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Probing the Origin of Challenge of Realizing Metallaphosphabenzene: Unfavorable 1,2-Migration in Metallapyridines Becomes Feasible in Metallaphosphabenzene

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Metallabenzenes have attracted considerable interest of both theoretical and experimental chemists. However, metallaphosphabenzene has never been synthesized. Thus, understanding the origin of the challenge of synthesizing metallaphosphabenzene is particularly urgent for experimentalists. Now density functional theory (DFT) calculations have been carried out to examine this issue. Our results reveal that the 1,2-migration in metallapyridines is unfavorable whereas such a 1,2-migration in metallaphosphabenzene is feasible, which can be rationalized by the reluctance of phosphorus to participate in π bonding. In addition, π -donor ligands and the 5d transition metals can stabilize metallaphosphabenzene. Compared with hydride and methyl migration, the chloride migration has a relatively lower activation barrier due to the polarization of the M=P bond. CO ligand could further decrease the reaction barrier of the migration due to the reduction of the interaction between the metal centre and the phosphorus atom. All of these findings could help synthetic chemists to realize the first metallaphosphabenzene.

The chemistry of transition-metal-containing aromatics has attracted continuously increasing attention^{1–6} since metallabenzene was first predicted by Hoffmann⁷ and isolated by Roper⁸. In contrast, the heteroatom-containing metallabenzenes such as metallapyrylium^{9,10}, metallathiabenzene^{11,12}, metallapyridine^{13,14}, metallapyrrole^{15,16}, and metallathiophene^{17,18} are relatively less developed. To the best of our knowledge, metallaphosphabenzene has not been synthesized so far, although its structure and property were investigated theoretically^{19,20}. The difficulties in the synthesis and isolation of metallaphosphabenzene could be due to the reluctance of phosphorus to participate in multiple bonds²¹, similar to our previous finding²² that 1,2-migration in metallasilabenzenes becomes favorable due to the reluctance of silicon to participate in π bonding. Thus, 1,2-migration in metallaphosphabenzene may also occur (Fig. 1A). Another reason for the difficulties in the synthesis of metallaphosphabenzene could be facile isomerization of metallaphosphabenzene **II** to the corresponding η^5 -phosphacyclopentadiene (PCp) metal complex **I**, similar to that of metallabenzenes^{23,24}. Indeed, our previous study²⁰ shows that substituents have a significant effect on the thermodynamics and kinetics of the rearrangement reactions. Thus, an interconversion between metallaphosphabenzene and the corresponding η^5 -PCp complexes can be achieved theoretically by simply tuning the substituents on the metallacycles. In comparison, the isomerization from metallaphosphabenzene **II** to nonaromatic analogue **III** has never been reported. Our ongoing interest in aromaticity^{25–32} and reaction mechanisms^{33–37} has led us to test the hypothetical isomerization of metallaphosphabenzene **II** to the nonaromatic

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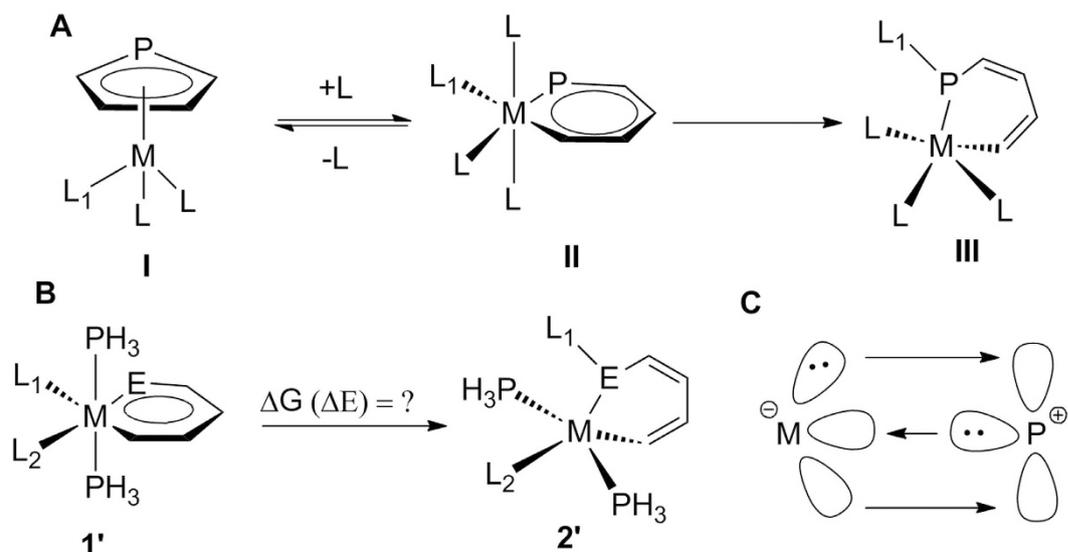


