

# Theoretical Study of the Interaction $d^{10}$ - $d^8$ Between Pt(0) and M(I) on the $[\text{Pt}(\text{PH}_3)_3\text{—M}(\text{PH}_3)]^+$ Complexes (M = Cu, Ag, Au)

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**ABSTRACT:** Ab initio calculations suggest that a series of complexes of type  $[\text{Pt}(\text{PH}_3)_3\text{—M}(\text{PH}_3)]^+$  (M = Au, Ag, Cu) are stable. We found that changes around the equilibrium distance Pt—M and in the interaction energies are sensitive to the electron correlation potential. This effect was evaluated using several levels of theory, including HF, MP2, and B3LYP. Both the magnitude of the interaction energies and distances Pt—M indicate a formal chemical bond, the latter being ratified by orbital diagram.

**Key words:** platinum bond; metal interaction; coinage metal

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## Introduction

Catalano et al. have synthesized and reported a series of compounds with bonding interactions in closed-shell systems between  $d^{10}$  Pt(0) or Pd(0) and  $s^2$  ions, such as Tl(I) or Pb(II) [1-4]. One of

those compounds is the  $[\text{Pt}(\text{PPh}_2\text{Py})_3\text{—Tl}]^+$  complex. Ab initio theoretical studies demonstrated that a charge-induced dipole term was found in such complex as the principal contribution in the stability between the platinum fragment and ion Tl(I) [5]. Near the equilibrium distance the dispersive interaction was smaller, but not negligible. Also, those results indicated a net nonbonding effect through the orbital interactions because of the inert character of the  $6s^2$  orbital of Tl(I).

On the contrary, it is possible to create a hypothetical complex between the fragments  $[\text{Pt}(\text{PR}_3)_3]$  (nucleophile) and  $\text{MPR}_3^+$  (electrophile) (M = Au, Ag, Cu; R = phosphine group), where we replaced the Tl(I), ion with the  $\text{MPR}_3^+$ , focusing on the  $d^{10}$ - $d^{10}$

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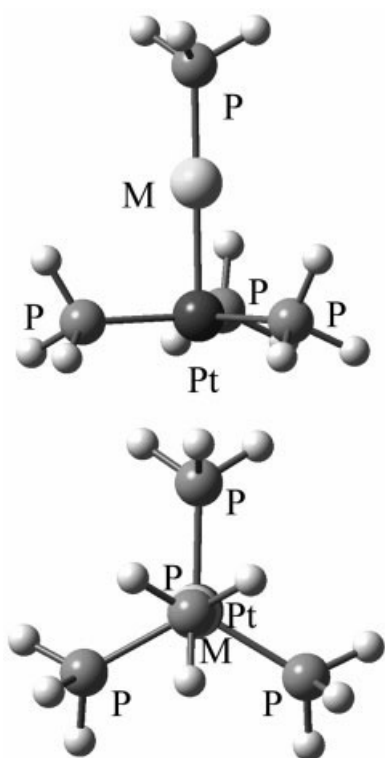
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Dedicated to Professor Pekka Pyykkö on the occasion of his 65th birthday.



**FIGURE 1.** The model of  $[\text{Pt}(\text{PH}_3)_3\text{—MPH}_3]^+$  ( $\text{M} = \text{Cu, Ag, Au}$ ).

strong closed-shell interaction. If the transition metal is thallium(I) ion ( $s^2$ ) of the complex is not formed according to the Dewar-Chartt-Duncanson model (synergistic combination of  $\sigma$ -donor and  $\pi$ -acceptor interaction) [6, 7]. This happens when the cations used are coinage transition metals ( $\text{Cu(I)}$ ,  $\text{Ag(I)}$  and  $\text{Au(I)}$ ) [8-10]. It has been shown that electrophilic gold fragments,  $\text{Ph}_3\text{PAu}^+$  which are isolobal with  $\text{H}^+$ , can be

added to electron-rich bi- or trinuclear platinum(II) complexes [11].

