Cycloaddition Reactions of Metalloaromatic Complexes of Iridium and Rhodium: A Mechanistic DFT Investigation

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Abstract: The mechanistic details of 1,2- and 1,4-cycloaddition reactions of acetone, CO, and CS2 to isostructural iridiabenzenes, iridiapyrromethene, and iridiathiabenzenes complexes, as well as their rhodium analogues, were elucidated by density functional theory (DFT) at the PCM/mPW1K/SDD-level of theory. The calculated reaction profiles concur with reported experimental observations. It was found that the first complex reacts via a concerted reaction mechanism, while the latter two react by a stepwise mechanism. Several factors affecting the reaction mechanisms and outcome were identified. They include the composition and size of the metal-aromatic ring, the length of the substrate C=X (X = O, S) bond, the geometry of the product, the symmetry of the frontier molecular orbitals, and the type of reaction mechanism involved.

Introduction

Kekulé’s discovery of the aromatic nature of benzene was possibly one of the greatest landmarks in chemistry.1 The impact has been felt in most fields of science. Aromaticity plays an important role in organic, industrial, and medicinal chemistry, and in life sciences where four amino acids (phenylalanine, tyrosine, tryptophan, and histidine) contain aromatic rings. Subsequent research included substituting one or more CH units of benzene. Initially this involved elements such as N, O, P, and S, but later progress included main group metals (e.g., B2, Si3,4 Ge,5 and As6,7) and even transition metals8,9 (e.g., Nb,10,11 Ta,10–12 Mo,13 W,14 Fe,15 Ru,16 Re,17,18 Os,19,20 Ni,23 Pt,24 and Ir25–35). Recently, examples of a 1,4-phosphaboratabenzen36 and an osmabenzyne37–39 were reported. In addition, metalloaromatic complexes have been suggested as intermediates in various reactions.15,16,40–42

Despite the recent extensive interest in metalloaromatic complexes, detailed mechanistic and theoretical investigations into the formation and reactivity of these interesting systems remain remarkably scarce.8 Before the first reported isolation

of a metallabenzene complex by Roper et al.,\textsuperscript{21} theoretical studies by Thorn and Hoffmann predicted that metallabenzene complexes of Mn and Rh may be viable synthetic targets.\textsuperscript{43} There are also a few theoretical reports on metalloaromaticity in metal chelate rings\textsuperscript{44} and aromaticity in all-metal clusters.\textsuperscript{45–48} More recently, we communicated on our initial calculations on the reactivity of metalloaromatic iridium complexes toward acetone.\textsuperscript{49}

There has been considerable debate whether metallabenzene complexes can be considered aromatic.\textsuperscript{8} The aromatic nature of these complexes is consistent with the Hückel rule (4n + 2 \pi electrons) and molecular orbital calculations.\textsuperscript{43} The flat metal-organic rings do not show alternating single and double bonds. In addition, their NMR spectra show downfield shifts attributed to aromatic ring currents.\textsuperscript{31} The aromatic nature is also apparent from the observed reactivity. For instance, osmabenzene undergoes electrophilic aromatic substitution much in the same way as benzene (Scheme 1).\textsuperscript{22}

The cycloaddition reactivity of acetone, CO\textsubscript{2}, CS\textsubscript{2}, and other substrates with metallabenzene (1C),\textsuperscript{3,4} metallapyrilium (1O),\textsuperscript{13} and metallathiabenzenes (1S)\textsuperscript{35} complexes of iridium reported by Beeke et al. seems to contrast the aromatic nature (Scheme 2). Remarkably, acetone reacts reversibly with the metallabenzene complex (1C) to give the 1,4-addition product (2) but not with the other two complexes (1C and 1S). Furthermore, the metallabenzenes complex (1C) adds CO\textsubscript{2} in a 1,2-manner (3) and the isovalent CS\textsubscript{2} in a 1,4-fashion (4). Although these selective addition reactions have been studied in detail, the strikingly different reactivity patterns are not fully understood. The use of transition metals in cycloadditions is common. There are numerous examples where the metal complex participates in the reaction and is one of the reactants and the metal is present in the product.\textsuperscript{50,51} In many cases, they assist in the reaction but are not part of the products.\textsuperscript{52–54}