Figure 1. (A) Isomerizations from metallaphosphabenzene (II) to η^5 -PCp metal complex (I) or non-aromatic complex (III). (B) 1,2-Migration of metallapyridines (E=N) and metallaphosphabenzene (E=P). (C) Schematic diagram of the M=P bonding in phosphinidene complex.

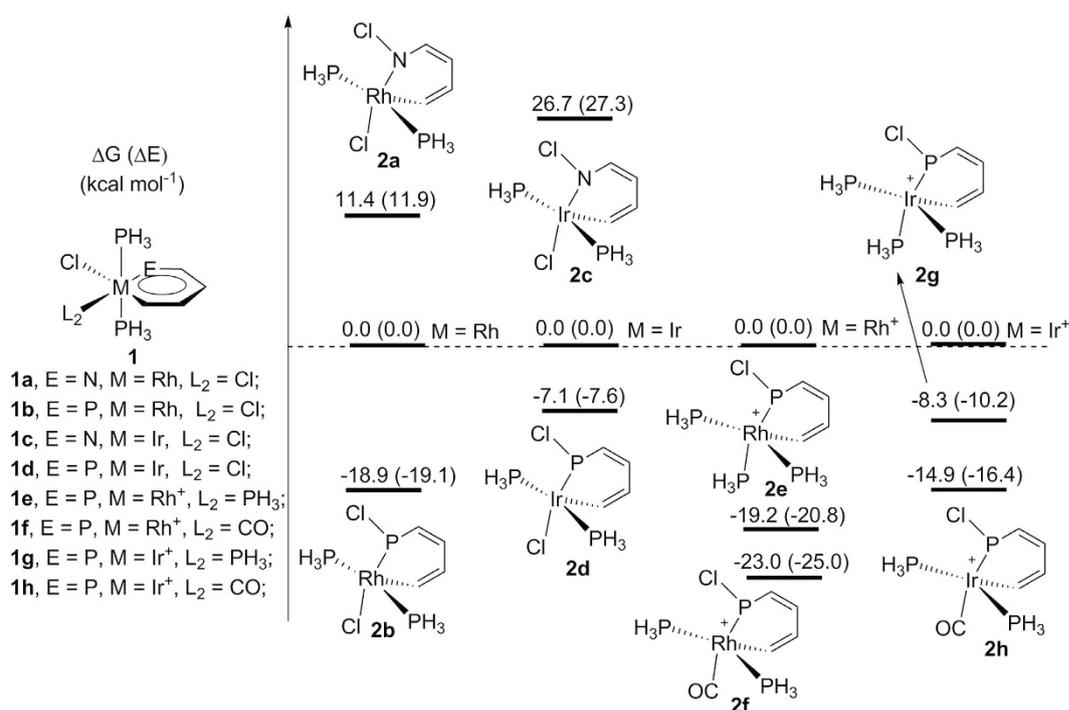


Figure 2. Thermodynamic stabilities of metallaphosphabenzene (1a–1h) compared with its nonaromatic analogues (2a–2h) formed by chloride migration.

analogue III as described in Fig 1A. Here we carry out thorough density function theory (DFT) calculations on this issue. How the ligands, metal centers affect the reaction mechanisms will be investigated in detail.