Complexes of the  $[\text{Pt}(\text{PR}_3)_3\text{—MPR}_3]^+$  ( $\text{M} = \text{Cu, Ag, Au}$ ) type have been reported neither at theoretical nor at experimental level. However, in the literature it is possible to find complexes of the type  $\text{Pt}_3$ -clusters with electrophiles  $\text{MPR}_3^+$  ( $\text{M} = \text{Cu, Ag, Au}$ ) forming half-sandwich structures:  $[\text{Pt}_3(\text{CO})_3\text{—}(\text{PCy}_3)_3\text{—MPR}_3]$  and  $[\text{Pt}_3(\text{SO}_2)_3(\text{PR}_3)_3\text{—MPR}_3]$  [12]. Extended Hückel calculations have reported that major bonding interactions arise between the LUMO  $\text{MPR}_3^+$  electrophile and HOMO platinum triangle fragment [13, 14].

The aim of this work is to study theoretically the intermolecular interaction  $d^{10}\text{—}d^{10}$  using the  $[\text{Pt}(\text{PH}_3)_3\text{—MPH}_3]^+$  complexes as models (Fig. 1), comparing the  $\text{Pt(0)—M(I)}$  distances and estimating the strength of the interaction at the HF, MP2, and B3LYP levels by means of scalar relativistic pseudopotentials (PPs).

## Computational Details

The calculations were performed with the Gaussian 98 program package [15]. For the heavy elements Pt, Au, Ag, and Cu, the Stuttgart pseudopotentials (PP) were used: 18 valence-electrons (VE) for Pt and 19-VE for the Au, Ag and Cu, [16] respectively. Two f-type polarization functions were added: Pt ( $\alpha_f = 0.70, 0.14$ ) [17], Au ( $\alpha_f = 0.20, 1.19$ ), Ag ( $\alpha_f = 0.22, 1.72$ ) and Cu ( $\alpha_f = 0.24, 3.70$ ) [18]. The P atom was also treated with PP, using a double-zeta basis set and adding one d-type polarization function [19]. For hydrogen, a valence-double-zeta basis set with p-polarization functions was used [20].

**TABLE I**  
Main geometric parameters of the model studied  $[\text{Pt}(\text{PH}_3)_3\text{—MPH}_3]^+$  ( $\text{M} = \text{Cu, Ag, Au}$ ).

System	Method	M—Pt (pm)	Pt—P (pm)	P—H (pm)	P—M (pm)	P—H (pm)	M—Pt—P (degrees)	H—P—Pt (degrees)	H—P—Pt (degrees)
$[\text{Pt}(\text{PH}_3)_3\text{—AuPH}_3]^+$	HF	264.1	243.1	141.1	237.4	140.5	90.3	119.0	116.5
	MP2	252.1	233.3	141.8	226.0	141.3	89.6	119.1	116.3
	B3LYP	260.4	239.6	142.9	231.0	142.3	90.9	119.7	116.8
$[\text{Pt}(\text{PH}_3)_3\text{—AgPH}_3]^+$	HF	271.8	241.2	141.2	258.4	140.7	90.8	119.4	117.5
	MP2	253.8	232.3	141.9	234.9	141.4	89.9	119.3	117.5
	B3LYP	263.2	238.3	143.1	242.0	142.5	91.1	120.0	117.9
$[\text{Pt}(\text{PH}_3)_3\text{—CuPH}_3]^+$	HF	248.0	241.5	141.1	235.9	140.7	90.5	119.2	117.3
	MP2	233.3	232.7	141.8	213.0	141.4	89.9	119.2	117.6
	B3LYP	240.9	238.7	143.0	220.9	142.5	90.9	119.9	117.8

**TABLE II**

Optimized Pt—M distance ( $R_e$ ) (in pm), interaction energies ( $\Delta E$ , in kJ/mol), with counterpoise correction, force constant ( $F$ ) Pt—M (in N m<sup>-1</sup>) and vibration frequency ( $\nu$ ) (in cm<sup>-1</sup>).

