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# Why do Cationic Hydridoiridium(III) Complexes with β-Aminophosphane Ligands Favour the Transfer Hydrogenation of Ketones over the Direct "$H_2$-Hydrogenation"?—A Computational Approach

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**Abstract:** Density functional theory and ab initio molecular orbital calculations show that the observed inability of cationic hydridoiridium(III) complexes with β-aminophosphane ligands to catalyse the direct hydrogenation of carbonyl compounds with dihydrogen ("$H_2$-hydrogenation") in contrast to their ruthenium(II) equivalents is due to the inability of $H_2$ to displace a coordinated solvent molecule from an intermediate hydrido complex.

**Keywords:** ab initio calculations · density functional calculations · hydrogenation · iridium · solvent effects

## Introduction

Among the most efficient known catalysts for the transformation of ketones to secondary alcohols with dihydrogen as a reductant (referred to as "$H_2$-hydrogenation" in the following) are the species formed in basic media from bis(phosphane)/diamine-coordinated ruthenium(II) complexes $[Ru(X)(Y)(PR_3)_2(H_2N\cap NH_2)]$ (X, Y, = Cl, H), in which $H_2N\cap NH_2$ stands for a chiral or achiral chelating 1,2-diamine and $(PR_3)_2$ represents two monodentate or one chiral bidentate phosphane, especially the binap (2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl) ligand. The actual catalysts are usually created in isopropanol solution by treating the $Ru^{II}$ precursors with a large excess of strong alkaline base (KOH, KO*t*Bu, and the like). $H_2$-hydrogenations supported by such systems are exceptional with respect to their consistently high enantioselectivity, their chemoselectivity for carbonyl over olefin reduction and the very large substrate-to-catalyst ratios (up to $10^6$) that can be reached.[1]

This unique catalytic behaviour arises from the addition of $H_2$ to initially formed 16e amido hydrides $[RuH(\square)(PR_3)_2(HN\cap NH_2)]$ (Scheme 1: **1**) to yield transient $Ru(\eta^2\text{-}H_2)$ intermediates $[RuH(H_2)(PR_3)_2(HN\cap NH_2)]$ **5**, which then undergo rate-determining deprotonation of their dihydrogen ligand by the amido nitrogen atom.[2,3] There is convincing experimental and computational evidence[2c,f,3a,b] that the resulting dihydrides $[RuH_2(PR_3)_2(H_2N\cap NH_2)]$ **2** are generated as the least stable and, hence, catalytically active *trans*-$RuH_2$ (*OC*-6-22) stereoisomers. Of particular note are their near-planar *syn*-H-Ru–N–H structural motifs, which are aligned by Ru-H···H–N hydridic–protonic interactions and have elongated Ru–H bonds because of the strong *trans* influence of hydrido ligands.[2b,c] These features make the H-Ru-N-H active sites particularly suitable for the rapid transfer of $H^{\delta-}/H^{\delta+}$ equivalents to the carbonyl dipole once the ketonic substrate has joined the second coordination sphere in a six-membered $Ru\text{–}H^{\delta-}\cdots>C^{\delta+}=O^{\delta-}\cdots H^{\delta+}\text{–}N$ transition state $\mathbf{3}^{\neq}$.[3] The concerted transfer of a hydride and a proton from the metal and the nitrogen atom to the >C=O bond represents the reversal of the dehydrogenation of a secondary alcohol such as isopropanol by the $Ru^{II}$ diamide $[(\eta^6\text{-}p\text{-cumene})Ru(HNCH(Ph)CH(Ph)NTs)]$ (Ts = *p*-$MeC_6H_4SO_2$) to give the amido–amine hydride $[(\eta^6\text{-}p\text{-cumene})Ru(H)(H_2NCH(Ph)CH(Ph)NTs)]$. The latter in turn can quickly transfer hydridic H from Ru and protic H from N to a >C=O function loosely bound in the outer coordination sphere and, hence, work as a catalyst for the transfer hydro-