Results

Thermodynamic aspect of chloride migration. In this work, we focus on *o*-metallaphosphabenzene (Fig. 2, 1a–1h) as a phosphorus atom at the ortho position on metallaphosphabenzene, which was reported to be more stable than those at the meta and para positions by Solà and co-workers¹⁹. As shown in Fig. 2, both 1a and 1c are much more stable than their nonaromatic analogues 2a and 2c thermodynamically. In sharp contrast, complexes 2b and 2d are thermodynamically more stable than metallaphosphabenzene 1b and 1d. This could be one of the reasons why some metallapyridines have been isolated whereas metallaphosphabenzene have never been

Complex(1')	M	E	L ₁	L ₂	PR(2')
1a'	Ru ⁻	N	Cl	Cl	35.1 (36.7)
1b'	Ru ⁻	P	Cl	Cl	-1.4 (-0.4)
1c'	Os ⁻	N	Cl	Cl	54.6 (56.7)
1d'	Os ⁻	P	Cl	Cl	10.4 (10.5)
1e'	Ru	P	Cl	PH ₃	-2.6 (-2.4)
1f'	Ru	P	Cl	CO	-8.7 (-9.7)
1g'	Os	P	Cl	PH ₃	7.8 (7.1)
1h'	Os	P	Cl	CO	1.8 (1.3)
1n'	Ru	P	H	PH ₃	-18.9 (-20.3)
1o'	Os	P	H	PH ₃	-5.4 (-7.2)
1p'	Ru	P	Me	PH ₃	-26.9 (-28.9)
1q'	Os	P	Me	PH ₃	-13.6 (-14.6)

Table 1. Calculated reaction energies for the 1,2-migration of metallaaromatics to its nonaromatic analogues based on Fig. 1B. The relative Gibbs free energies at 298 K and electronic energies (in parentheses) are given in kcal mol⁻¹.

	Charge (M)	Charge (E)	Electron population (E)
1a	-0.69	-0.32	1.23
1b	-1.14	+0.88	0.83
1c	-0.57	-0.37	1.27
1d	-1.09	+0.82	0.86

Table 2. The charges and electron populations of M=E bonds (E=N, or P) in 1a–1d.

synthesized. Apparently, the stability of iridaphosphabenzene and iridapyridine relative to their nonaromatic analogues increases dramatically in comparison with rhodaphosphabenzene and rhodapyridine due to more diffuse *d* orbitals, in line with previous results that 5*d* metallacycles are more stable than their 4*d* analogues^{1–3,19}. These results are also applicable to ruthenaphosphabenzene and osmaphosphabenzene (Fig. 1B, 1a'–1d' in Table 1). Especially for ruthenapyridine 1a' and osmapyridine 1c', both of them are much more stable than their nonaromatic 2a' and 2c' by fixing the N–Cl bond with the value of 1.78 Å (the N–Cl bond length in 2a) because 2a' and 2c' always rearranged to 1a' and 1c' by normal optimization.

What causes this significant difference between metallapyridines and metallaphosphabenzene? It is well-known that the phosphorus atom has larger size difference in *s* and *p* valence orbitals than the nitrogen atom, leading to a lower tendency for hybridization to form multiple bonds²¹. Thus, the back donation from the *d* orbital of the metal center to the vacant *p* orbital of the phosphorus atom (Fig. 1C) will become weaker. Indeed, according to the NBO analysis of complexes 1c–1d (Table 2), the results indicate that the M=P bond^{38–41} is highly polarized toward M^{δ-}–P^{δ+}. For example, the nitrogen atom has contributed 1.27 electron population in the Ir=N double bond of 1c. In sharp contrast, the contribution from the phosphorus atom is reduced by 0.41 electron in 1d than that from the nitrogen atom in 1c. Meanwhile, the NBO charge on the phosphorus atom becomes positive, which contrasts sharply with the negative charge on the nitrogen. Therefore, the reversed M=P bond polarization plays an important role in 1,2-migration in metallaphosphabenzene. All these results indicate that the phosphorus atom is reluctant to participate in π bonding so that 1,2-migration in metallaphosphabenzene could become thermodynamically favorable whereas such a migration in metallapyridine is unfavorable.