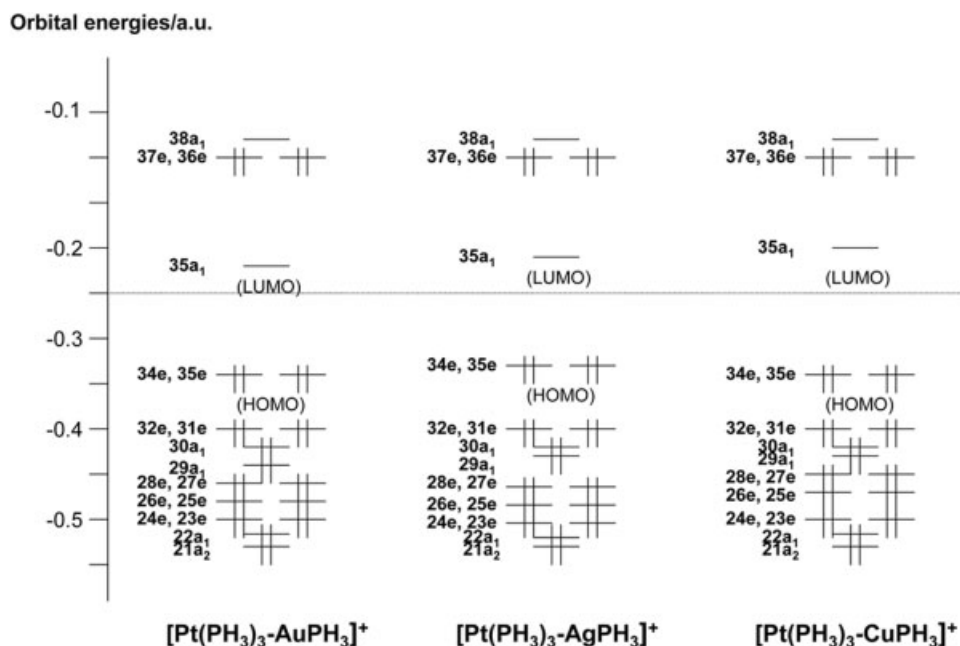
System	Method	Pt—M	$\Delta E$	$F$	$\nu$
[Pt(PH <sub>3</sub> ) <sub>3</sub> —AuPH <sub>3</sub> ] <sup>+</sup>	HF	264.1	-188.0	18.8	146.8
	MP2	252.0	-306.1	36.2	183.4
	B3LYP	260.4	-251.8	22.8	153.9
[Pt(PH <sub>3</sub> ) <sub>3</sub> —AgPH <sub>3</sub> ] <sup>+</sup>	HF	271.8	-134.3	9.7	127.0
	MP2	253.8	-223.9	26.6	177.2
	B3LYP	263.2	-197.7	32.3	182.9
[Pt(PH <sub>3</sub> ) <sub>3</sub> CuPH <sub>3</sub> ] <sup>+</sup>	HF	248.0	-161.9	14.9	146.9
	MP2	233.3	-257.2	32.9	201.6
	B3LYP	240.9	-230.9	23.3	171.3

The structures assume a C<sub>3v</sub> point symmetry. Fully optimized geometries were determined by applying the HF, MP2, and B3LYP methods. Though computational methodologies do not consider spin-orbit interactions, the complexes under investigation are closed-shell singlets; therefore, they should only be of minor importance. The counterpoise correction for the basis-set superposition error (BSSE) was used for the interaction energies calculated. The vibrational frequencies were computed on the models with different methods to obtain a thoroughly optimized geometry, without imaginary frequencies.