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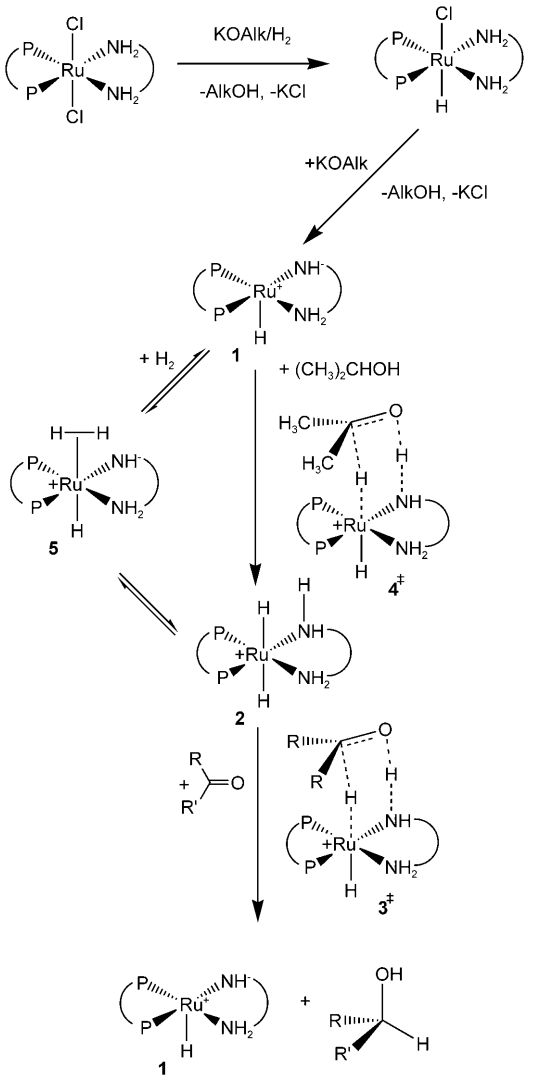



Scheme 1. Key steps of $Ru^{II}$-catalysed $H_2$ and transfer hydrogenations of carbonyl compounds.

genation of ketones with isopropanol as the reducing agent.[4]

As $Ru^{II}$-catalysed transfer hydrogenations are mechanistically linked to $H_2$-hydrogenations through transition states of the same kind (Scheme 1: **3**$^{\ddagger}$ and **4**$^{\ddagger}$),[5–8] catalysts that work in the hydrogenation of ketones with molecular hydrogen in isopropanol solution should also catalyse the transfer of $H^{\delta-}/H^{\delta+}$ equivalents from the solvent to the substrate. As a result, $H_2$-hydrogenations and transfer hydrogenations can become competitive[9] and there are, in fact, a few Ru-[2d,5d,f,10a] and Rh-based[10b] systems for which activity in both modes of C=O reduction has been established.

Usually, however, (pre)catalysts used for transfer or $H_2$-hydrogenations are dealt with completely separately because the two ways of transforming ketones into alcohols are widely used as alternatives. $H_2$-hydrogenations are attractive for reactions run on a multi-100 g scale because several "advanced", that is, extremely active, catalytic systems have been introduced for this technology. Transfer hydrogenations, on the other hand, are only used for small-to-medium scale transformations as they can only make use of less highly developed catalysts.

Hartmann and Chen showed that the activation of the pre-catalyst $[RuCl_2\{(S)\text{-binap}\}\{(S,S)\text{-}H_2NCH(Ph)CH(Ph)\text{-}NH_2\}]$ for efficient $H_2$-hydrogenation not only needs an excess of an arbitrary strong base, but also requires a source of alkali metal cations, $K^+$ being particularly efficacious (the "potassium effect"). They postulated that the role of the potassium ion is to coordinate to the amido nitrogen atom of a dehydrochlorinated intermediate **1**, whereby the transient $Ru(\eta^2\text{-}H_2)$ amide **5** is rendered cationic and thus sufficiently acidic for enhanced heterolysis of the dihydrogen ligand. As a result, its turnover-limiting cleavage into $H^-$ and $H^+$ (Scheme 1: **5**→**2**) is accelerated, such that the transfer of hydridic and protic H from the solvent (Scheme 1: **1**→**4**$^{\ddagger}$→**2**) is no longer competitive.[9]

This raised the question as to whether the positive charge of cationic P,N-coordinated hydridoiridium(III) compounds would contribute to their functioning as active catalysts for direct C=O hydrogenation by $H_2$, notwithstanding that iridium complexes are known predominantly as transfer-hydrogenation catalysts.[11] In previous work,[12] we isolated the bis(β-aminophosphane)-chelated cation (*OC*-6-43)-$[Ir(H)(Cl)(Ph_2PCH_2CH_2NH_2)_2]^+$ **6** as the chloride salt and obtained the *trans*-dihydride (*OC*-6-22)-$[IrH_2(Ph_2PCH_2CH_2\text{-}NH_2)_2]Cl$ (**7**, Figure 1) by combination of **6** with KOH in isopropanol.