Formally, the organic moiety of a metallabenzene complex can be viewed as a vinyl carbene ligand (Scheme 3), although experimental and theoretical studies show that these complexes are best considered as aromatic (vide supra).\textsuperscript{8} However, the cycloaddition chemistry might be reminiscent of carbene complexes and of organic alklenes and dienes. A number of related reactions of metalla-carbenes with ketones, CO\textsubscript{2}, and CS\textsubscript{2} have been reported (Scheme 4). For instance, the tungsten complexes Cl\textsubscript{2}W(O)(\textsuperscript{=CH\textsubscript{2}}) and Cl\textsubscript{2}W(O)(\textsuperscript{=CH\textsubscript{3}}) react with ketones and aldehydes to give substituted olefins (eq 1).\textsuperscript{55} The iridium complex Cp\textsuperscript{+}(PM\textsubscript{3})\textsubscript{2}Ir=CH\textsubscript{2}, formed by the photocatalytic extrusion of acetone from a 2-oxoiridacycle, reacts with CO\textsubscript{2} to give the 1,2-addition product (eq 2).\textsuperscript{56} The similar nickel complex (dtbpe)Ni=CH\textsubscript{2} reacts with 2 equivalents of CO\textsubscript{2} yielding a six-membered metallacycle (eq 3).\textsuperscript{57} The chromium complex [(CO)\textsubscript{6}Cr=CPh\textsubscript{2}(OMe)]\textsuperscript{2+} seems to react with CO\textsubscript{2} in a similar fashion (eq 4).\textsuperscript{58} The tungsten complex (PM\textsubscript{3})\textsubscript{2}I\textsubscript{2}(CO)\textsubscript{2}Ni=CH\textsubscript{2} reacts with CS\textsubscript{2} in the presence of PPh\textsubscript{3} to give the \eta\textsuperscript{2}-alkynethiol complex (eq 5).\textsuperscript{59}

Density functional theory (DFT) has become a powerful tool in recent years in the investigation of transition metal reactions,\textsuperscript{60,61} especially due to the rapid increase in available computer power and the development of new methods. For example, we have used DFT to investigate H/D scrambling in TpPtMeH\textsubscript{2} (Tp = hydrido-tris-pyrazolylborate),\textsuperscript{62} the rhodium

catalyzed hydrogenation of acetone, the palladium catalyzed Heck reaction, stabilization strategies of silanones, and C–H versus C–C bond activation by rhodium complexes. The challenge here is clear: is it possible by means of DFT to identify the transition states were confirmed by having only one imaginary vibrational mode suitable for the desired reaction. In addition, an imaginary reaction coordinate (IRC) calculation was performed on each transition state to confirm connectivity with the reactant(s) and the product.

Bulk solvation effects were approximated by single-point mPW1K/SDB-cc-pVDZ energy calculations using a polarized continuum (overlapping spheres) model (PCM). Either acetone (ε = 20.7) or tetrahydrofuran (ε = 7.58) was used depending on the solvent used in the experimental procedures. Energies at this level of theory are denoted PCM/mPW1K/SDB-cc-pVDZ//mPW1K/SDD.

Since Gaussian 98 uses the same number of radial grid points throughout the periodic table, the “ultrafine” grid, that is, a pruned (99,590) grid, was used throughout the calculations as recommended in ref 89. Nevertheless, due to the size of the systems with PMe3 ligands (vide infra), such a grid makes the calculations far too computationally expensive and the default grid, that is, a pruned (75,302) grid, was used for the mPW1K/SDD geometry optimizations and the ultrafine grid for the mPW1K/SDB-cc-pVDZ single-point energy calculations, both in the gas phase calculations and with the PCM model. Likewise, the lengthy IRC calculations were carried out using the default integration grids.

Results and Discussion

The following naming scheme will be used hereinafter for the calculated complexes and transition states. Each complex is assigned a name comprised of three components: its place in the reaction profile (a number, 5–10), type of metalloaromatic ring (C = metallabenzenes, O = metallypyrylium, S = metallathiabenzene), and the type of adduct formed (α = acetone, α = CO2, s = Cs2). Transition states are labeled according to the two minima they connect. The two aromatic methyl groups are present in the experimental complexes (1C, 1O, and 1S; Scheme 2) due to synthetic requirements but are not expected to dramatically affect their reactivity and, therefore, are replaced by hydrogens in the calculations. Likewise, the bulky PEt3 ligands are replaced by the smaller PH3.

