Mechanistic aspects of acetone addition to metalloaromatic complexes of iridium: a DFT investigation†

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DFT calculations were used to reveal the unexpected reactivity and mechanism of the addition of acetone to metallabenzene, metallapyrylium and metallathiabenzene complexes of iridium.

The discovery of the aromatic nature of benzene was a landmark discovery in chemistry. The unique properties of aromatic compounds have driven many chemists to substitute aromatic CH units. Initial goals included 'organic' moieties such as O, N, P and S. Later targets involved using main group metals (*e.g.*, B,[1a] Si,[1b] Ge,[1c] As[1d,e]) and even transition metals (*e.g.*, Os,[2a,b] Ru,[2c–e] Pt,[2f] Ni,[2g] Mo,[2h] Ir[2i,j,3,4]). There is also a metallabenzyne complex of osmium.[5] Despite the significant amount of experimental data available on metalloaromatic complexes,[2–5] theoretical[6] and kinetic studies are scarce.[4]

Recently, Bleeke *et al.* published an interesting series of papers on the synthesis and unusual reactivity of metalloaromatic complexes of Ir(I), [Me$_2$C$_4$H$_2$XIr(PEt$_3$)$_3$]$^{n+}$, specifically a metallabenzene (**1C**, X = CH, *n* = 0),[3b] a metallapyrylium (**1O**, X = O, *n* = 1, as BF$_4^-$ salt)[3c,d] and a metallathiabenzene (**1S**, X = S, *n* = 1, as BF$_4^-$ salt).[3e,f] The fascinating reactions of these complexes with a variety of organic substrates is intriguing yet not well understood. For instance, the metallabenzene (**1C**) and metallathiabenzene (**1S**) complexes are unreactive towards acetone while the metallapyrylium complex (**1O**) reversibly adds acetone in a 1,4-fashion [eqn. (1)]. The facile reversibility of this reaction and the colour change observed upon dissolving the purple metallapyrylium complex in acetone to give the yellow adduct (**2O**) may be useful in several applications, including chemical sensors.

$$\tag{1}$$
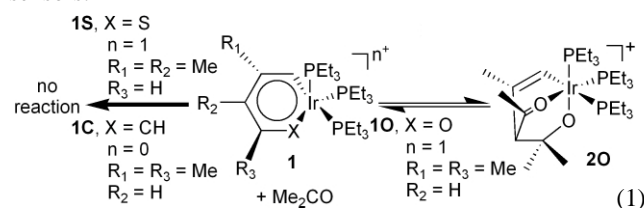
We report herein the 1,4-addition of acetone to the model complexes [C$_4$H$_4$XIr(PH$_3$)$_3$]$^{n+}$ (**3C**, X = CH, *n* = 0; **3O**, X = O, *n* = 1; **3S**, X = S, *n* = 1) using DFT methods (Fig. 1). We selected the mPW1K[7]/SDB-cc-pVDZ//mPW1K/SDD level of theory having previously recommended its use in investigating reaction mechanisms.[8] All calculations used Gaussian 98[9] (see ESI† for full computational details). The identities of the transition states were confirmed by intrinsic reaction coordinate (IRC) calculations.

A stepwise and a concerted reaction mechanism for the reversible acetone addition to **3** are considered here. In the former, an intermediate would be formed prior to C–C bond formation where the acetone is η^1-coordinated to the metal. In the latter, the Ir–O and C–C bonds are formed in a concerted

(Diels–Alder) fashion. At present, it is unknown which mechanism transpires.

The metalloaromatic complexes **3** were optimised and they have a square pyramidal geometry with apical phosphine ligands. The calculated C–C bond lengths show little variation and are all near the calculated value for benzene (1.396 Å). In fact, the C$_{ortho}$–C$_{meta}$ and C$_{meta}$–C$_{para}$ lengths in **3C** are 1.395 and 1.398 Å, respectively. The calculated structures of **3C** and **3S** agree satisfactorily with the reported X-ray structures of **1C**[3b] and **1S**.[3e] In all three cases, the six-membered rings are basically flat as appropriate for aromatic systems.

From **3O** and **3S**, an η^1-coordinated acetone complex is initially formed yielding **4O** and **4S**, respectively. In both complexes there is some alternation of the ring C–C bonds, suggesting partial loss of aromaticity. In these two complexes, the Ir–O (acetone) bond lengths are 2.131 Å (**4O**) and 2.140 Å (**4S**).[10] This bond length in **4O** gives an indication of the nature of the aromatic Ir–O bond of **3O** and **4O**. In these two complexes, the ring Ir–O bonds are 1.997 and 2.030 Å, respectively, further emphasizing the aromatic nature of the former and the reduced aromaticity of the latter. In complexes **4O** and **4S**, the acetone C=O bonds have been lengthened from 1.235 Å (free acetone) to 1.256 Å.[10] Such an intermediate would be expected for a step-wise addition reaction mechanism.

For **3C**, acetone coordination could not be found. Instead, a long-range complex (**4C**) was located. In this complex, the acetone is not coordinated to the metal centre but rather lies parallel to the metallabenzene plane and to the Ir···C$_{para}$ axis. The metallabenzene moiety and the acetone C=O bond lengths remain unchanged, the latter 1.241 Å. The distances between the two fragments are 2.991 Å (Ir···O) and 5.250 Å (C···C).