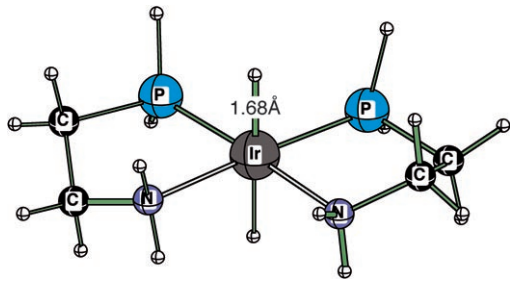
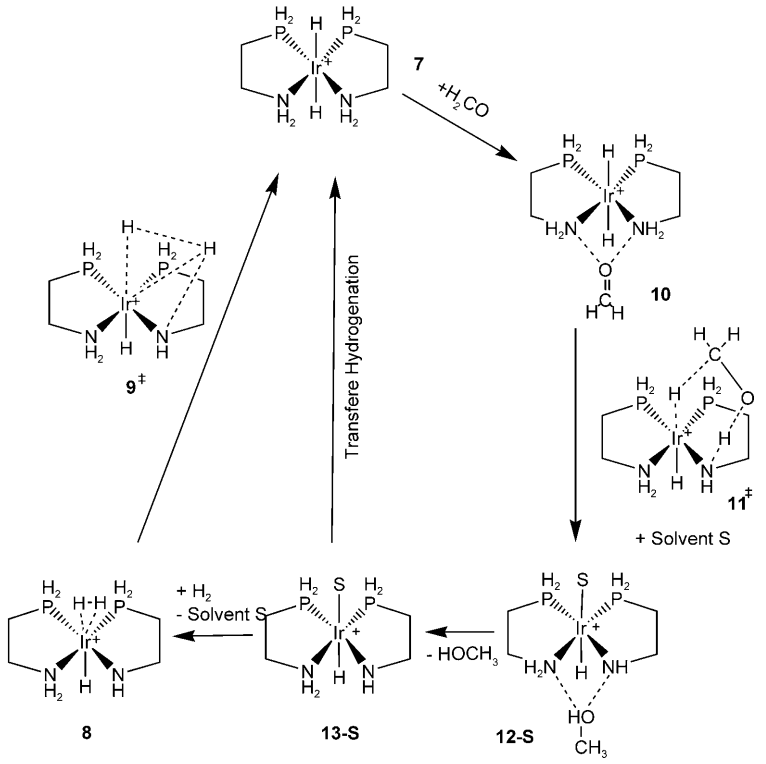



Figure 1. B3LYP/LACV3P+**-optimised structure of cationic complex **7**. The Ir–H bond length is given in Å.

These two $Ir^{III}$ compounds bear a direct structural resemblance both to the established Noyori–Morris pre-catalysts (*OC*-6-43)-$[Ru(H)(Cl)(PR_3)_2(H_2N\cap NH_2)]$ and the real active species (*OC*-6-22)-$[RuH_2(PR_3)_2(H_2N\cap NH_2)]$. Unlike their closely matching $Ru^{II}$-analogues (*OC*-6-13)-$[RuCl_2(Ph_2PCH_2CR_2NH_2)_2]$ (R = H, Me) and (*OC*-6-43)-$[Ru(H)(Cl)(Ph_2PCH_2CH(R)NH_2)_2]$ (R = H, Me), which in the presence of potassium alkoxide furnished active catalysts for the $H_2$-hydrogenation of acetophenone[2e,10a] and could also be used for the transfer hydrogenation of the ketone,[10a] however, the two iridium complexes did not act as $H_2$-hydrogenation (pre)catalysts: potassium alkoxide-activated $[Ir(H)(Cl)(Ph_2PCH_2CH_2NH_2)_2]Cl$ only catalysed transfer hy-