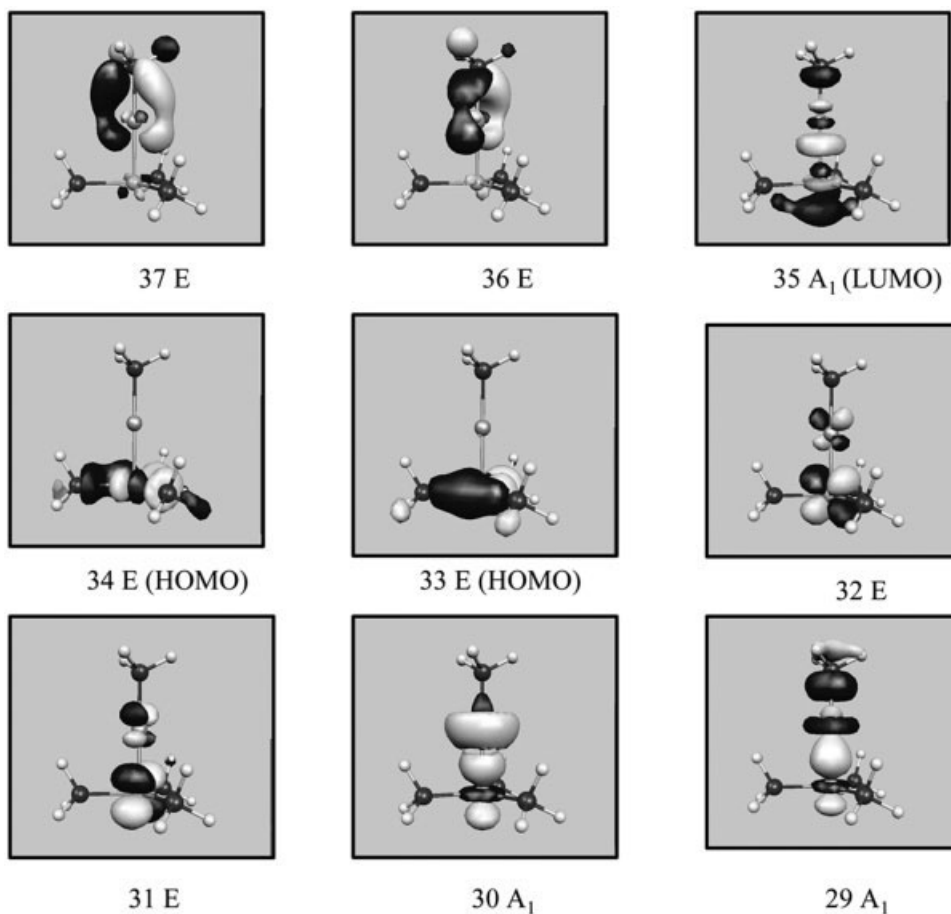
## Results and Discussion

All hypothetical complexes were found to be of local minima, with all real harmonic frequencies in a singlet ground state. Tables I and II summarize key geometric parameters, interaction energies and the force constants Pt—M obtained for the optimized geometries at several theoretical levels.

As for the Pt—M distance and the interaction energy (see Table II), it is clear that electronic correlation effects play an important role in the stability of the system. The Pt—M distances obtained with all meth-



**FIGURE 2.** The B3LYP orbital energies of [Pt(PH<sub>3</sub>)<sub>3</sub>—MPH<sub>3</sub>]<sup>+</sup> (M = Cu, Ag, Au).



**FIGURE 3.** The B3LYP frontier molecular orbitals of  $[\text{Pt}(\text{PH}_3)_3\text{-AuPH}_3]^+$ .

ods are close to simple bond, the distance obtained with the MP2 method being the shortest. It is worth noting that the MP2 approximation over-estimates the metallic interactions [21, 22]. The Pt—M force constants ( $F$ ) calculated in the complexes (shown in the Table II) are indicative of a strong interaction.

On the other hand, the M—Pt—P° angle in the complexes shows only a minor deviation compared to the  $[\text{Pt}(\text{PH}_3)_3]$  free. Such angle has a magnitude of  $\sim 90^\circ$ . Thus, a rehybridization of the platinum fragment is not observed, resulting in a pyramidalization of the complexes.

The magnitude of the interaction energies obtained varies according to the method used between 198 kJ/mol (HF) and 251 kJ/mol (B3LYP). Such magnitude is generally associated with covalent bonds. This might be indicative of an orbital stabilization due to the formation of stable adducts between the fragments of platinum and the metal ions. The complexes are already stabilized at the HF level as shown in Table I.

To obtain a better insight on such stabilization, B3LYP orbital energies for  $[\text{Pt}(\text{PH}_3)_3\text{-M}(\text{PH}_3)]^+$  ( $M = \text{Au, Ag, Cu}$ ) complexes have been depicted in Figure 2. The positions of frontier molecular orbitals in the orbital energy spectra of the three complexes are very similar, the HOMO-LUMO gap for all complexes being  $\sim 3.1$  eV. Figure 3 depicted the three important orbitals:  $35a_1$  (LUMO),  $30a_1$  and  $29a_1$ . In the case of the gold complex, these orbitals are analogous to the silver and copper remainder complexes. The orbitals generate the bonding ( $30a_1$  and  $29a_1$ ) and antibonding ( $35a_1$ ) sigma levels from  $5d_{z^2}$  (Pt) and  $5d_{z^2}$  (M), respectively. These two bonding molecular orbitals are doubly occupied, while the antibonding orbital is empty (LUMO). These results clearly indicated a net bonding effect through orbital interactions between the platinum and metal fragments.