Geometries. Selected complexes are depicted in Figure 1 and all are presented in the Supporting Information. The iridiaromatic complexes (5) are square pyramidal complexes with apical phosphine ligands and basically flat rings. The agreement is satisfactory between the structures of 5C and 5O and the X-ray structures of 1C11 and 1S, respectively. In these calculated complexes, there is minimal variation in the aromatic C=C bond lengths, which are around the calculated bond lengths for the latter basis set; this level of theory is conventionally denoted as mPW1K/SDB-cc-pVDZ/mPW1K/SDD. We have previously recommended this level of theory as better suited than the more popular B3LYP79,80/ALANL2DZ81 to investigate reaction mechanisms.

The identities of the transition states were confirmed by having only one imaginary vibrational mode suitable for the desired reaction. In addition, an imaginary reaction coordinate (IRC) calculation was performed on each transition state to confirm connectivity with the reactant(s) and the product. 

With this functional, two basis set—RECP (relativistic effective core potential) combinations were used. The first, denoted SDD, is the barrier heights than B3LYP or other “conventional” exchange-correlation functionals. It has been shown (e.g., refs 62, 71, 78) that with this functional, two basis set—Dresden basis set combination76 on transition metals. The second, denoted SDB-cc-pVDZ, combines the Dresden cc-pVDZ basis set77 on the main group elements and the Stuttgart—Dresden basis set—RECP on the transition metals with an added f-type polarization exponent taken as the geometric average of the two f-exponents given in the Appendix to ref 78. Geometry optimizations were carried out using the former basis set, while the energetics of the reactions were calculated at these geometries with the

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Computational Details

All calculations were carried out using Gaussian 98 revision A11. The mPW1K (modified Perdew—Wang 1-parameter for kinetics) DFT exchange-correlation functional of Truhlar and co-workers was used. The latter basis set; this level of theory is conventionally denoted as mPW1K/SDB-cc-pVDZ//mPW1K/SDD. We have previously recommended this level of theory as better suited than the more popular B3LYP/ALANL2DZ to investigate reaction mechanisms. It has been shown (e.g., refs 62, 71, 78) that with this functional, two basis set—Dresden basis set combination on transition metals. The second, denoted SDB-cc-pVDZ, combines the Dresden cc-pVDZ basis set77 on the main group elements and the Stuttgart—Dresden basis set—RECP on the transition metals with an added f-type polarization exponent taken as the geometric average of the two f-exponents given in the Appendix to ref 78. Geometry optimizations were carried out using the former basis set, while the energetics of the reactions were calculated at these geometries with the

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benzene of 1.396 Å. In fact, the C\textsubscript{ortho}−C\textsubscript{meta} and C\textsubscript{meta}−C\textsubscript{para} bond lengths in 
5C are 1.395 and 1.398 Å, respectively, in line with expectations for an aromatic system. Phosphine dissociation from 
5 was examined and found not to occur (vide infra).

The next step is the substrate coordination (L = acetone, CO\textsubscript{2}, or CS\textsubscript{2}) to the iridium center to afford [(C\textsubscript{4}H\textsubscript{4}YIr)(L)(PH\textsubscript{3})\textsubscript{3}]\textsuperscript{+} (6). Two types of coordination complexes were found. The cationic 5O and 5S form \textgamma\hyperscript{1}-complexes. Upon coordination, a pattern of alternating C\textsubscript{s}C and C\textsubscript{d}C bonds emerges in the 
metal-ring system (similar in lengths as in the 1,2- and 1,4-
addition products 7O and 7S; vide infra), suggesting loss of 
aromaticity and formation of a cyclohexadiene-like structure. The ring bond lengths are similar within each set of three 
coordination complexes (6O\textsubscript{aos} and 6S\textsubscript{aos}). The formation of the substrate coordination complexes is made possible by an 
additional resonance structure that allows for the chalcogen to 
accept electron density preventing the formation of formally

\begin{align*}
\text{Ir}−\text{O(acetone)} \text{bond distances in 6O\textsubscript{a} and 6S\textsubscript{a} are 2.131 and 2.140 Å, respectively, which are significantly shorter than the Ir−O(acetone) distances, thereby emphasizing the aromatic nature of these complexes. In the acetone coordination complexes 6O\textsubscript{a} and 6S\textsubscript{a}, the C=O bond of acetone has lengthened from 1.235 Å (calculated for free acetone at the same level of theory) to 1.256 Å, consistent with the abovementioned crystallographically characterized Ir-acetone complexes (C=O: 1.248(10) Å and 1.232(7) Å).}^{92,93} \text{The analogous CO\textsubscript{2} (6O\textsubscript{o} and 6S\textsubscript{o}) and CS\textsubscript{2} (6O\textsubscript{s} and 6S\textsubscript{s}) coordination complexes are structurally similar. In these complexes, the C=\texttextsubscript{d}X=\texttextsubscript{d}C\texttextsubscript{d}X angle remains nearly linear (178.5° in 6S\textsubscript{o}, 178.6° in 6O\textsubscript{o} and 6O\textsubscript{s}, and 179.3° in 6S\textsubscript{s}).}
\end{align*}