drogenations with methanol or isopropanol as proton/hydride sources. In these transformations, dihydrido complex **7** was ascribed the role of the actual catalyst, as it was seen to maintain the catalytic cycle even in the absence of base. It therefore seems clear that there exists neither a "$K^+$ effect" nor a beneficial influence of positive charge in the case of the two $Ir^{III}$ hydrides. This could be owed to a different mechanism involving addition of the ketone to a site made vacant by dissociation of a ligand. The catalytic activity of base-free (*OC*-6-22)-$[IrH_2(Ph_2PCH_2CH_2NH_2)_2]Cl$ (**7**), which as a low-spin $d^6$ system should be quite inert to ligand substitution, however, suggests that an $Ir{-}H^{\delta-}\cdots C^{\delta+}{=}O^{\delta-}\cdots H^{\delta+}{-}N$ interaction similar to that observed for $Ru^{II}$ is actually operative in the catalytic loop.




Scheme 2. Key steps, transition states and intermediates of the $Ir^{III}$-catalysed $H_2$- and transfer hydrogenations of carbonyl compounds.

In the following we present a computational study designed to clarify the situation by comparing $H_2PCH_2CH_2NH_2$- rather than $Ph_2PCH_2CH_2NH_2$-coordinated complexes as simplified models for $Ir^{III}$-catalysed transfer and $H_2$-hydrogenation of ketones. Prior to this work, computational methods have only been used once to elucidate the mechanism of iridium-catalysed transfer hydrogenations, to draw comparisons between model systems for the hydrogen transfer among alcohols and ketones in the presence of amino alcohol complexes of $Ir^I$ and $Ru^{II}$.[13] The concerted $H^-/H^+$ transfer in the second coordination sphere outlined above[5–8] was confirmed for the ruthenium-based systems, but, in contrast, the calculations suggested the iridium-catalysed reaction to involve hydrogen transfer between simultaneously coordinated alcohol and ketone.

## Results and Discussion

The calculated reaction pathways for the gas-phase reaction are shown in Scheme 2. The hydrido–dihydrogen complex **8** reacts via transition state $\mathbf{9}^{\ddagger}$ to give the dihydrido complex **7** with an activation energy of only 10–14 kcal mol$^{-1}$. This reaction is calculated to be exothermic by approximately 22 kcal mol$^{-1}$ and should therefore proceed rapidly under the experimental conditions. Complex **7**, in turn, can react with formaldehyde (as model carbonyl compound) via hydrogen-bonded precursor complex **10** and transition state $\mathbf{11}^{\ddagger}$ to give methanol complex **12**. This reaction is calculated to have a barrier (relative to **10**) of 10–12 kcal mol$^{-1}$ and to be exothermic by approximately 10 kcal mol$^{-1}$. Loss of the coordinated methanol to give the hydrido species **13** is calculated to be 10–13 kcal mol$^{-1}$ endothermic. Table 1 shows the calculated energies relative to **7**. The calculated total and zero-point energies are shown in Table S1 of the Supporting Information, as are the optimised Geometries as Gaussian Archive files.

Transition state $\mathbf{11}^{\ddagger}$ (shown in Figure 2) is particularly interesting as it represents a concerted process in which the hydride and the proton are transferred simultaneously. The nature of the process has been the subject of some speculation for the equivalent reaction in the ruthenium system.[6a,7,5a,c] Whereas Anderson and co-workers[6a] and Noyori et al.[5a,c] favour the concerted mechanism found here for iridium, van Leeuwen et al.[7] have proposed a stepwise process. However, to be sure that $\mathbf{11}^{\ddagger}$ is the correct transition state (i.e. that it connects **10** to **12**) we have performed nudged elastic band (NEB) calculations to confirm the reaction path.

