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

Richard D. Adams,* Vitaly Rassolov,* and Qiang Zhang

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States

S *Supporting Information*

ABSTRACT: Variable-temperature NMR studies of the compound $Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-}C_6H_5)(\mu\text{-}AuPPh_3)$ (**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, $\Delta H^{\ddagger}$ = 73.33(42) kJ/mol and $\Delta S^{\ddagger}$ = −2.66(1.25) J/(K mol), were determined by analysis of variable-temperature ^{1}H 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 $Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-}Py)(\mu\text{-}AuPPh_3)$ (**2**; Py = 2-$C_{15}H_9$) was synthesized and was found to exhibit a similar rotation of the bridging pyrenyl ligand about the metal−metal bond: $\Delta H^{\ddagger}$ = 70.93(61) kJ/mol and $\Delta S^{\ddagger}$ = −6.98(1.83) J/(K mol).
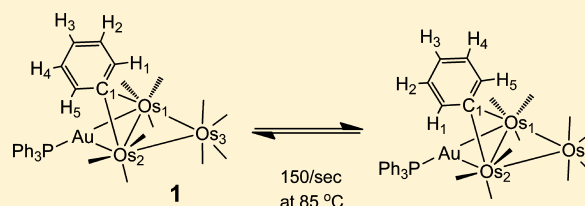
Dynamic NMR spectroscopy has played a key role in developing our understanding of the molecular dynamics of small organic molecules, ligands, metal complexes, reversible isomerizations, and a variety of chemical transformations, including the coordination and activation of hydrogen by metal complexes.[1,2] 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 η^1-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.

A
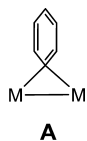
η^1-bridging aryl ligands are commonly found in polynuclear aryl−copper compounds.[5] There are also a number of examples of polynuclear metal carbonyl complexes containing bridging aryl ligands.[6] We have recently described the electronically unsaturated 46-electron complex $Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-}C_6H_5)(\mu\text{-}AuPPh_3)$ (**1**), which was obtained by the oxidative addition of $PhAu(PPh_3)$ to $Os_3(CO)_{10}(NCMe)_2$.[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
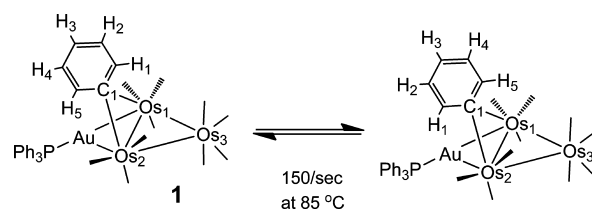
Due to the low molecular symmetry of **1**, all of the hydrogen atoms on the phenyl ring are inequivalent. ^{1}H NMR spectra of the phenyl ring protons of **1** at several different temperatures are shown in Figure 1. As the temperature is raised, the two ortho-positioned protons H_1 and H_5 (Figure 1A) observed as doublets due to coupling to their neighboring hydrogen nuclei H_2 and H_4, respectively, broaden and collapse into the baseline of the spectrum. Likewise, the inequivalent meta protons H_2 and H_4 (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 H_1 and H_5, 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-d_8 solvent that was used. As expected, the resonance of the para proton H_3 does not undergo any changes with temperature and thus is not shown in Figure 1.
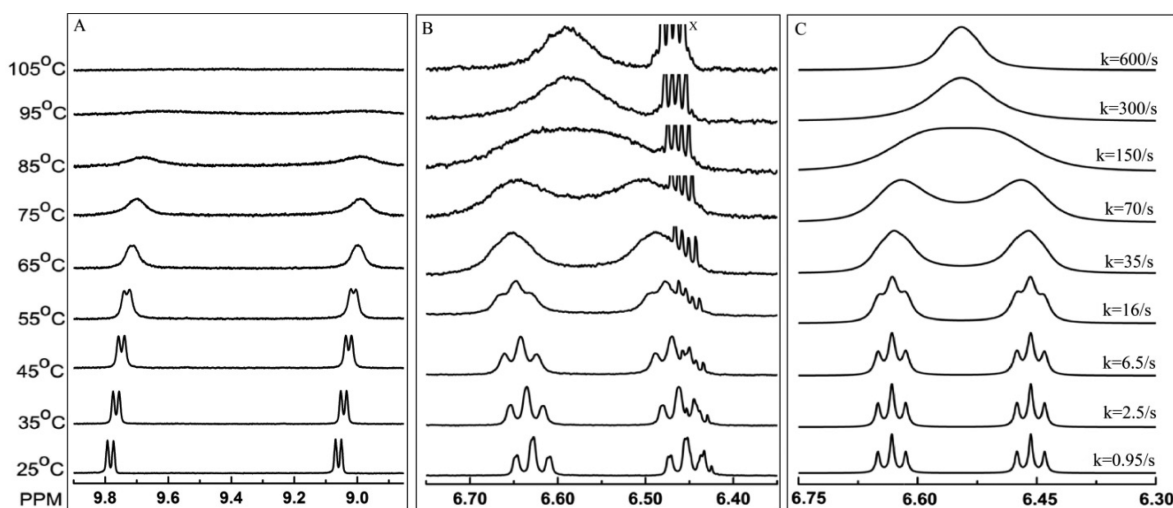
Figure 1. Variable-temperature ^{1}H NMR spectra of **1** in the phenyl region of the spectrum recorded in toluene-d_8. Spectra A (left) show two doublets at room temperature corresponding to the inequivalent ortho hydrogen atoms H_1 and H_5 of the bridging phenyl ligand. Spectra B (center) show two triplets due to the inequivalent meta hydrogen atoms H_2 and H_4; the resonances X are due to the compound $Os_3(CO)_9(\mu_3\text{-}C_6H_4)(\mu\text{-}AuPPh_3)(\mu\text{-}H)$ (**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.

