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STABILIZATION OF THREE COORDINATE d^8 METAL COMPLEXES THROUGH INTRAMOLECULAR LIGAND—METAL INTERACTIONS: A THEORETICAL STUDY OF THE ION $[Rh(PPh_3)_3]^+$

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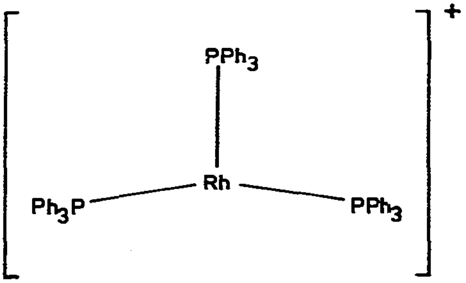
Summary

A theoretical analysis of the distortions in the $[Rh(PPh_3)_3]^+$ cation has been carried out using ab-initio LCAO-MO-SCF calculations. From these calculations, molecular and electrostatic intramolecular interactions between the phenyl group and the rhodium center appear to be at the origin of the observed distortions. A possible relationship to orthometallation reactions is briefly discussed.

Three-coordinate ML_3 d^8 metal complexes have been postulated as reaction intermediates in some organometallic reactions [1—8] or in some rearrangements [9—12]. Such 14-electron systems are rather unstable, but a few of them have been isolated and characterized [13—15] by using bulky phosphine ligands such as PCy_3 [13] (Cy = cyclohexyl) or PBu^t_3 [14] (Bu^t = tert-butyl). Despite a smaller cone angle of the PPh_3 ligand [16] the $[Rh(PPh_3)_3]ClO_4$ complex is also stable. The X-ray crystal structure [15] of the $[RhPPh_3]^+$ cation (1) displays



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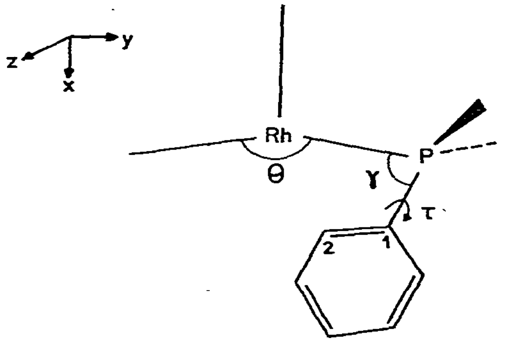
some striking features. First there is a distortion from trigonal planarity towards the T-shape geometry ($\theta = 159.5°$) which leads to the diamagnetism of the complex. It is one of the two distortions expected [17] in this Jahn-Teller system, the other being towards the Y shape. But a more important distortion is found for one phosphine ligand, and is depicted schematically in **2**; the small γ angle ($\gamma = 75.6°$) has been traced [15] to some interaction between the rhodium center (which is coordinatively unsaturated) and the α carbon atom (C(1)) of the phenyl ligand and to an additional (but weaker) interaction of Rh with the *ortho* carbon atom (C(2)) and its hydrogen atom.



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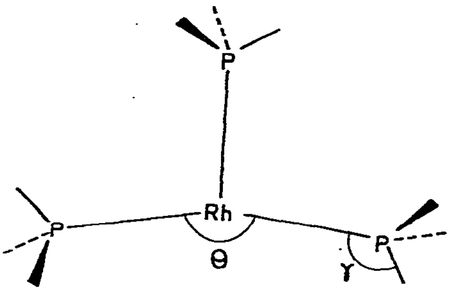
These interactions (which are supposed to be attractive) have therefore been tentatively advanced as the explanation of the stabilization of the $[Rh(PPh_3)_3]$-ClO_4 complex and of some other coordinatively unsaturated reaction intermediates having at least one triphenylphosphine ligand [15]. This may well be the case for the $RhCl(PPh_3)_2$ system, which is often thought to be the actual catalyst in the $RhCl(PPh_3)_3$-catalyzed homogeneous hydrogenation of alkenes [2,3,18]. These interactions may also have some significance [19] in the context of orthometallation processes [20], the mechanism of which is largely unknown.