The above results suggest that the iridium complex should react similarly to its ruthenium equivalent, in contrast to the experimental results described above. The gas-phase calculations therefore do not explain why the ruthenium catalyst can perform $H_2$-hydrogenation, whereas its iridium equivalent is limited to transfer hydrogenation. To resolve this difference, we performed further calculations in which we took the effect of a coordinating solvent molecule into account. Scheme 2 shows the systems considered. As model solvents,

Table 1. Calculated energies [kcal mol$^{-1}$] relative to **7** for the species shown in Scheme 2. The calculation levels are defined in the footnote.[a]

| | **7** | **8** | **9**$^{\ddagger}$ | **10** | **11**$^{\ddagger}$ | **12** | **12-ACE** |
|---|---|---|---|---|---|---|---|
| B-LANL2DZp | 0.0 | 27.5 | 39.8 | −11.0 | −2.0 | −11.4 | −20.9 |
| B-LACV3P+** | 0.0 | 24.1 | 35.6 | −9.4 | +0.6 | −10.8 | −18.4 |
| MP2(fc) | 0.0 | 24.2 | 36.3 | −11.9 | −0.2 | −11.0 | −25.9 |
| P-LANL2DZp | 0.0 | 25.1 | 35.8 | −12.1 | −11.8 | −14.3 | −28.2 |
| P-LACV3P+** | 0.0 | 21.1 | 31.4 | −10.4 | -9.4 | −13.8 | −25.0 |
| | **12-*i*Pro** | **12-THF** | **13** | **13-ACE** | **13-*i*Pro** | **13-THF** | |
| B-LANL2DZp | −19.9 | −19.2 | 0.2 | −7.4 | −4.9 | −3.2 | |
| B-LACV3P+** | −16.5 | −17.3 | −0.9 | −6.7 | −3.2 | −3.7 | |
| MP2(fc) | −24.6 | −28.0 | 2.0 | −9.4 | −6.9 | −9.7 | |
| P-LANL2DZp | −27.1 | −25.7 | −1.0 | −10.9 | −8.4 | −6.4 | |
| P-LACV3P+** | −23.2 | −23.8 | −2.2 | −10.5 | −6.9 | −11.2 | |

[a] The calculation levels are abbreviated in the table and are defined as follows: B-LANL2DZp: RB3LYP/LANL2DZp+ZPE(B3LYP/LANL2DZp); B-LACV3P+**: RB3LYP/LACV3P+**+ZPE(B3LYP/LANL2DZp); MP2(fc): RMP2(fc)/LACV3P+**//B3LYP/LACV3P+**+ZPE(B3LYP/LANL2DZp); P-LANL2DZp: RPW91PW91/LANL2DZp+ZPE(PW91PW91/LANL2DZp); P-LACV3P+**: RPW91P91/LANL2DZp+ZPE(PW91/LANL2DZp)

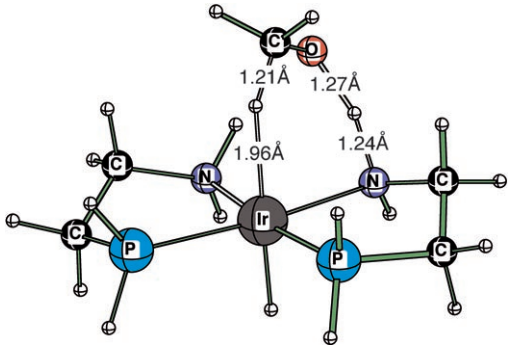



Figure 2. B3LYP/LACV3P+**-optimised structure of the transition state **11**$^{\ddagger}$. Bond lengths are given in Å.

**S**, we used acetone (**ACE**), isopropanol (***i*Pro**) and tetrahydrofuran (**THF**).

The key reaction is that of **13-S** with $H_2$ to give **8** (i.e. displacement of the coordinated solvent molecule by dihydrogen). This process is found to be endothermic by 7–11, 7–14 and 10–13 kcal mol$^{-1}$ for isopropanol, THF and acetone, respectively. Thus, this step prevents the $H_2$-hydrogenation in coordinating solvents.

The question therefore remains as to whether $H_2$ can displace the same solvent molecules from the ruthenium complex. Table 2 shows the calculated energies needed to displace a coordinated solvent molecule from **13-S** for the Ir$^{III}$ (**13Ir-S**) and Ru$^{II}$ (**13Ru-S**) complexes by dihydrogen.

The results shown in Table 2 provide a convincing rationalisation for the observed difference between the two types of complex. The calculated heats of reaction for displacing the solvent molecule by dihydrogen are all slightly endothermic, thermoneutral or slightly exothermic, depending on the level of calculation and the solvent. The calculations all agree, however, that displacing the solvent by $H_2$ is 6–12 kcal mol$^{-1}$ less favourable for the iridium catalyst than for the ruthenium equivalent. Thus, the key step that distinguishes between transfer and $H_2$-hydrogenation becomes energetically inaccessible for the iridium catalyst, which therefore can only catalyse transfer hydrogenation.