A resonance structure where electron density is localized on the carbon ortho to the iridium center is not favorable with 5C, and indeed substrate coordination does not occur. Instead, in 6C the incoming substrate hovers above the ring forming a long-range complex and does not coordinate to the metal center. The metallabenzenoid moiety remains unaffected (changes in ring C=−C bond lengths are \textless 0.002 Å). The bond lengths in the 
substrate are likewise not substantially different from those in

the free substrate, and the \( \text{X} = \text{C}=\text{X} \) angles remain linear (175.5° in 6Co and 179.9° in 6Cs).

The products of 1,2- and 1,4-cycloaddition (7 and 8, respectively) were identified, and their geometries exhibit the expected distinct single and double bonds. Complex 7 has a 1-iridia-2,4-cyclohexadiene-like core, whereas 8 has a 1-iridia-2,5-cyclohexadiene-like core. This is apparent in the shorter single and longer double bonds than in 8 where the double bonds are not conjugated. In the CX₂ cycloaddition products (X = O, S), the X=C–X angles are in the expected range of \( 121° - 128° \). The calculated structure of 7Co compares satisfactorily with the reported X-ray crystal structure of 3.³⁰

These cycloaddition reactions may either follow a concerted (i.e., Diels–Alder) or nonconcerted reaction pathway. The metallabenzenzene complex (5C) reacts with all three substrates in a concerted fashion, and the C–Ir–X (X = O, S) bonds are formed simultaneously. This is apparent from the transition states found, TS(6C-7C) for 1,2-addition and TS(6C-8C) for 1,4-addition, where both the Ir–X (X = O, S) and the C–C bonds are formed in a concerted step. The other two complexes (5O and 5S) react with the substrates in a nonconcerted manner, and a substrate coordination complex (6O or 6S) is formed prior to C–C bond formation. From the coordination complex, there is a transition state for C–C bond formation.

The transition state for 1,4-cycloaddition, TS(6–8), has the ring \( \text{C} \text{para} \) bent toward the substrate carbon atom, which likewise is bent toward the ring. In the adducts of CX₂ (X = O, S), the X=C–X angle is \( 147° - 157° \), intermediate between the reactants (\( 180° \)) and the products (\( 125° \)). The 1,2-cycloaddition transition states, TS(6Cos-7Cos), for the addition of CX₂ (X = O, S) have the substrate aligned perpendicular to the Ir–Cortho bond. The CX₂ substrate rotates during the reaction to form the cycloaddition product, as confirmed by IRC calculations (see Computational Details section). Such a transition state is expected from orbital considerations (vide infra).

For acetone, such a transition state could not be found, probably because the greater bulk of the acetone substrate makes it more difficult to rotate. In this case, the transition state, TS(6Ca-7Ca), is like that for the 1,4-addition where the substrate is aligned parallel to the Ir–Cortho bond.

### Reaction Energies

The calculated energies of the various complexes relative to 5 + L (L = acetone, CO₂, or CS₂) are presented in Table 1. From these results, one can clearly understand the observed experimental reactivity (Scheme 2).³¹,³³,³⁵

The reaction of the metallapyrrolaylum complex (5O) with acetone leads to reversible formation of the 1,4-addition product 8Oa. Here, the formation of the acetone complex (6Oa) is exergonic. The addition barrier, TS(6Oa-8Oa), is relatively low (\( \Delta G^\ddagger_{298} = 14.5 \text{ kcal/mol} \)), and the addition is almost thermoneutral (\( \Delta G_{298} = 1.2 \text{ kcal/mol} \)). The experimentally unobserved 1,2-addition reaction of 5O with acetone has a higher reaction barrier (\( \Delta G^\ddagger_{298} = 18.9 \text{ kcal/mol} \)) and is endergonic (\( \Delta G_{298} = 7.1 \text{ kcal/mol} \)). The other two metalloaromatic complexes (5C and 5S) are known not to react with acetone.³¹,³³,³⁴ Even though the calculated reaction barriers for the reaction of 5S with acetone are not too high (\( \Delta G^\ddagger_{298} = 23.4 \text{ kcal/mol} \)), the overall reaction is not expected to occur.