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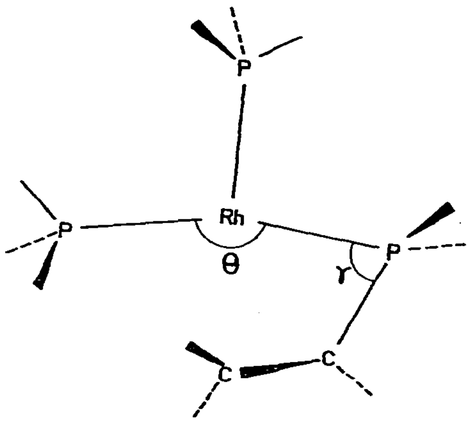

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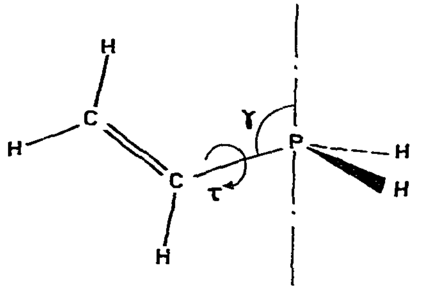
As part of our comprehensive theoretical study of the $RhCl(PPh_3)_3$-catalyzed hydrogenation of olefins [21—23], we present here an analysis of these intramolecular phenyl—metal interactions in the $[Rh(PPh_3)_3]^+$ system. Our conclusions are derived from ab initio LCAO-MO calculations [24] carried out on the systems $[Rh(PH_3)_3]^+$ (**3**), $[Rh(PH_3)_2(PH_2vy)]^+$ (**4**, vy = vinyl) [30] and on the $Ru(PH_3)_2(PH_2vy)$ complex (which is isoelectronic to $[Rh(PH_3)_2(PH_2vy)]^+$). In these systems PH_3 and PH_2vy (**5**) serve as models for the non-interacting and interacting phosphine ligands, respectively. Our strategy is to determine the potential energy curves as a function of the θ and γ angles for the $[Rh(PH_3)_3]^+$ (**3**), $[Rh(PH_3)_2(PH_2vy)]^+$ (**4**) and (PH_2vy) (**5**) (γ angle only) systems [32] and to compare their profiles. The corresponding results are then analyzed in terms of orbital and electrostatic interactions. We finally discuss a possible relationship to orthometallation reactions.



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Results and discussion

We first consider the variation of the θ angle in the $[Rh(PH_3)_3]^+$ model system. An almost perfect T-shaped geometry is found, the total energy being minimum for $\theta \simeq 175°$ (see Table 1). This is traced to a four-electron destabilizing interaction **6** between the metal d_{xy} orbital and the b_2 combination (in the

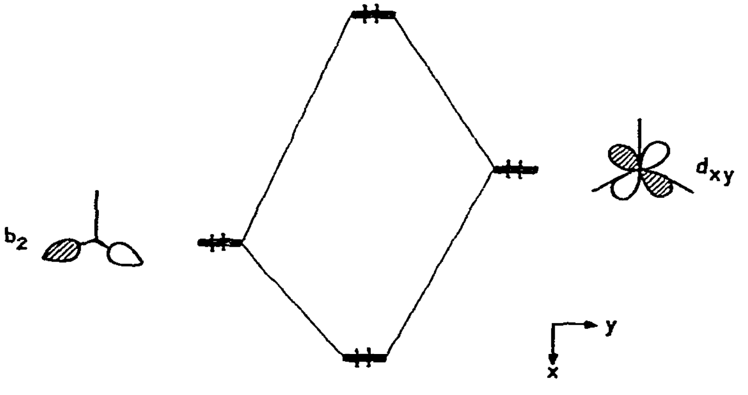

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TABLE 1

TOTAL ENERGIES (in a.u.) AND RELATIVE ENERGIES (in kcal/mol) FOR THE $[Rh(PH_3)_3]^+$ AND $[Rh(PH_3)_2(PH_2vy)]^+$ SYSTEMS AS A FUNCTION OF THE θ ANGLE (γ being kept at 75° for the $[Rh(PH_3)_2(PH_2vy)]^+$ system)

System	θ angle	Total energy	Relative energy
$[Rh(PH_3)_3]^+$	180	−5699.4006	0
	170	−5699.4000	+0.4
	160	−5699.3925	+5.1
	140	−5699.3628	+23.7
	100	−5699.3473	+33.5
$[Rh(PH_3)_2(PH_2vy)]^+$	180	−5776.1693	0
	160	−5776.1779	−5.4
	140	−5776.1548	+9.1

C_{2v} pseudo symmetry) of the phosphorus lone pairs which is minimum when $\theta = 180°$. We refer the reader to the two papers by Hoffman et al. [17], where an extensive theoretical analysis of distortions in a planar three-coordinate 14-electron complex is carried out. The patterns of the valence levels for the $[Rh(PH_3)_3]^+$ system (this work) and for the $Au(CH_3)_3$ system (ref. 17a) are indeed quite similar [34]. We also find a rather important destabilization of the Y geometry (33.5 kcal/mol for $\theta = 100°$ [36], see Table 1). The experimental θ value of 159.3° in the $[Rh(PPh_3)_3]^+$ system is therefore indicative either of some steric repulsion between the adjacent triphenylphosphine ligands (the cone angle being much greater in PPh_3 than in PH_3 [16]) or (see ref. 15) of some interaction between a phenyl ring and the rhodium center.

