Dynamic Rotation of Bridging Aryl Ligands in Unsaturated Metal Carbonyl Cluster Complexes

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Supporting Information

ABSTRACT: Variable-temperature NMR studies of the compound Os₃(CO)₁₀(μ-η¹⁻C₆H₅)(μ-AuPPh₃) (1) have revealed a dynamic process of hindered rotation of the bridging phenyl ligand about the metal–metal bond. The activation parameters for the process, ΔH° = 73.33(42) kJ/mol and ΔS° = −2.66(1.25) J/(K mol), were determined by analysis of variable-temperature ¹H NMR spectra. A density functional theory analysis has provided a mechanism that involves a shift of the ligand out of the bridging position with the formation of an agostic interaction of one of the ortho-positioned CH bonds of the phenyl ring to the neighboring metal atom. The related compound Os₃(CO)₁₀(μ-η⁻⁻Py)(μ-AuPPh₃) (2; Py = 2-C₆H₅) was synthesized and was found to exhibit a similar rotation of the bridging pyrenyl ligand about the metal–metal bond: ΔH° = 70.93(61) kJ/mol and ΔS° = −6.98(1.83) J/(K mol).

Dynamic NMR spectroscopy has played a key role in developing our understanding of the molecular dynamics of small organic molecules, ligands, metal complexes, reversible isomerizations, and a variety of chemical transformations, including the coordination and activation of hydrogen by metal complexes.¹,² The hindered rotation of aryl rings is a topic of considerable interest and importance. The rotation behavior of aryl rings is dominated by steric effects and is strongly influenced by the size of the substituents at the ortho positions.³ The hindered rotation of aryl rings serves as a basis for the creation of molecular propellers,³ and it imparts configurational stability to chiral phosphines so that they may be used as auxiliaries for asymmetric induction in homogeneous catalysis by metal complexes.⁴

We have now discovered the first examples of hindered rotation of σ-bonded aryl ligands having the η¹-bridging coordination mode across two metal atoms A. For these ligands, the ipso carbon atom is bonded to both metal atoms and the plane of the aryl ring generally lies approximately perpendicular to the vector between the two metal atoms.

η¹-bridging aryl ligands are commonly found in polynuclear aryl–copper compounds.⁵ There are also a number of examples of polynuclear metal carbonyl complexes containing bridging aryl ligands.⁶ We have recently described the electronically unsaturated 46-electron complex Os₃(CO)₁₀(μ-η¹⁻C₆H₅)(μ-AuPPh₃) (1), which was obtained by the oxidative addition of PhAu(PPh₃)₂ to Os₃(CO)₁₀(NCMe)₈.⁷ We have now found that the phenyl ligand of 1 undergoes a facile dynamic rearrangement that is tantamount to a 180° rotation of the plane of the ring about the bridging carbon atom C₁ and perpendicular to the Os–Os bond (see Scheme 1).

Scheme 1

Due to the low molecular symmetry of 1, all of the hydrogen atoms on the phenyl ring are inequivalent. ¹H NMR spectra of the phenyl ring protons of 1 at several different temperatures are shown in Figure 1. As the temperature is raised, the two ortho-positioned protons H₄ and H₅ (Figure 1A) observed as doublets due to coupling to their neighboring hydrogen nuclei H₂ and H₃, respectively, broaden and collapse into the baseline of the spectrum. Likewise, the inequivalent meta protons H₁ and H₆ (Figure 1B), observed as triplets, also broaden as the temperature is raised, but since the chemical shift difference between them is much smaller than that for H₁ and H₆, these two resonances actually coalesce and re-form as a broad averaged resonance at 105 °C, the highest temperature that could be recorded in the toluene-d₈ solvent that was used. As expected, the resonance of the para proton H₃ does not undergo any changes with temperature and thus is not shown in Figure 1.

Supporting Information

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Computer simulations of the exchange broadened spectra (Figure 1C) have provided exchange rates, from which we have been able to calculate the activation parameters for the exchange process: \( \Delta H^\ddagger = 73.33(42) \text{ kJ/mol} \) and \( \Delta S^\ddagger = -2.66(1.25) \text{ J/(K mol)} \). Assuming that the exchange process is not dissociative, two intramolecular mechanisms for the rearrangement are readily envisaged. (1) Simple 180° rotation of the plane of the ring about the bridging carbon atom takes place, as shown in Scheme 1. This rearrangement would encounter significant steric interactions between the ortho ring protons \( H_1 \) and \( H_5 \) and two pairs of carbonyl ligands on the metal atoms Os1 and Os2.7 (2) A process takes place in which the phenyl ring shifts to a terminal position on one of the metal atoms, generating an intermediate such as B, shown in Scheme 2, followed by a rotation about the Os–C bond and a return to the bridging position. Although the terminal phenyl ring in B would be less crowded by the ligands on the metal atom Os(1), the shift of the ring to a terminal position would require breaking one of the Os–C bonds and that would formally generate an “vacant” coordination site on the neighboring metal atom, Os(2). The generation of a vacant coordination site would clearly be energetically unfavorable.