The good agreement between the calculated (Table 2) and experimentally observed reactivities (Scheme 2) reactions allows an estimation of the reaction enthalpies.

### Table 1. Calculated Relative Energies (kcal/mol) of Complexes 5–8 and 10

<table>
<thead>
<tr>
<th>Complex</th>
<th>+ acetone(( \Delta G^\ddagger_{298} ))</th>
<th>+ CO₂(( \Delta G^\ddagger_{298} ))</th>
<th>+ CS₂(( \Delta G^\ddagger_{298} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5C/SO/SS</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>5C/CO/SS</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>5C/CS/SS</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>6O</td>
<td>24.3</td>
<td>24.3</td>
<td>24.3</td>
</tr>
<tr>
<td>6S</td>
<td>21.9</td>
<td>21.9</td>
<td>21.9</td>
</tr>
<tr>
<td>7O</td>
<td>21.9</td>
<td>21.9</td>
<td>21.9</td>
</tr>
<tr>
<td>7S</td>
<td>21.9</td>
<td>21.9</td>
<td>21.9</td>
</tr>
<tr>
<td>10O + PH₃</td>
<td>21.9</td>
<td>21.9</td>
<td>21.9</td>
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<tr>
<td>10S + PH₃</td>
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</table>

\( \Delta G^\ddagger_{298} = 26.2 \text{ kcal/mol} \) for 1,2-addition, the overall reactions are endergonic. The metallabenzenzene complex (5C) is unreactive toward acetone as it involves excessive barriers (\( \Delta G^\ddagger_{298} = 33.2 \text{ kcal/mol} \)) for 1,4-addition and \( \Delta G^\ddagger_{298} = 41.9 \text{ kcal/mol} \) for 1,2-addition.

The additions of CO₂ and CS₂ to the metallabenzenzene complex (5C) lead to the 1,2-addition (7Co) and 1,4-addition (8Cs) products, respectively. These two reactions are not expected to be reversible. The addition of CO₂ has reaction barriers of \( \Delta G^\ddagger_{298} = 33.8 \text{ kcal/mol} \) for 1,2-addition and \( \Delta G^\ddagger_{298} = 39.0 \text{ kcal/mol} \) for 1,4-addition. These barriers include both the transition state and the formation of the CO₂ complex because the latter is endergonic due to loss of entropy. CS₂ adds in a 1,4-manner to 5C as, in this case, this barrier is lower (\( \Delta G^\ddagger_{298} = 28.1 \text{ kcal/mol} \)) and the reaction is quite exergonic (\( \Delta G_{298} = -20.8 \text{ kcal/mol} \)).

While the gas phase computational results are fairly satisfactory, there are some minor discrepancies. For instance, the addition of acetone to the metallapyrrolaylum (5O) is slightly endergonic (8Oa compared to 6Oa), yet when an acetone solution of 1O is cooled to \( -40 ^\circ \text{C} \), the 1,4-addition product (2) is clearly detected by NMR. At room temperature, broad peaks are observed.³³ The barrier of the CO₂ 1,2-addition to 5C (\( \Delta G^\ddagger_{298} = 33.8 \text{ kcal/mol} \)) is a bit too high for the reaction to proceed at room temperature, and the reaction is slightly endergonic (\( \Delta G_{298} = 1.8 \text{ kcal/mol} \)). At the same time, the barrier for 1,4-addition of acetone to 5C is \( \Delta G^\ddagger_{298} = 33.2 \text{ kcal/mol} \), and this reaction is not reported experimentally. These issues are resolved when the bulk solvent effects are taken into account, as shown in Table 2, using the PCM solvation model (vide supra Computational Details). The addition of acetone to 5O is now calculated to be slightly exergonic (\( \Delta G_{298} = -1.0 \text{ kcal/mol} \)) in agreement with experimental observations.³³ Furthermore, the addition of CO₂ to 5C has a barrier of \( \Delta G^\ddagger_{298} = 24.3 \text{ kcal/mol} \) and is exergonic (\( \Delta G_{298} = -4.0 \text{ kcal/mol} \)). The barrier for acetone 1,4-addition is \( \Delta G^\ddagger_{298} = 37.6 \text{ kcal/mol} \), and thus this reaction is not expected to occur.
product distribution of the following four similar mechanistic reactions. The reaction of CO₂ with the metallabenzene (SS) is unlikely to occur as both 1,2- and 1,4-additions are fairly endergonic (ΔG₂₉₈ = 12.3 and 14.9 kcal/mol, respectively). In the reaction of the metallapyrylium complex (SO) with CO₂, both 1,2- and 1,4-additions are thermoneutral (ΔG₂₉₈ = 0.6 and 0.8 kcal/mol, respectively) and both reaction barriers (ΔG¹₂₉₈ = 19.8 and 19.2 kcal/mol, respectively) are of similar heights. Therefore, one can expect a mixture of both CO₂ addition products and unreacted starting material. The reactions of CS₂ with both complexes (SO and SS) are exergonic (ΔG₂₉₈ = -19.5 and -18.4 kcal/mol, respectively, for SO and ΔG₂₉₈ = -7.6 and -5.0 kcal/mol, respectively, for SS) and again, in each case, involve barriers of similar height (ΔG¹₂₉₈ = 14.4 and 13.0 kcal/mol, respectively, for SO and ΔG₂₉₈ = 17.8 kcal/mol for SS). Thus, again, one might expect nonselective reactions; however, this has not been verified experimentally.