In order to assess the origin of the $[Rh(PPh_3)_3]^+$ distortions, one PH_3 ligand of the $[Rh(PH_3)_3]^+$ system was replaced by the PH_2vy ligand (see **3** and **4**). This substitution does not lead to more steric repulsion with the *cis* phosphine ligand, but is expected to model the interacting part of the phenyl ring in $[Rh(PPh_3)_3]^+$. Calculations on the resulting $[Rh(PH_3)_2(PH_2vy)]^+$ system (**4**) were carried out varying either θ or γ [37]. The corresponding results are given in Tables 1 and 2. In both cases the total energy is a minimum for values (θ =

TABLE 2

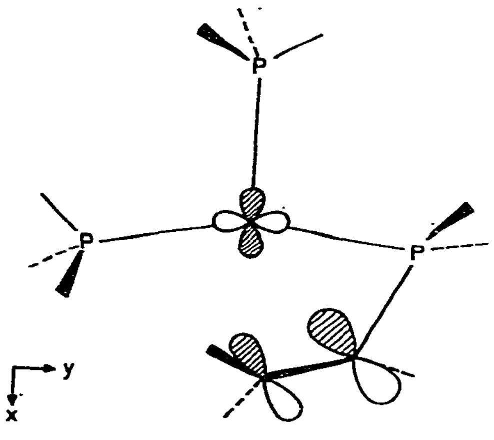
TOTAL ENERGIES (in a.u.) AND RELATIVE ENERGIES (in kcal/mol) FOR THE $[Rh(PH_3)_3]^+$, $[Rh(PH_3)_2(PH_2vy)]^+$ AND $[Ru(PH_3)_2(PH_2vy)]$ SYSTEMS AS A FUNCTION OF THE γ ANGLE (θ being kept at 160°)

System	γ Angle	Total energy	Relative energy
$[Rh(PH_3)_3]^+$	122.85 [a]	−5699.3896	0
	100	−5699.3945	−3.1
	75	−5699.3662	+14.7
$[Rh(PH_3)_2(PH_2vy)]^+$	122.85 [a]	−5776.1594	0
	100	−5776.1767	−10.9
	75	−5776.1779	−11.6
	65	−5776.1670	−4.8
$[Ru(PH_3)_2(PH_2vy)]^+$	122.85 [a]	−5532.3639	0
	75	−5532.3733	−5.9

[a] Experimental γ value for PH_3 [33].

165°, $\gamma = 86°$) which are close to the experimental ones for $[Rh(PPh_3)_3]^+$. But more important is the comparison, as γ varies, of the energy profiles for the $[Rh(PH_3)_2(PH_2vy)]^+$ system (**4**) and for the PH_2vy ligand (**5**) alone, as shown in Fig. 1. As γ is diminished the $[Rh(PH_3)_2(PH_2vy)]^+$ system is stabilized (by 11.6 kcal/mol for $\gamma = 75°$) whereas the PH_2vy system is destabilized (by 13.9 kcal/mol). These results are clearly indicative of some stabilizing interactions of an electronic nature between the vinyl moiety and the rhodium center (since, as mentioned above, no extra steric repulsion is introduced by the vinyl substitution). The same type of interactions between the phenyl ring and the rhodium center probably operates in the $[Rh(PPh_3)_3]^+$ system.

Our next concern is the nature of these electronic interactions. We can think of some orbital interactions or, perhaps more simply, of some electrostatic attraction between the positive metal center (especially for a cationic system) and the π electronic density of the vinyl moiety. The orbital interactions are rather difficult to characterize owing to the lack of symmetry of the wave function. We find, however, some stabilizing interaction, **7**, though weak, between the occupied π_u orbital of the vinyl moiety and $4d_{x^2-y^2}$ (which is formally empty) of the rhodium atom [38]. This is best illustrated by the increase in the $4d_{x^2-y^2}$ atomic population from 0.75 to 0.87 when γ varies from 122.85° to 75°. Note that the torsion of the vinyl entity (or of the phenyl ring) around the P—C bond is not only dictated by steric constraints, but is also a necessary condition for this stabilizing interaction to occur. For a torsional angle of 0°, i.e. with the C_2H_3 plane into the RhPC plane, the nodal properties of the π_u orbital would lead to a zero overlap between π_u and $4d_{x^2-y^2}$ (see **8**), precluding any interaction between these two orbitals.



