for more complete optimization of the structures.[33] The basis sets and effective core potentials differed somewhat from ours. Still, the results are similar though they uniformly find bond lengths somewhat shorter than those reported here.

III. Energetics

A. Metal–Ligand Bond Energies. Even though we were primarily interested in examining processes of the form

$$Pt(PH_3)_2 + XY \rightarrow PtXY(PH_3)_2$$

the nature of the platinum–phosphine bonds was also examined. The bond energies for the mono- and bis(phosphine)platinum(0) adducts are outlined in Table VI. If the ground state of Pt (^{3}D) is chosen as the asymptotic reference, the calculated energetics appear unreasonable, since the monophosphine is not bound with respect to these ground-state asymptotes. The more appropriate reference, however, is the d^{10} (^{1}S) state of the platinum, as this is the atomic configuration expected to be dominant in the Pt(0) molecular environment. If this is used as a reference, a very consistent picture emerges, the average Pt–PH_3 bond being approximately 23 kcal/mol. We make this diversion primarily to show that despite our use of PH_3 as a ligand—which one would expect to be a poorer π acceptor than its trialkyl derivative—the complexes are nonetheless stable with respect to ligand dissociation.

In Table VII, the energetics for the reactions

$$Pt(PH_3)_2 + XY \rightarrow Pt(PH_3)_2XY$$

are presented. The calculations were done at the SCF level and hence are expected to have only qualitative significance. The stabilities of the Cl_2 adducts in Table VII are expected

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Table VIII. Population Analyses for $Pt(PH_3)_2XY$ Systems

	net charge on each ligand[a]			
syst	Pt	PH_3	X	Y
$Pt(PH_3)_2$	0.38+ (0.23−)	0.19− (0.12+)		
cis-$Pt(PH_3)_2H_2$	1.23+ (0.33−)	0.33− (0.18+)	0.29− (0.01−)	0.29− (0.01−)
trans-$Pt(PH_3)_2H_2$	1.01+ (0.46−)	0.01− (0.31+)	0.50− (0.08−)	0.50− (0.08−)
cis-$Pt(PH_3)_2HCl$	1.20+ (0.22−)	0.10− (0.35+)	0.23− (0.07+)	0.74− (0.49−)
trans-$Pt(PH_3)_2HCl$	1.09+ (0.21−)	0.06+ (0.37+)	0.28− (0.05+)	0.89− (0.58−)
cis-$Pt(PH_3)_2Cl_2$	1.28+ (0.18−)	0.06+ (0.42+)	0.69− (0.33−)	0.69− (0.33−)
trans-$Pt(PH_3)_2Cl_2$	1.18+ (0.05−)	0.17+ (0.47+)	0.76− (0.53−)	0.76− (0.45−)

[a] Mulliken assignments are in parentheses.

to be overestimated since a poorer description of the diatomic bond strengths is obtained at the SCF level. Even at a more sophisticated level the addition of polarization functions (2p on H and 3d on Cl) and the use of two-configuration GVB-1 wave functions properly treating the XY → X + Y dissociation process yields bond energies of 93, 88, and 25 kcal/mol for H_2, HCl, and Cl_2, respectively. When these are compared to the experimental values of 104, 106, and 58 kcal/mol, this leads to respective errors of 11, 16, and 33 kcal/mol for H_2, HCl, and Cl_2.

Despite the larger underestimates of the HCl and Cl_2 bond energies, the description of H_2 and its addition to the Pt(0) adduct are very reasonable even at this rather modest level of calculation. Even without the inclusion of correlation effects, we calculate an average metal–hydrogen bond strength of 50 kcal/mol. Although there do not appear to be experimental bond strengths for Pt, this value is similar to the 60 kcal/mol average bond strength[34,35] for the metal–hydrogen bonds in $H_2IrCl(CO)(P(C_6H_5)_3)_2$. Still it is promising that a qualitatively reasonable description of the energetics of both the reactant and product asymptotes for the addition of H_2 to a Pt(0) complex can be attained without requiring a highly correlated wave function. This offers hope that useful information might be obtained by a partial mapping of the reaction surface at a modest computational level.

The energetics for the addition of the chlorine to $Pt(PH_3)_2$ are less satisfactory owing in large measure to the difficulty in describing the bond in diatomic chlorine without including correlation effects. We reiterate however that the platinum–chlorine bond as characterized by its bond length and vibrational frequencies is well represented by these calculations. Nonetheless, mapping the reaction surface for the additions of Cl_2 to Pt(0) would require much more sophisticated wave functions.