To check the possibility of phosphine dissociation playing a part in the cycloaddition reactions, the complexes cis-[(C₆H₅-YIr)(PH₃)]²⁺ (9) were optimized. The dissociation of the third phosphine is highly endergonic in all three cases, even when solvent effects are considered (PCM model, see Computational Details) with ΔG₂₉₈ = 18.6 (9C), 17.4 (9O), and 16.3 kcal/mol (9S). The reported exchange of one PEt₃ ligand in 1C with PMe₃ proceeded via a dissociative mechanism with a rate-determining phosphine dissociation step of ΔG²₂₉₈ = 23 kcal/mol.34 In a similar manner, phosphine dissociation for the coordination complexes 8 to give complexes 10 is also fairly endergonic (see Tables 1 and 2).

### Table 2. Calculated Relative Free Energies (ΔG₂₉₈, kcal/mol), Including Bulk Solvent Effects, of the Calculated Complexes 5–8 and 10

<table>
<thead>
<tr>
<th>Product</th>
<th>+ acetone (a)</th>
<th>+ CO₂ (o)</th>
<th>+ CS₂ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5C/5O/5S</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>6C</td>
<td>9.5</td>
<td>7.7</td>
<td>11.4</td>
</tr>
<tr>
<td>TS(6C-7C)</td>
<td>45.6</td>
<td>24.3</td>
<td>29.0</td>
</tr>
<tr>
<td>7C</td>
<td>8.2</td>
<td>-4.0</td>
<td>-24.8</td>
</tr>
<tr>
<td>TS(6C-8C)</td>
<td>37.6</td>
<td>37.4</td>
<td>27.1</td>
</tr>
<tr>
<td>8C</td>
<td>3.8</td>
<td>-2.6</td>
<td>-24.9</td>
</tr>
<tr>
<td>10C + PH₃</td>
<td>21.0</td>
<td>20.9</td>
<td>18.6</td>
</tr>
<tr>
<td>6S</td>
<td>-6.7</td>
<td>10.1</td>
<td>8.2</td>
</tr>
<tr>
<td>TS(6S-7S)</td>
<td>10.7</td>
<td>19.8</td>
<td>14.4</td>
</tr>
<tr>
<td>7S</td>
<td>-2.7</td>
<td>0.6</td>
<td>-19.5</td>
</tr>
<tr>
<td>TS(6S-8S)</td>
<td>7.0</td>
<td>19.2</td>
<td>13.0</td>
</tr>
<tr>
<td>8S</td>
<td>-7.6</td>
<td>0.8</td>
<td>-18.4</td>
</tr>
<tr>
<td>10O + PH₃</td>
<td>11.8</td>
<td>12.8</td>
<td>12.1</td>
</tr>
<tr>
<td>6S</td>
<td>-6.0</td>
<td>9.8</td>
<td>8.1</td>
</tr>
<tr>
<td>TS(6S-7S)</td>
<td>18.2</td>
<td>24.8</td>
<td>17.8</td>
</tr>
<tr>
<td>7S</td>
<td>10.1</td>
<td>12.3</td>
<td>-7.6</td>
</tr>
<tr>
<td>TS(6S-8S)</td>
<td>15.9</td>
<td>26.0</td>
<td>17.8</td>
</tr>
<tr>
<td>8S</td>
<td>6.5</td>
<td>14.9</td>
<td>-5.0</td>
</tr>
<tr>
<td>10S + PH₃</td>
<td>16.3</td>
<td>16.1</td>
<td>25.7</td>
</tr>
</tbody>
</table>