Notably, we have observed comparably dominant effects of coordinated solvent molecules twice previously. Both the anomalous effects of N-alkylation on the properties of Ni$^{I}$, Ni$^{II}$, Cr$^{II}$ and Cr$^{III}$ cyclam complexes[14] and the relative abilities of cob(II)alamine and cob(III)alamine to complex NO in aqueous solution are determined by the strength of coordination of solvent molecules to the metal centres.[15,16] In all these cases, DFT and ab initio calculations played an important role in defining the effect of solvent. Note that all these examples involve the microscopic (i.e. molecular) effect of a single solvent molecule rather than the more general macroscopic solvent effect.

Why is this effect more important for the Ir$^{III}$ complexes than for their Ru$^{II}$ equivalents? The answer is almost disappointingly simple. Charged complexes are much stronger Lewis acceptors than neutral ones, so that the interactions of the cationic Ir$^{III}$ species with Lewis donor solvents is far stronger than that of the neutral Ru$^{II}$ complexes. This effect does not play as strong a role in binding $H_2$ as metal–$H_2$ interactions depend strongly on the strength of the M−H bond and less so on the Lewis acceptor characteristics of the metal. Thus, the balance between metal-solvent and metal-$H_2$ interactions shifts to the advantage of the former for cationic complexes.

Noyori and co-workers[17] have suggested that an equivalent mechanism for splitting $H_2$ involving diamine and diphosphine ligands may be operative for ruthenium catalysts. As shown below, $H_2$-addition for these species is calculated (P-LACV3P+**) to be exother-

Table 2. Calculated energies for the reaction **13-S**+$H_2$→**8**+**S**. The results are shown for the Ir$^{III}$ and Ru$^{II}$ complexes and for the three different solvents. The calculation levels are as defined in the footnote of Table 1.

| | **13Ir-ACE** | **13Ir-*i*Pro** | **13Ir-THF** | **13Ru-ACE** | **13Ru-*i*Pro** | **13Ru-THF** |
|---|---|---|---|---|---|---|
| B-LANL2DZp | 14.9 | 12.4 | 10.7 | 3.1 | [a] | 2.6 |
| B-LACV3P+** | 10.3 | 6.8 | 7.3 | 0.1 | [a] | 1.2 |
| MP2(fc) | 13.4 | 10.9 | 13.7 | 2.7 | [a] | 6.3 |
| P-LANL2DZp | 16.5 | 14.0 | 12.0 | 3.3 | [a] | 1.2 |
| P-LACV3P+** | 11.4 | 7.8 | 12.1 | 0.0 | [a] | −0.3 |

[a] No bound isopropanol complex found.

mic enough to displace solvent in all cases and not to depend strongly on the exact $(PN)_2$ or $P_2,N_2$ architecture of the ligands.

## Conclusion

Our calculations show that the fundamental mechanisms of transfer and $H_2$-hydrogenation are very similar for the ruthenium and iridium-based catalyst systems. However, the observed inability of the cationic iridium system to catalyse $H_2$-hydrogenation can be traced back to the substitution reaction in which molecular hydrogen displaces a donor solvent molecule. This substitution is calculated to be significantly endothermic for the cationic iridium system, but close to thermoneutral for the well-known ruthenium catalysts. This change is due to the more effective electrostatic coordination of the donor solvent molecules to the cationic iridium complex compared with the neutral ruthenium equivalent.

## Experimental Section

All structures were fully optimised by using the B3LYP hybrid density functional[18–20] and the LANL2DZp basis set, i.e., with pseudopotentials on iridium and phosphorus and the valence basis set augmented with polarisation functions,[21,22] and characterised as minima or transition states by calculating the normal vibrations within the harmonic approximation.[23] Structures were subsequently refined at the B3LYP/LACV3P+** level,[24] i.e., with diffuse functions on non-hydrogen atoms, to minimise the basis set superposition error (BSSE).[25] Zero-point energies were calculated at the B3LYP/LANL2DZp level. Single-point energy calculations were performed at the MP2/LACV3P+**//B3LYP/LACV3P+** level.[26] All calculations used the Gaussian03 suite of programs.[27]

## Acknowledgements

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