Effect of ligands on the chloride migration in metallaphosphabenzene. The effect of ligands has also been investigated to tune the stability of metallaphosphabenzene. Our results indicated the ligands have a remarkable effect on the relative stability of metallaphosphabenzene in comparison with the nonaromatic analogues (1e–1h and 2e–2h in Fig. 2, 1e'–1h' in Table 1). Specifically, when π -acceptor ligand CO is introduced to replace the chloride, reaction energies (Gibbs free energies) for the formation of 2f and 2h from 1f and 1h are -23.0 and -14.9 kcal mol⁻¹, respectively, indicating that metallaphosphabenzene prefer π -donor ligands. When the chloride is replaced by one ligand PH₃, the instability of 1e and 1g is increased slightly in comparison with 1b and 1d in Fig. 2. This is understandable because the M=P double bond in metallaphosphabenzene is strongly polarized toward M^{δ-}–P^{δ+}, indicating that the phosphorus atom is highly electron-deficient. Therefore, π -acceptor ligand CO can decrease the electron density of the metal center, thus weakening the bonding between the metal center and metal-bonded phosphorus. In other words, the M=P double bond will become weaker and the polarization will be enhanced, leading to relatively high stability of nonaromatic 2f and 2h. The stabilizing effect of ligands in metallaphosphabenzene increases in the order CO < PH₃ < Cl. Therefore, π -donor and π -acceptor ligands are suggested for the synthesis of metallaphosphabenzene and nonaromatic analogues, respectively.

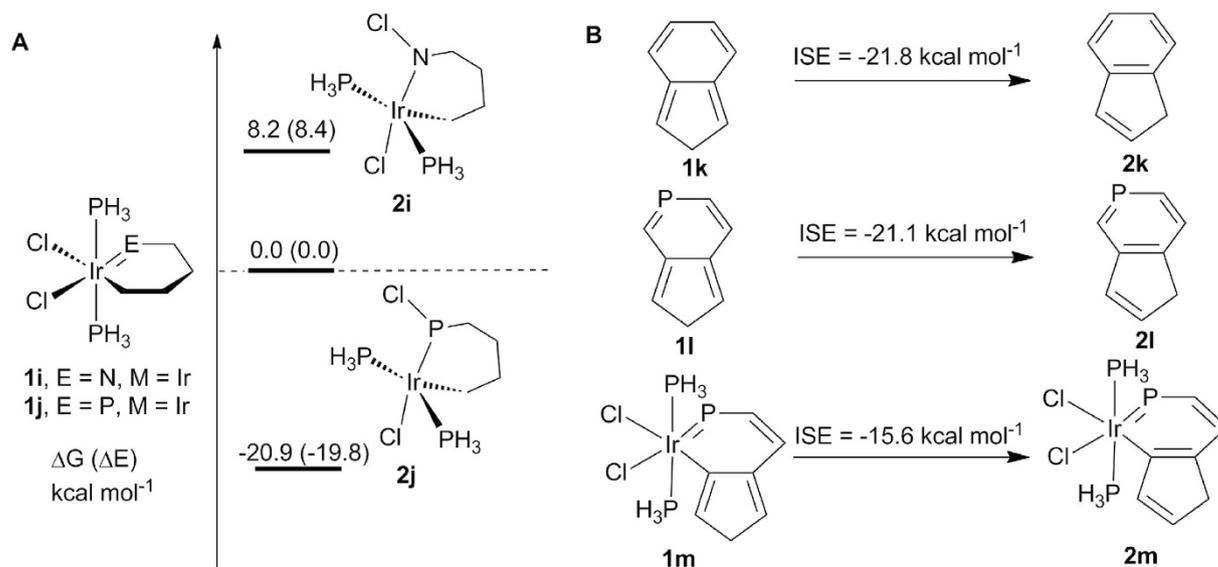


Figure 3. (A) Energy profiles calculated for the corresponding chloride migration of nonaromatic complexes. (B) Indene-isoindene ISE evaluations of the aromaticity of **1k-2m**.