In order to establish the mechanism of the rearrangement in greater detail, DFT computational analyses were performed. We have used the PBEsol functional with TZP basis set and small frozen core, as implemented in the ADF program.4 Intermediate and ground-state structures were located by using full geometry optimization. The approximate transition states were computed as maxima of total energy along the reaction coordinate with full geometry optimization of all other coordinates. This analysis has revealed a mechanism that can be viewed as a combination of the two mechanisms described above. As represented in Scheme 3, as the phenyl ring begins to twist, one of the Os–C bonds, Os(1)–C(1), weakens. Simultaneously a weak bonding interaction forms to one of the ortho-positioned carbon atoms and its hydrogen atom H(1). This process proceeds to the formation of the intermediate C, in which the Os(1)–C(1) bond has been coordinate with full geometry optimization of all other coordinates. This analysis has revealed a mechanism that can be viewed as a combination of the two mechanisms described above. As represented in Scheme 3, as the phenyl ring begins to twist, one of the Os–C bonds, Os(1)–C(1), weakens. Simultaneously a weak bonding interaction forms to one of the ortho-positioned carbon atoms and its hydrogen atom H(1). This process proceeds to the formation of the intermediate C, in which the Os(1)–C(1) bond has been.

Figure 1. Variable-temperature \(^1\)H NMR spectra of \( 1 \) in the phenyl region of the spectrum recorded in toluene-\( d_8 \). Spectra A (left) show two doublets at room temperature corresponding to the inequivalent ortho hydrogen atoms \( H_1 \) and \( H_5 \) of the bridging phenyl ligand. Spectra B (center) show two triplets due to the inequivalent meta hydrogen atoms \( H_2 \) and \( H_4 \); the resonances X are due to the compound \( \text{Os}_3(\text{CO})_9(\mu_3-\text{C}_6\text{H}_4)(\mu-\text{AuPPh}_3)(\mu-H) \) (3), which is formed from \( 1 \) at elevated temperatures.\(^7\) Spectra C are simulations of the changing spectra of the triplets shown in B at different rates of exchange.
cleaved and an agostic interaction between the ortho-positioned carbon atom and H(1) has formed. Intermediate C lies +9.88 kcal/mol above the ground state 1. There is a transition state TS1 that lies +13.06 kcal/mol above going from 1 to C. The HOMO-27 of C, shown in Figure 2, reveals a significant orbital component representing this agostic CH−Os bond. HOMO-27 lies at −0.313 eV, in comparison with −0.194 eV for the HOMO and −0.107 eV for the LUMO of C.

Formation of the agostic interaction in C, the “vacant” site problem anticipated in B was avoided. As the twisting process is continued, a related second agostic C−H bonded intermediate D is formed, which lies +11.58 kcal/mol above 1. An approximate transition state TS2 that lies +21.77 kcal/mol above 1 is traversed in going from C to D. In search of this transition state, TS2, a reaction coordinate was defined as the bond angle Au−Os(1)−H(1) and scanned between its values in C and D, with all other coordinates optimized. A significant geometry rearrangement occurs past the TS value of the reaction coordinate of 78.8° and results in a flip of the tilted phenyl ring from one side of the Os−Os bond to the other. The actual computational transition state is likely to be a couple of kilocalories per mole lower than the approximate value calculated here. Exact transition states are difficult to locate for two reasons. First, analytic Hessians are not available for the PBEsol functional in the current version of ADF. Second, and more important, it is difficult to define and constrain a proper reaction coordinate (see the Supporting Information for details). Intermediate D continues to 1′, which is equivalent to 1, via the lower energy transition state TS3 (15.27 kcal/mol above 1) to complete the exchange.

Figure 2. HOMO-27 for intermediate C, showing the agostic CH−Os bonding in red, which is encircled in green.

An energy profile of the rotational transformation via the various intermediates and transition states is shown in Figure 3.

In order to investigate these rotational transformations further, we prepared and structurally characterized the related complex Os3(CO)10(μ-η1-Py)(μ-AuPPh3)2 (2; Py = 2-C6H5). Selected bond distances (Å): Os1−C35 = 2.291(12), Os2−C35 = 2.345(13), Os1−Os2 = 2.748(7), Os1−Os3 = 2.7518(7), Os2−Os3 = 2.7515(7), Os1−Au1 = 2.7515(7), Os2−Au1 = 2.7518(7).

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Scheme 4

Figure 4. ORTEP diagram of the molecular structure of Os3(CO)10(μ-η1-Py)(μ-AuPPh3)2. Selected bond distances (Å): Os1−C35 = 2.291(12), Os2−C35 = 2.345(13), Os1−Os2 = 2.748(7), Os1−Os3 = 2.7518(7), Os2−Os3 = 2.7515(7), Os1−Au1 = 2.7515(7), Os2−Au1 = 2.7518(7).

In contrast, a transition state for phenyl ring rotation with both Os−C bonds held equal, i.e. without any selective Os−C bond weakening, has a computed TS energy of +56 kcal above 1.

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Herein, we have described the first examples of hindered rotation of bridging aryl ligands about a metal—metal bond in polynuclear metal carbonyl complexes. Computational analyses have revealed that the twisting rearrangement involves a cleavage of one of the metal—carbon bonds to the bridging carbon atom accompanied by the formation of intermediates containing agostic interactions to one of the ortho-positioned CH bonds of the aryl ring. The rearrangement appears to be facilitated by the intrinsic electronic unsaturation in the complexes themselves.

**REFERENCES**


(10) See the Supporting Information.