The expected products (**6**) were identified and exhibit a puckered ring. The alternating ring C–C bond lengths clearly
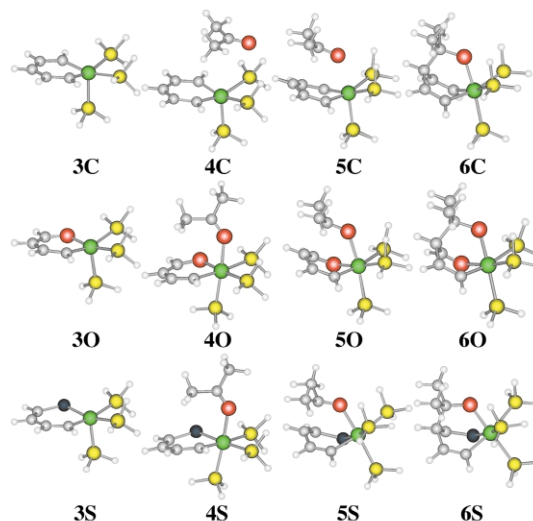

Fig. 1 Calculated structures of complexes **3–6**. Colour scheme: Ir: green, C: grey, H: white, O: red. S: blue, P: yellow.

resemble a 2,4-cyclohexadiene system with, in **6C** for example, C_{ortho}–C_{meta} of 1.340 Å and C_{meta}–C_{para} of 1.515 Å.

The transition states (**5**) for the addition of acetone were found and the bond lengths in the transition states are intermediate between the reactants (**4**) and the products (**6**). For **4O** and **4S**, the acetone ligand has rotated so that the methyl groups are parallel to the metalloaromatic ring and the acetone ligand is now bent towards the ring. The C_{para}–Ir–O angle decreases from 100.0 to 60.6 to 53.4° for X = O and 102.4 to 55.8 to 51.3° for X = S. Furthermore, the ring becomes puckered during the transition state (**5**), but to a lesser degree than in the product complexes (**6**). The two transition states are characterised by a single imaginary vibrational frequency whose normal coordinate corresponds to C–C bond formation. Overall, the obtained transition states (**4O** and **4S**) are what would be expected for stepwise addition of acetone across the metalloaromatic system.

For the X = CH system, the transition state (**5C**) was also as expected. Again, the bond lengths are intermediate between **4C** and **6C**. The acetone moiety remains basically parallel to the metallabenzene plane throughout the reaction. The metallabenzene ring has become puckered and the Ir···O and C···C distances have decreased to 2.411 and 2.689 Å, respectively. This transition state, characterised by a single imaginary frequency for simultaneous Ir–O and C–C bond formations, is indicative of a concerted reaction mechanism.

The calculated structures of the complexes **3–6** are depicted in Fig. 1. One can clearly understand the observed experimental results [eqn. (1)][3] from the energetic data for the three reactions in Table 1. Of the three complexes (**3**), only the metallapyrylium (**3O**) reacts with acetone. This reaction has the lowest reaction barrier with $\Delta G^{\ddagger}_{298} = 14.5$ kcal mol^{-1}. The fact that the overall reaction is only mildly exothermic, with $\Delta G_{298} = -6.8$ kcal mol^{-1}, is essential for the process to be reversible. If the reaction would be too exothermic, the barrier for the reverse reaction would be too large. In this case, $\Delta G^{\ddagger}_{298} = 13.3$ kcal mol^{-1} for the reverse reaction.

On the other hand, the situation is not as favourable for the other two systems. For the metallathiabenzene (**3S**), the reaction barrier is not unreasonably high at room temperature. Nonetheless, the overall reaction is endothermic and, therefore, the rate of the reverse reaction would be approximately 14 orders of magnitude faster. In the case of the metallabenzene (**1C**), the reaction barrier is simply too high to allow the reaction to proceed, even though the overall reaction is thermoneutral.

The main question that remains is why there is this remarkable difference in reactivities between **3** and acetone. There are two potential contributions to the observed reaction pattern. The metallabenzene complex (**3C**) is neutral while the other two (**3O** and **3S**) are cationic. A significant stabilisation can be obtained by coordination of the electronegative oxygen of acetone to the cationic metal centre. In fact, in all three cases the formation of **4** is exoenergetic, but the formation of **4C** is not sufficiently so to overcome the loss of entropy and the formation of **4C** is thus slightly endothermic. The formation of the η^1-coordinated acetone complexes **4O** and **4S** directs, and thus facilitates, the addition reaction.

The second important factor is the Ir···C_{para} diagonal of the metalloaromatic ring. The acetone C=O bond has to stretch across the ring during the reaction, and this is energetically unfavourable. In the transition state, the C=O bond of acetone

are 1.277 Å (**5C**), 1.313 Å (**5O**) and 1.325 Å (**5S**). The Ir···C_{para} distances for **3O**, **3C** and **3S** are 3.400, 3.456 and 3.602 Å, respectively. Not surprisingly, this follows the same order as the single bond covalent radii of 0.66, 0.77 and 1.05 Å for O, C and S.[11]

In summary, the addition of acetone was investigated for a series of isostructural metalloaromatic complexes of Ir(ı). The calculated reactivities fully agree with the experimental observations.[3] It was found that **1O** and **1S** follow a step-wise mechanism while **1C** would react in a concerted manner. The addition of acetone to the metallathiabenzene (**3S**) does not proceed because of the high barrier caused by the relatively large ring size and the endothermicity of the reaction. Both the larger ring size of the metallabenzene complex (**3C**) and the non-concerted transition state make the addition to this metal centre difficult. We are currently examining other addition reactions to this class of complexes.

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Table 1 Calculated energies of complexes **3–6** (in kcal mol^{-1})

Complex	C		O		S	
	ΔE	ΔG_{298}	ΔE	ΔG_{298}	ΔE	ΔG_{298}
3	0.0	0.0	0.0	0.0	0.0	0.0
4	−6.7	3.3	−22.5	−7.9	−21.9	−7.6
5	18.6	33.2	−9.5	6.6	−0.2	15.8
6	−17.8	−0.2	−22.4	−6.8	−9.8	6.7