Effect of aromaticity on the chloride migration. The aromaticity effect has also been examined in metallaphosphabenzene with similar migration of nonaromatic cyclic complexes by changing the $M=E$ double bond to $M-E$ single bond (Fig. 3A). Apparently, the 1,2-migration in nonaromatic cycles become more favorable thermodynamically. The reaction energy (ΔG) from **1i** to **2i** is computed to be 8.2 kcal mol^{-1} whereas that from **1j** to **2j** becomes $-20.9 \text{ kcal mol}^{-1}$. It is understandable because when aromaticity in the reactants is lost, such a chloride migration should become thermodynamically more favorable. The contribution from aromaticity in iridaphosphabenzene **1d** is thus evaluated quantitatively ($-13.8 \text{ kcal mol}^{-1}$) by computing the energy difference between the reaction from **1d** to **2d** and that from **1j** to **2j**.

To gain an insight into the aromaticity in metallaphosphabenzene, we employed the “isomerization stabilization energy” (ISE) method, a convenient tool to evaluate the magnitude of the aromaticity in the ground state and the lowest triplet state^{25,28,42,43}. The indene-isoindene ISE approach is homodesmotic and has the advantage that all carbon atoms in the six-membered ring are sp^2 -hybridized in both the reactants and products. As shown in Fig. 3B, benzene and phosphabenzene have comparable ISE values (-21.8 and $-21.1 \text{ kcal mol}^{-1}$, respectively). Nevertheless, the ISE value of iridaphosphabenzene is just 71.6% of that in benzene, indicating the aromaticity in metallaphosphabenzene is fairly reduced. In addition, the ISE value ($-15.6 \text{ kcal mol}^{-1}$) of iridaphosphabenzene is comparable to the aromaticity contribution ($-13.8 \text{ kcal mol}^{-1}$), indicating the reliability of our calculations.

1,2-Migration of hydride and methyl groups in metallaphosphabenzene. To examine the scope of our findings, we investigated the 1,2-migration of hydride and methyl groups (Fig. 4, and **1n'-1q'** in Table 1). The negative values indicate that these migrations are also feasible. The results in Fig. 4 show that the thermodynamic stability of metallaphosphabenzene relative to its nonaromatic analogues with the hydride and methyl groups are higher than those with the chloride ligand, which could be mainly attributed to the higher bond strength of $P-C$ and $P-H$ bond than that of $P-Cl$ in the products.

Kinetics of chloride, hydride and methyl migration. To have a deeper understanding of the reaction mechanisms, we have examined the kinetics of 1,2-migration from metallaaromatics to its nonaromatic analogues (Fig. 5 and Table 3). The calculations show that reaction barriers are particularly low. All these values are lower than $24.2 \text{ kcal mol}^{-1}$ at 25°C according to the Eyring equation⁴⁴. In addition, iridaphosphabenzene complexes have relative higher reaction barriers for 1,2-migration than rhodaphosphabenzene analogues. It could be due to the second-row transition metal rhodium has less diffuse d orbitals in comparison with iridium. Therefore, the $Rh=P$ bond becomes relatively weak as evidenced by the Wiberg bond index (WBI) (1.00 and 1.07 for the $Rh=P$ bond and $Ir=P$ bond in **1b** and **1d**, respectively). The lowest barrier is found when the ligand is CO. As a strong π acceptor ligand, CO can reduce the interaction between the metal center and the phosphorus atom, thus weakening the metal-phosphorus bonds in metallaphosphabenzene⁴¹. In addition, as shown in Table 3, the reaction barriers for the migration of hydride and methyl are a little higher than that of chloride. A plausible explanation for these general observations is clarified below. The results could be understandable because the $Rh-Cl$ in **1e** has a weaker bond strength (WBI: 0.62) than $Rh-H$ in **1n** (WBI: 0.65) and $Rh-C$ in **1p** (WBI: 0.66), respectively. In addition, it is known that the $M=P$ bond is highly polarized in metallaphosphabenzene, and the ligand with higher electronegativity could promote the migration. Hence, a lower barrier for migration of chloride is expected in the reaction. In sharp contrast, all the metallapyridines are thermodynamically more stable than their nonaromatic analogues (Supplementary Fig. S1 and Table S1).