Scheme 2
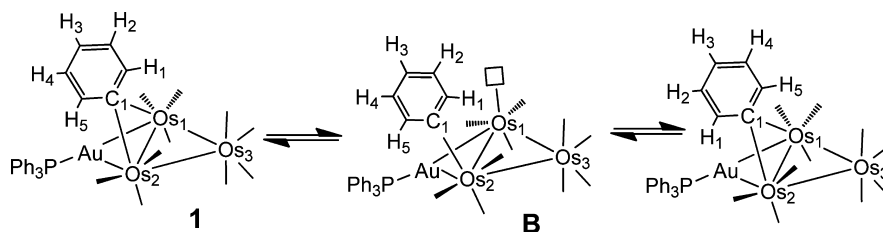
Computer simulations of the exchange broadened spectra (Figure 1C) have provided exchange rates, from which we have been able to calculate the activation parameters for the exchange process: $\Delta H^{\ddagger} = 73.33(42)$ kJ/mol and $\Delta S^{\ddagger} = -2.66(1.25)$ J/(K mol). Assuming that the 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 Os_1 and Os_2.[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.[8] 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. 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

Scheme 3
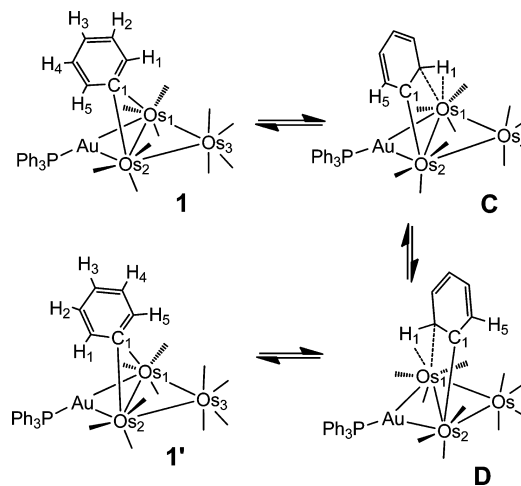
cleaved and an agostic interaction between the ortho-positioned carbon atom and H(1) has formed. Intermediate **C** lies +9.88 kcal/mol above the ground state **1**. There is a transition state TS_1 that lies +13.06 kcal/mol above **1** on going from **1** to **C**. The HOMO-27 of **C**, shown in Figure 2, reveals a
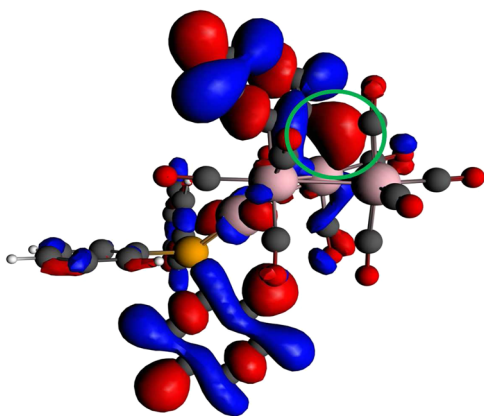

Figure 2. HOMO-27 for intermediate **C**, showing the agostic CH−Os bonding in red, which is encircled in green.

significant orbital component representing this agostic CH(1)−Os(1) 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**.

By 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 the ground state **1**. An approximate transition state TS_2 that lies +21.77 kcal/mol above **1** is traversed in going from **C** to **D**. In search of this transition state, TS_2, 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 TS_3 (15.27 kcal/mol above **1**) to complete the exchange. 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**.