### Table 3. Calculated Gas-Phase and Solution (PCM) Relative Energies (kcal/mol) of the PMe₃ Complexes 5–8

<table>
<thead>
<tr>
<th>Product</th>
<th>+ acetone</th>
<th>+ CO₂</th>
<th>+ CS₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>5C</td>
<td>gas phase</td>
<td>PCM</td>
<td>gas phase</td>
</tr>
<tr>
<td>5O</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>6C</td>
<td>4.5</td>
<td>14.4</td>
<td>4.8</td>
</tr>
<tr>
<td>7C</td>
<td>6.6</td>
<td>11.7</td>
<td>6.5</td>
</tr>
<tr>
<td>8C</td>
<td>28.1</td>
<td>34.8</td>
<td>9.8</td>
</tr>
</tbody>
</table>

* A fully optimized mPW1K/SDD structure was not found. Reported values are calculated mPW1K/SDB-cc-pVDZ single-point energies at the minimum energy structure obtained during the optimization. A vibrational frequencies calculation resulted in only one imaginary frequency, apropos for a transition state structure.

This may be due to steric interaction with the larger phosphine ligand. In 6Oa and 6Os there might be a weak interaction between the acetone and the apical PH₃, yet this does not have a significant impact on the reaction barriers. The barrier for 1,4-addition of acetone to the metallapyrylium complex (SO) is now ΔG²₉₈ = 15.1 kcal/mol instead of 13.7 kcal/mol. Moreover, the unobserved 1,2-addition barrier has increased to ΔG²₉₈ = 22.0 kcal/mol, making this reaction even more unfavorable.

### Reactivity

Several factors influencing the reactivity of 5 have been identified. These include the type of reaction mechanism (concerted versus nonconcerted), orbital symmetry considerations, size of the electrophile, and geometry of the reaction product.

The metallabenzene complex (5C) reacts via a concerted mechanism, as evident from the substrate complexes 6C where the substrate “lies” above the aromatic ring, and the transition states where both the Ir–X (X = O, S) and the C–C bonds are formed simultaneously in one step. The metallapyrylium (5O) and metallabenzene (5S) complexes react via a nonconcerted mechanism. They are cationic, unlike 5C, and are stabilized by coordination of the electronegative O or S. The formation of these coordination complexes is facilitated by the resonance structure of 5O and 5S where electron density can be localized on the chalcogen atom (Scheme 5, vide supra). The formation of all nine coordination complexes (6) is exoenergetic, but loss of entropy makes the formation of most of them endergonic (i.e., on the G₂₉₈ surface; see Table 2). The addition of acetone has a greater effect on the coordination energy than the linear CX₂ (X = O, S) substrates, possibly because it has a dipole moment.

The frontier orbitals of 5C, 5O, acetone, and CO₂ are illustrated in Figure 2; those of 5S and CS₂ are similar to 5O and CO₂, respectively. If one examines those of acetone, CO₂, and CS₂, one can clearly see that the reaction is an electrophilic attack of the substrate on the aromatic ring. The HOMO (highest occupied molecular orbital) of acetone is contained within the molecular plane, but the reaction with the metallaoromatic ring transpires perpendicular to this plane. The LUMO (lowest unoccupied molecular orbital) of acetone is the C=O π* orbital and, hence, is perpendicular to the molecular plane and is antisymmetric (i.e., + on C and − on O). Likewise, the HOMOs of CO₂ and CS₂ do not have any contributions from the carbon atoms and thus cannot interact with the metallaoromatic complexes, while the LUMO, which is antisymmetric with...
respect to the C and the O/S atoms, can. Moreover, the symmetry of the metalloaromatic HOMO and the electrophile LUMO have the appropriate orbital symmetries for 1,4-addition. This is expected as this is a [4 + 2] electron cycloaddition reaction, and the Woodward–Hoffmann rules predict such a reaction to be symmetry allowed. In addition, it is apparent that the 1,2-addition reaction is symmetry forbidden, although this does not preclude it from occurring.