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One might also think that the stabilization could be induced by some modification in the direction and in the shape of the lone pair of the PH_2vy ligand when γ goes from 122.85° to 75°. The directional effect is shown schematically in **9** and **10**. In **9** the lone pair axis coincides with the Rh—P bond, whereas in **10** this axis is tilted upwards, off the nodal plane of the empty $d_{x^2-y^2}$ orbital. Moreover, since the phosphorus atom is less pyramidal in **10**, the lone pair

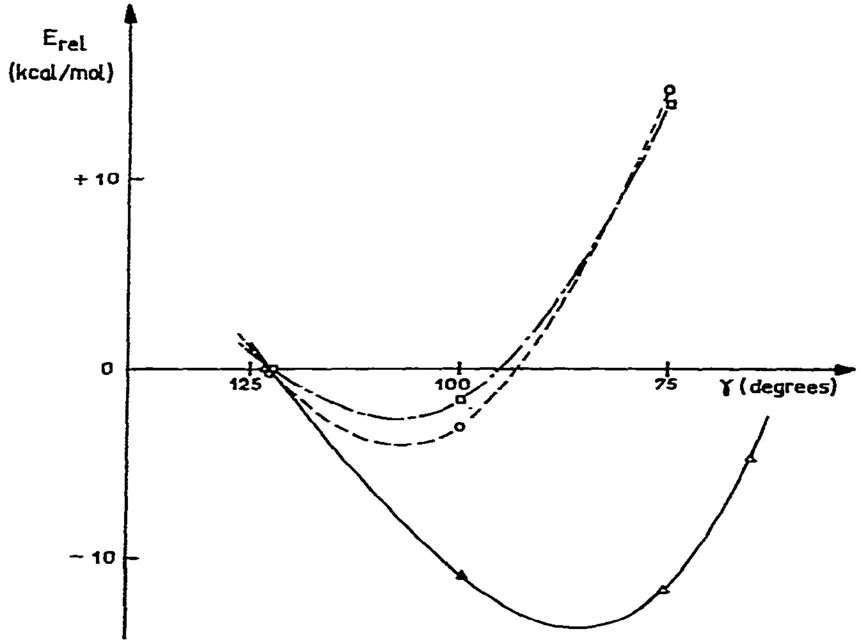
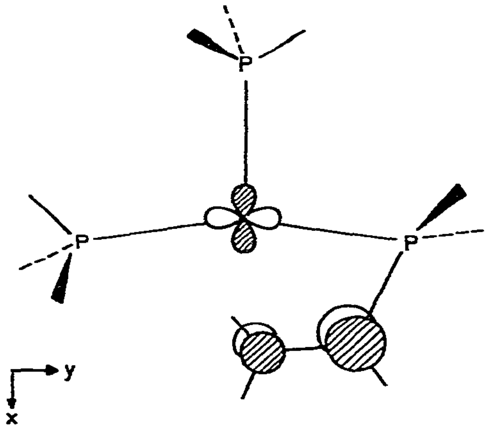


Fig. 1. Potential energy curve for the γ angle distortion in the $[Rh(PH_3)_2(PH_2vy)]^+$ (——△——), $[Rh(PH_3)_3]^+$ (– – ○ – –) and PH_2vy (–•–□–•–) systems. The energy zero refers to $\gamma = 122.85°$.

should have more p character [39]. Both factors should therefore lead to a greater overlap between the lone pair and $d_{x^2-y^2}$, and consequently to a greater stabilizing interaction. In addition the lone pair/d_{xy} destabilizing interaction



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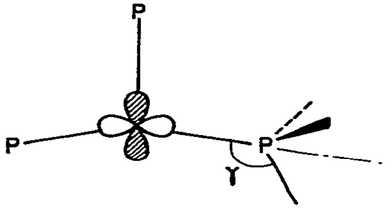
should be smaller. This again would result from the tilting of the lone pair, its increased p character leading in this case to a smaller overlap with d_{xy}. To test this hypothesis we carried out calculations on the $[Rh(PH_3)_3]^+$ system in which the γ angle is varied [40]. The same effects should operate. They are far from



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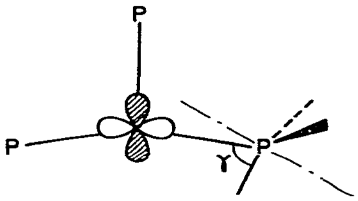

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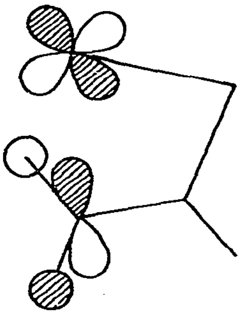
being dominant, however, and as γ is decreased from 122.85° to 75° an overall destabilization is found (see Table 2 and Fig. 1). Also, the potential energy curves for $[Rh(PH_3)_3]^+$ and PH_2vy are parallel, suggesting that the $[Rh(PH_3)_3]^+$ destabilization can be traced to the phosphine ligand deformation.