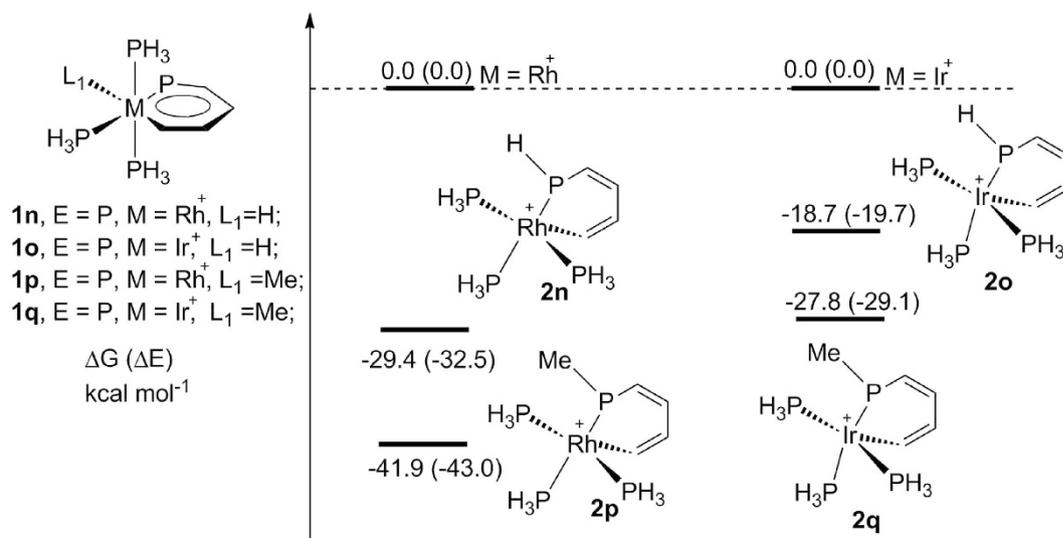


Figure 4. Thermodynamic stabilities of metallaaromatics (**1n–1q**) compared with its nonaromatic analogues (**2n–2q**) formed by hydride and methyl migration.

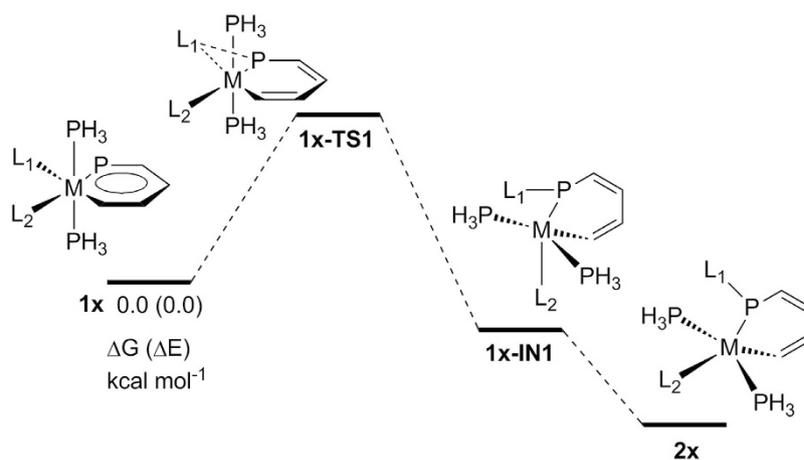


Figure 5. Energy profiles calculated for the 1,2-migration of metallaaromatics to its nonaromatic analogues.