Table III show the natural bond orbital (NBO) [23] population analysis based on the B3LYP density for the complexes. This table shows a charge transfer from the  $[\text{Pt}(\text{PH}_3)_3]$  fragment towards the

**TABLE III**  
**NBO analysis of the B3LYP density of [Pt(PH<sub>3</sub>)<sub>3</sub>—MPH<sub>3</sub>]<sup>+</sup> (M = Cu, Ag, Au).**

System	Atom	Natural	Natural electron configuration
[Pt(PH <sub>3</sub> ) <sub>3</sub> —AuPH <sub>3</sub> ] <sup>+</sup>	Au	+0.3011	6s <sup>0.88</sup> 5d <sup>9.80</sup> 6p <sup>0.01</sup>
	Pt	-0.1611	6s <sup>0.68</sup> 5d <sup>9.41</sup> 5f <sup>0.01</sup> 6d <sup>0.01</sup> 7p <sup>0.04</sup>
	P	+0.0700	3s <sup>1.46</sup> 3p <sup>3.42</sup> 3d <sup>0.03</sup> 4p <sup>0.02</sup>
	P	+0.1611	3s <sup>1.42</sup> 3p <sup>3.37</sup> 3d <sup>0.03</sup> 4p <sup>0.01</sup>
	H	+0.0400	1s <sup>0.96</sup>
	H	+0.0600	1s <sup>0.94</sup>
[Pt(PH <sub>3</sub> ) <sub>3</sub> —AgPH <sub>3</sub> ] <sup>+</sup>	Ag	+0.5485	5s <sup>0.52</sup> 4d <sup>9.91</sup> 5p <sup>0.01</sup> 7p <sup>0.01</sup>
	Pt	-0.2296	6s <sup>0.68</sup> 5d <sup>9.48</sup> 5f <sup>0.01</sup> 6d <sup>0.01</sup> 7p <sup>0.04</sup>
	P	+0.0605	3s <sup>1.46</sup> 3p <sup>3.42</sup> 3d <sup>0.03</sup> 4p <sup>0.02</sup>
	P	+0.0213	3s <sup>1.47</sup> 3p <sup>3.47</sup> 3d <sup>0.03</sup> 4p <sup>0.02</sup>
	H	+0.0400	1s <sup>0.96</sup>
	H	+0.0600	1s <sup>0.94</sup>
[Pt(PH <sub>3</sub> ) <sub>3</sub> —CuPH <sub>3</sub> ] <sup>+</sup>	Cu	+0.5342	4s <sup>0.56</sup> 3d <sup>9.88</sup> 5p <sup>0.01</sup> 6p <sup>0.01</sup>
	Pt	-0.2449	6s <sup>0.69</sup> 5d <sup>9.48</sup> 5f <sup>0.01</sup> 6d <sup>0.02</sup> 7p <sup>0.03</sup>
	P	+0.0650	3s <sup>1.46</sup> 3p <sup>3.42</sup> 3d <sup>0.03</sup> 4p <sup>0.02</sup>
	P	+0.0349	3s <sup>1.46</sup> 3p <sup>3.46</sup> 3d <sup>0.03</sup> 4p <sup>0.01</sup>
	H	+0.0400	1s <sup>0.96</sup>
	H	+0.0600	1s <sup>0.94</sup>
[Pt(PH <sub>3</sub> ) <sub>3</sub> ]	Pt	-0.2135	6s <sup>0.62</sup> 5d <sup>9.56</sup> 6d <sup>0.01</sup> 7p <sup>0.01</sup>
	P	-0.0800	3s <sup>1.48</sup> 3p <sup>3.38</sup> 3d <sup>0.03</sup> 4p <sup>0.03</sup>
	H	-0.0019	1s <sup>0.99</sup>

metal electrophile ions in the [Pt(PH<sub>3</sub>)<sub>3</sub>—MPH<sub>3</sub>]<sup>+</sup> complexes. The charge on metal ions (Au, Ag, and Cu) is mainly due to a charge transfer from the phosphorus and hydrogen atoms. The platinum shows no charge variability. The gross population per atom shell shows changes in the bond among the metal fragments due to electronic transfers.

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