Can we ascribe the stabilizing deformation of the $[Rh(PH_3)_2(PH_2vy)]^+$ system to some electrostatic interaction between the positive rhodium center and the π electronic density of the vinyl entity? We first note that the +1 positive charge is not concentrated on the rhodium center but is rather delocalized over the whole system; from the population analysis the charge of the rhodium atom is about +0.35. Nevertheless, to probe the possibility of an electrostatic interaction between the rhodium center and the vinyl entity, the isoelectronic but neutral $Ru(PH_3)_2(PH_2vy)$ system has been considered (see Table 2). Again some stabilization is found for a γ angle of 75°, but it is much smaller, 5.9 kcal/mol. The charge of the ruthenium atom in this system is +0.12, suggesting that the electrostatic interaction is probably a significant component of the stabilization caused by the phosphine distortion in $[Rh(PH_3)_2(PH_2vy)]^+$ and in $[Rh(PPh_3)_3]^+$. It could also be important for the stabilization of the three-coordinate $RhCl(PPh_3)_2$ intermediate involved in the $RhCl(PPh_3)_3$-catalyzed hydrogenation of olefins, where the rhodium atom is likely to bear a positive charge (from the population analysis of the model system $RhCl(PH_3)_2$ [21] the rhodium atomic charge is +0.51).

The computed stabilization for the $[Rh(PH_3)_2(PH_2vy)]^+$ system (as γ goes from 122.85° to 75°, see Table 2) amounts to 11.6 kcal/mol. One could argue that this results mainly from a basis set superposition error, since the geometrical deformation considered here can be viewed as bringing together two separate entities. In our case, however, one would have to take into account the intrinsic destabilization (13.9 kcal/mol) of the PH_2vy ligand during the process and the superposition error would therefore have to be more than 25.5 kcal/mol to offset the computed stabilization of the $[Rh(PH_3)_2(PH_2vy)]^+$ system. We also note that the coordination of PPh_3 to $RhCl(PPh_3)_2$ has been found experimentally to be exothermic by about 12.5 kcal/mol [41].

Finally, the relevance of this stabilizing effect to orthometallation reactions may be considered, and more precisely to the initial interaction between the C—H bond (or the hydrogen atom of the C—H bond) and the metal. Experimentally, no evidence of orthometallation has been found upon heating the $[Rh(PPh_3)_3]ClO_4$ complex [15]. If an intramolecular C—H oxidative addition [42] were likely to occur, one should find, by analogy with the H_2 oxidative addition [22,43], some kind of two-electron orbital interaction (11) between an empty orbital being C—H antibonding in character and an occupied *d* metal



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orbital of the proper symmetry with which to interact. We do not find such an interaction in the wave function of the $[Rh(PH_3)_2(PH_2vy)]^+$ system. The torsion of the vinyl entity around the P—C bond destroys a possible interaction with the d_{xy} metal orbital (see **2** for our choice of axes), but does not allow any substantial interaction with either d_{xz} or d_{z^2}. This situation is quite similar to the one observed by Deeming and Rothwell for some palladation reactions [44,20d], and may therefore explain why $[Rh(PPh_3)_3]ClO_4$ does not undergo an orthometallation reaction.

Acknowledgments

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35 For $\theta = 140°$ the energy of the $(xz)^2(yz)^2(z^2)^2(x^2-y^2)^2$ configuration is computed to be —5699.2653 a.u., i.e. 2.65 eV above the energy of the $(xz)^2(yz)^2(z^2)^2(xy)^2$ configuration.
36 We consider here the $(xz)^2(yz)^2(z^2)^2(x^2-y^2)^2$ configuration (which is the lowest).
37 The angle variations are considered separately. γ is set to 75° (experimental value) when θ is varied, θ is set to 160° (experimental value) when γ is varied.
38 In fact, the situation is more complicated. There is a four-electron destabilizing interaction between $4d_{xy}$ and π_u which is somewhat released through the interaction with the empty $4d_{x^2-y^2}$. The π_u orbital of the PH_2vy ligand is polarized as indicated in 7. This results in a greater overlap between the Rh atom and the C_α atom.
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