	1X		1X-TS1	1X-IN1	2X
M = Os	$L_2 = PH_3$	$L_1 = Cl$	22.2 (20.8)	18.7 (18.6)	7.8 (7.1)
M = Os	$L_2 = CO$	$L_1 = Cl$	14.0 (12.5)	12.8 (11.5)	1.8 (1.3)
M = Os	$L_2 = PH_3$	$L_1 = H$	17.3 (16.7)	0.7 (−0.7)	−5.4 (−7.2)
M = Ru	$L_2 = PH_3$	$L_1 = Cl$	14.6 (14.0)	5.9 (6.3)	−2.6 (−2.4)
M = Ru	$L_2 = CO$	$L_1 = Cl$	9.5 (7.8)	−1.5 (−1.3)	−8.7 (−9.7)
M = Ru	$L_2 = PH_3$	$L_1 = H$	10.9 (11.3)	−14.6 (−14.6)	−18.9 (−20.3)
M = Rh ⁺	$L_2 = PH_3$	$L_1 = Cl$	6.5 (6.1)	−11.2 (−9.0)	−19.2 (−20.8)
M = Rh ⁺	$L_2 = CO$	$L_1 = Cl$	5.9 (4.7)	−11.1 (−10.6)	−23.0 (−25.0)
M = Rh ⁺	$L_2 = PH_3$	$L_1 = H$	8.8 (8.2)	−22.3 (−23.2)	−29.4 (−32.5)
M = Rh ⁺	$L_2 = PH_3$	$L_1 = Me$	8.4 (8.9)	−33.1 (−32.4)	−41.9 (−43.0)
M = Ir ⁺	$L_2 = PH_3$	$L_1 = Cl$	12.3 (10.5)	4.2 (4.2)	−8.3 (−10.2)
M = Ir ⁺	$L_2 = CO$	$L_1 = Cl$	8.1 (6.5)	0.9 (0.4)	−14.9 (−16.4)
M = Ir ⁺	$L_2 = PH_3$	$L_1 = H$	14.2 (14.6)	−9.1 (−8.9)	−18.7 (−19.7)
M = Ir ⁺	$L_2 = PH_3$	$L_1 = Me$	14.5 (14.6)	−17.2 (−15.9)	−27.8 (−29.1)

Table 3. Calculated reaction energies and barriers for the 1,2-migration of metallaaromatics to its nonaromatic analogues based on Fig. 5. The relative Gibbs free energies at 298 K and electronic energies (in parentheses) are given in kcal mol⁻¹.

Discussion

The 1,2-migration on a series of metallaphosphabenzenes and metallapyridines have been studied thoroughly by DFT calculations. The effects of metal centers, ligands, aromaticity, and migration groups were examined systematically. Our results reveal that due to the reluctance of phosphorus to participate in π bonding, such a migration in metallapyridines is thermodynamically unfavorable whereas it becomes feasible in metallaphosphabenzenes, which could be the origin of challenge of realizing metallaphosphabenzenes. The 4d transition metals and π -acceptor ligands have the tendency to form nonaromatic analogues rather than metallaphosphabenzenes whereas π -donor ligands and the 5d transition metals can stabilize metallaphosphabenzenes. In addition, the chloride migration has relatively lower reaction barrier due to the weaker bond strength of M-L₁ in metallaphosphabenzene in comparison with hydride and methyl migrations. All these findings could be useful for synthetic chemists to realize the first metallaphosphabenzene.