B. Relative Energies of Isomers. Now we turn to a comparison of the relative energies of the isomers, a question not clouded by whether we can properly treat the asymptotes. As has been noted for the dihydrides, it is generally not possible to isolate an analogous cis isomer of the many known trans species. The paucity of stable cis isomers often is attributed to a kinetic lability, an argument based on symmetry considerations. Thermodynamically, one might even argue that it ought to be the more stable isomer, since the hydride ligand is considered to exert a strong trans-labilizing influence and hence to disfavor mutual trans arrangement of the hydrogen.[27] We do not observe this, but as shown in Table VII, we find a difference in stability of only 2.1 kcal/mol. The close thermodynamic order of these two, which might easily be reversed if relaxation of the metal–phosphine bond were included in the geometry optimizations, suggests that there is little inherent instability of the cis isomer of thermodynamic origin.

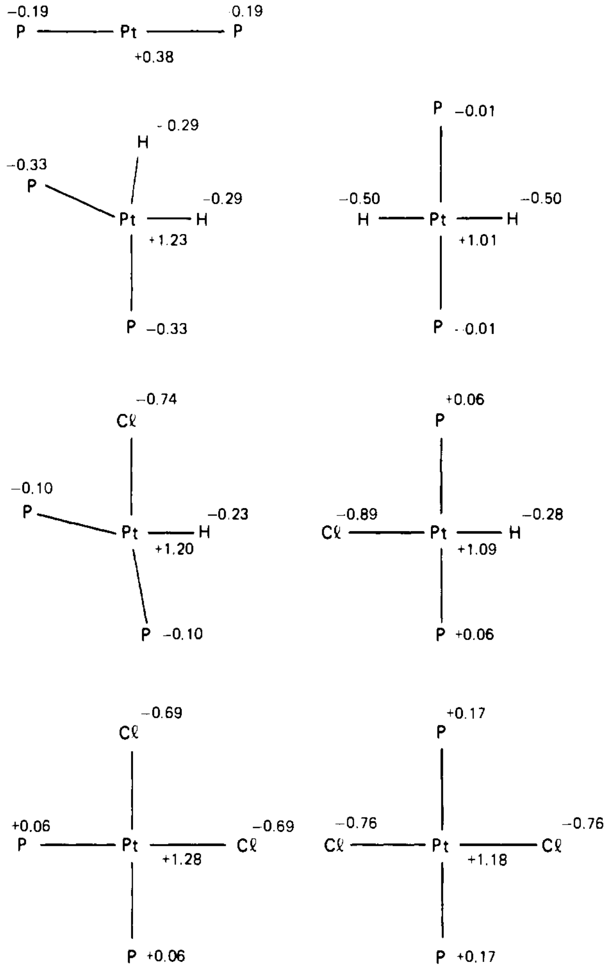

Figure 2. Calculated charge distributions for $(PH_3)_2PtXY$ isomers.

For both the HCl and Cl_2 additions, a clear thermodynamic preference for the trans isomer was observed by 16.9 and 33.5 kcal/mol, respectively. These results are to be expected in light of the analogous result for the dihydride. Replacement of the strongly labilizing hydride ligands with a more moderate chlorine should preferentially stabilize the trans adduct.

IV. Population Analysis

During this work we attempted to correlate the data with qualitative notions regarding the character of the ligands. Conventional population analyses failed for the reasons cited in the previous paper, and the alternate analysis was developed, which appears to partition the electrons more equitably in transition-metal systems. In Table VIII and Figure 3, net ligand and metal charges are collated for the equilibrium geometries of each of the systems considered. Populations deploying standard Mulliken analyses are also presented in the table. The standard analysis yields results discordant with intuition in that reduction of the metal is implied in some instances during the oxidative process! In the modified

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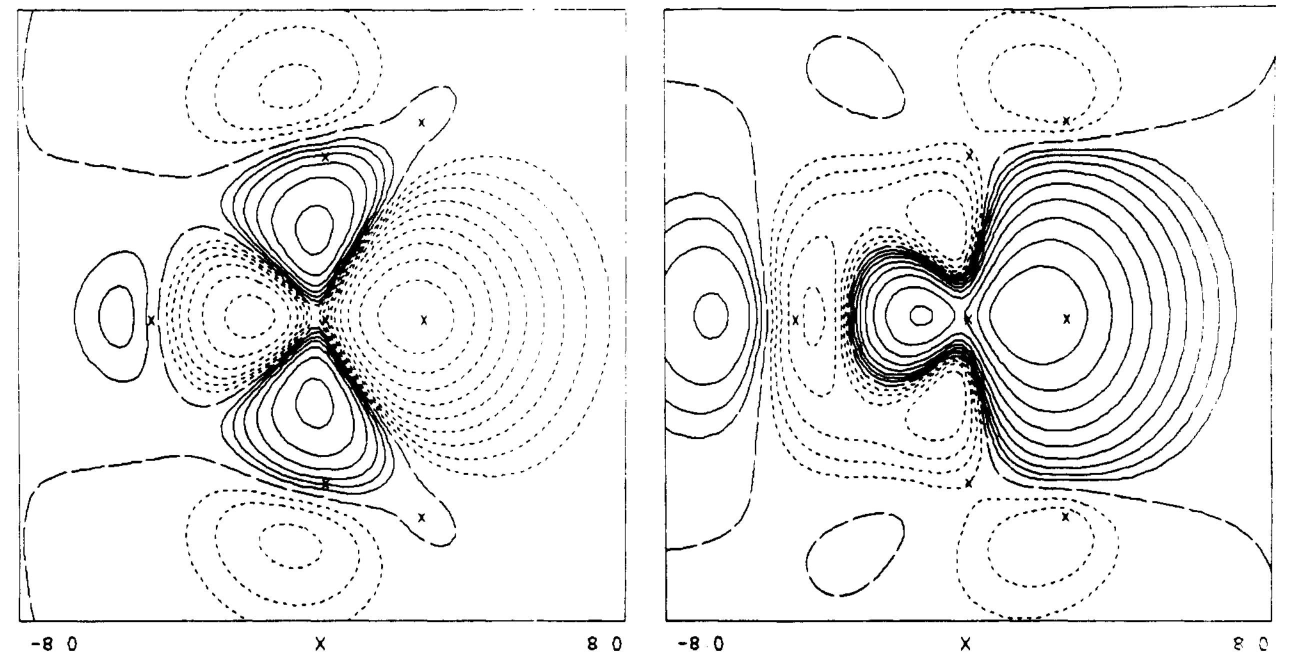