The orbital symmetry also explains the geometry of TS(6C*-8C*). It is observed experimentally that CO₂ reacts with the metallabenzenoid complex to give a 1,2-addition product. Because the HOMO of 5C (vis-à-vis the Ir and C_{ortho} centers) and the LUMO of CO₂ have different symmetries, the CO₂ cannot approach parallel to the Ir−C_{ortho} bond, and thus the perpendicular transition state is obtained. In this reaction, first an interaction occurs between the carbon of CO₂ and C_{ortho} of 5C and then the CO₂ rotates to form the Ir−O bond, all in one concerted step. A similar transition state is obtained for the 1,2-addition of CS₂ to 5C.

Another factor affecting reactivity is the length of the electrophile C=X (X = O or S) bond. The 1,4-addition requires this double bond to stretch across the metalloaromatic ring. The more stretching required, the less favorable the overall process. The calculated C=X bond lengths in free CO₂, acetone, and CS₂ are 1.178, 1.235, and 1.576 Å, respectively. For the 1,4-addition, these bonds have to stretch across the Ir−C_{para} diagonal, which are 3.400 Å (5O), 3.465 Å (5C), and 3.602 Å (5S). This Ir−C_{para} diagonal is another parameter influencing reactivity. These factors are clearly observable in the various reported reactions. The smallest electrophile, CO₂, would rather react with 5C in a symmetry forbidden 1,2-manner than stretch across the ring. With the smaller 5O, both reactions have similar barriers but are thermoneutral. The reaction of CO₂ with 5S is not expected to occur. The largest electrophile, CS₂, can react with all three complexes (5COS) in a 1,4-fasion. The midsized metallabenzenoid complex 5C reacts 1,2 with CO₂, will not react with acetone, and reacts 1,4 with CS₂.

Another key factor is the geometry of the addition products. In the 1,2-addition products, a strained four-membered ring is formed. This is apparent from the Y−Ir−P_{apical} (Y = the ring C, O or S) angles of approximately 67°−71° in the 1,2-products and 86°−90° in the 1,4-products. This deviation from the ideal 90° in the 1,2-products introduces significant strain in the system and raises the energy of the addition products. This ring strain, however, is mitigated by the conjugated C=C bonds that are present in the 1,2- but not the 1,4-addition products. While, in the three acetone additions, the 1,4-addition products (8Ca, 8Oa, and 8Sa) are lower in energy than the 1,2-addition products (7Ca, 7Oa, and 7Sa), in the additions of CO₂ and CS₂, the latter are lower or similar in energy to the former.

**Rh Complexes.** The cycloaddition reactions were examined with the analogous rhodium complexes (5R). To the best of our knowledge, there are no reported rhodiaaromatic complexes. The results are summarized in Table 4. The calculated cycloaddition reactivities for iridium and for rhodium are nearly identical suggesting that the reaction outcome is metal independent. This is in line with the studies of Thorn and Hoffmann that suggest that rhodium metallabenzenoid complexes may be stable but their formation might be problematic for kinetic reasons.

### Summary and Conclusions

We reported here on our DFT investigation at the PCM/mPW1K/SDB-cc-pVDZ/mPW1K/DDD level of theory into the 1,2- and 1,4-cycloaddition reactions of acetone (a), CO₂ (o), and CS₂ (s) to metallabenzenoid, metallaarylpyridium, and metalla-thiabenzenoid complexes of Ir (5COS) and Rh (5COS*). From the calculated barrier heights and reaction energies, one can note that the calculated reactivities are fully consistent with reported
experimental observations.\textsuperscript{31,33,35} For the first time, the complicated reaction patterns of this class of metalloaromatic complexes have been mapped out in detail. Moreover, several factors affecting the reactivity and product distribution were identified. It was found that the metallabenzene complex (5C) reacts via a concerted reaction mechanism while the other two (5O and 5S) react in a stepwise manner. The presence of a heteroatom (O or S) in the ring allows for an additional resonance structure whereby an additional ligand can coordinate permitting a stepwise reaction mechanism. The size of the ring and the length of the substrate C=X bond have a significant impact on the reaction barriers. The geometry of the product, including both ring strain and double bond conjugation, also has a dramatic impact. The symmetry of the frontier molecular orbitals, as with most reactions, is also a major factor with 1,2-addition being symmetry forbidden and 1,4-addition symmetry being allowed.

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\textbf{Supporting Information Available:} Full coordinates in .xyz format of all complexes are available free of charge at the Uniform Resource Locator (URL) http://theochem.weizmann.ac.il/web/papers/cycloaddition.html. This material is available free of charge via the Internet at http://pubs.acs.org. JA036723A