Methods

Computational details. The M05⁴⁵ level of density functional theory was applied to optimize all of the structures studied in the gas phase. Frequency calculations at the same level of theory have also been performed to identify all stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency). Calculations of intrinsic reaction coordinates (IRC)^{46,47} were also carried out on transition states to ensure that such structures are indeed connecting two minima. The LanL2DZ basis set⁴⁸ was employed to describe Ru, Os, Rh, Ir, P and Cl whereas the 6-31G(d) basis set⁴⁹ was used for all other atoms. Polarization functions were added for P ($\xi(d) = 0.340$), Cl ($\xi(d) = 0.514$), Ru ($\xi(f) = 1.235$), Os ($\xi(f) = 0.886$), Rh ($\xi(f) = 1.350$), and Ir ($\xi(f) = 0.938$)^{50,51}. In order to examine the effect of function for these complexes, the density functional M06L⁵² has been used with basis sets unchanged. The relative Gibbs free energies of **2b** to **1b**, **2d** to **1d** are -13.1 and -4.1 kcal mol⁻¹, respectively, which are comparable to those (-18.9 and -7.1 kcal mol⁻¹) at the M05/6-31G(d) level, indicating that the functional dependence is small. To examine the effect of basis sets, we employed a larger 6-311 + G(d) basis set⁵³ to optimize the complexes **1a-1d**, **2a-2d** (Fig. 2). The additional calculations show that the basis set dependence is small. For example, using the 6-31G(d) basis set in the gas phase, the relative free energies of **2a-2d** to **1a-b** are 0.0, 11.4, -18.9 , 26.7 and -7.1 kcal mol⁻¹, respectively. Using the larger 6-311 + G(d) basis set, the relative free energies are 0.0, 9.6, -20.1 , 24.6 and -8.3 kcal mol⁻¹, respectively. To examine the solvent effect^{54,55}, we optimized the structures (**1b**, **1d**, **2b** and **2d**) using the PCM model⁵⁶ with benzene as the solvent. The additional calculations show that the solvent effect is small. For example, the relative free energies of **2b** to **1b**, **2d** to **1d** are -16.1 and -5.0 kcal mol⁻¹ (-18.9 and -7.1 kcal mol⁻¹ in Fig. 2) when the solvent effect is included. Moreover, the solvent effect is also small for the transition states. For instance, when the solvent effect is included, the reaction barriers of **1e-TS1** and **1f-TS1** become 8.7 and 5.8 kcal mol⁻¹, which are close to those in Table 3 (6.5 and 5.9 kcal mol⁻¹, respectively). In addition, the polar solvents (ethanol and DMSO) are also been taken into account (see Supplementary Table S2), and the results for the polar solvents suggest that the solvent effect is also small. In order to examine the ligand effect of the simplified PH₃, we use PMe₃ to replace PH₃. The results show that the ligand effect is small. For instance, using the ligand PMe₃, the relative free energy of **2b** to **1b** is -14.0 kcal mol⁻¹, which is close to -18.9 kcal mol⁻¹ with the PH₃ ligand in Fig. 2. Calculations on complexes **1a-1h** indicate that all of them in the singlet ground state are lower in energy than those in the lowest triplet state (Supplementary Table S3), indicating all of them have the close-shell singlet ground state. In addition, the thermodynamics of 1,2 migration on complexes **1a-1h** in the lowest triplet state are also examined and the results are similar to those in Fig. 2. Specifically, the relative Gibbs free energies of **2a-2h** to **1a-1h** are 14.6, -17.1 , 40.8, -5.0 , -19.3 , -30.2 , -10.1 and -16.3 kcal mol⁻¹, respectively. The natural bond orbital (NBO, Version 3.1) was also used to obtain Wiberg bond indices (bond orders)⁵⁷. All calculations were carried out with the Gaussian 03 package⁵⁸ except the M06L calculations, which were performed by Gaussian 09 package⁵⁹. All the relative Gibbs free energies calculated at 298 K and electronic energies (in parentheses) are given in kcal mol⁻¹.

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Author Contributions

J.Z. conceived and directed the project. J.W. and Y.H. performed theoretical calculations. J.W. and J.Z. wrote the paper. All authors discussed the results and contributed to the preparation of the final manuscript.

Additional Information

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