Figure 3. Pt–H bonding orbitals in *trans*-$(PH_3)_2PtHCl$. Each of the nonorthogonal generalized valence bond orbitals describe one electron. The orbital on the left is primarily Pt 5d$_{x^2-y^2}$ with some hydrogen admixture, while the right is mainly H 1s with some metal 5d admixture. Positive (solid) and negative (dashed) contours are shown in the *xy* plane with *x*'s denoting the position of the nuclei.

analysis, the oxidative process results in hydrogens with appreciable—but not complete—anionic character, 0.50 e in the *trans*-dihydride case. This view is consistent with its reputation as a trans-labilizing ligand. Reduced anionic character (0.23– to 0.29–e) is observed in the *cis*-dihydride and the hydrochlorides (Figure 2).

Treated as an anion, the influence of the hydrogen on the lability of the ligand trans to it may be viewed as deriving from its strong basicity and concomitant σ donation of electrons to the metal.[35] Following this argument, one would expect to find a correlation between the net charge observed on the hydrogen and the labilizing effect it had on the trans ligand. The more ionic the hydrogen—implying less donation of charge from the H^- reference—the less marked should be its influence on the trans ligand. It is therefore significant to note that the hydrogen is markedly more anionic in the trans as compared with the cis analogue. This may explain why the nominally unfavorable situation of having the two labilizing ligands trans to each other was actually found to be the preferred conformer. It appears that the net effect of two labilizing ligands trans to one another is not so strong as might be expected upon their the basis of individual effect on other, less basic ligands.

Finally a representative example of the Pt–H bonding orbitals in these compounds is shown in Figure 3 for the case of the trans-HCl complex. Instead of showing the Hartree–Fock orbital (in either canonical or localized form) we have chosen to depict the generalized valence bond[36] (GVB) orbitals, which also give localized representations of the bonding. In this description the doubly occupied orbital representing the electron pair—$\phi(1)\bar{\phi}(2)$—is replaced by a valence-bond pair where each electron is allowed a separate orbital—$\phi_a(1)\bar{\phi}_b(2) + \phi_b(1)\bar{\phi}_a(2)$. ϕ_a and ϕ_b are optimized and permitted to be nonorthogonal. To the extent that the HF description is valid, the GVB orbitals will be nearly identical.

As shown in Figure 3, the hydrogen atom has penetrated well into the region of high 5d density on the metal. As a result is sees increased electronic charge, as evidenced by the overall charge (0.29–) on the hydrogen.

V. Conclusions

Several key points have emerged from the present study. First, ground-state geometrical properties of complexes involving a third-row transition-metal atom may be quite reliably reproduced even at the Hartree–Fock level. In addition, for some processes such as the oxidative addition of hydrogen, the energetics can also be reasonably treated at modest computational levels. The reaction path leading to formation of *cis*-$Pt(PH_3)_2H_2$ will be explored in a subsequent paper. Finally, the modified population analysis offers a qualitative guide to aid in interpreting the results.

Registry No. $Pt(PH_3)_2$, 76830-85-8; *trans*-$Pt(PH_3)_2HCl$, 55642-77-8; *cis*-$Pt(PH_3)_2HCl$, 79389-90-5; *cis*-$Pt(PH_3)_2Cl_2$, 79329-16-1; *trans*-$Pt(PH_3)_2Cl_2$, 79389-91-6; *cis*-$Pt(PH_3)_2H_2$, 76832-29-6; *trans*-$(PH_3)_2H_2$, 76830-84-7.

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