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 $Os_3(CO)_{10}(\mu-\eta^1-Py)(\mu-AuPPh_3)$ (**2**; Py = 2-$C_{16}H_9$) (see Figure 4 and ref 10). The ortho protons of the coordinated pyrenyl ring of **2** are inequivalent, just as they are in **1**. Their resonances appear as separate singlets in the ${}^1H$ NMR spectrum at room temperature. However, at elevated temperatures these resonances are broadened in a pattern similar to that of **1**, which is consistent with a similar rotational exchange
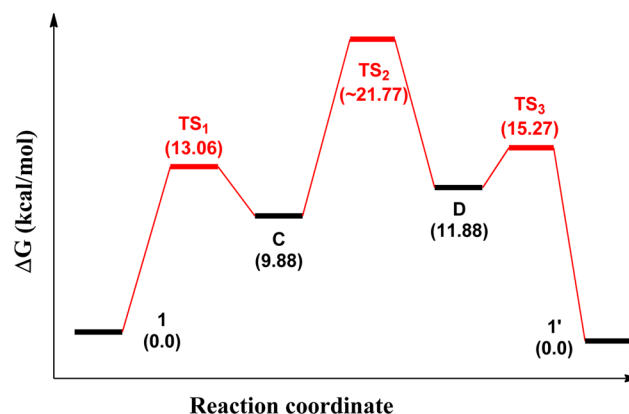

Figure 3. Calculated gas-phase free energy profile in kcal/mol for the rotation of the phenyl ring about the Os−Os bond in **1** as represented in Scheme 3.
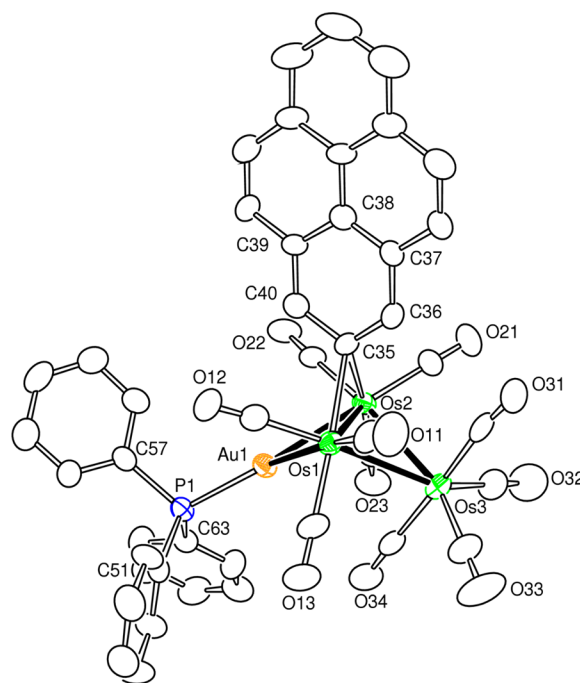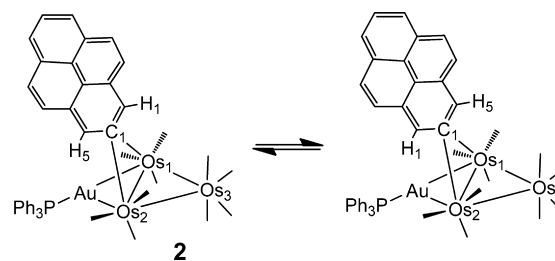

Figure 4. ORTEP diagram of the molecular structure of $Os_3(CO)_{10}(\mu-\eta^1-Py)(\mu-AuPPh_3)$ (**2**). Selected bond distances (Å): Os1−C35 = 2.291(12), Os2−C35 = 2.345(13), Os1−Os2 = 2.7485(7), Os1−Os3 = 2.8780(7), Os2−Os3 = 2.8863(7), Os1−Au1 = 2.7515(7), Os2−Au1 = 2.7518(7).

process (see Scheme 4).[9] The activation parameters for the process in **2** are very similar to those for **1**: $\Delta H^{\ddagger}$ = 70.93(61) kJ/mol and $\Delta S^{\ddagger}$ = −6.98(1.83) J/(K mol).

Scheme 4

2

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.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, figures, and a CIF file giving details of the synthesis and characterizations of compound **2**, computational analyses for **1**, and the structural analysis of compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for R.D.A.: Adamsrd@mailbox.sc.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) (a) Pregosin, P. S., *NMR in Organometallic Chemistry*; Wiley-VCH: Weinheim, Germany, 2012; Chapter 8. (b) *Dynamic NMR Spectroscopy*, Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975. (c) Pregosin, P. S.; Trabesinger, G. *Dalton Trans.* **1998**, 727–734.

(2) Kubas, G. J. *Metal Dihydrogen and σ-Bond Complexes*; Kluwer Academic/Plenum: Dordrecht, The Netherlands, 2001; Chapter 6.

(3) (a) Brydges, S.; Harrington, L. E.; McGlinchey, M. J. *Coord. Chem. Rev.* **2002**, *233–234*, 75–105. (b) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26–33.

(4) Hayashi, T. *Acc. Chem. Res.* **2000**, *33*, 354–362.

(5) (a) van Koten, G. *J. Organomet. Chem.* **1990**, *400*, 283–301 and references therein. (b) Eriksson, H.; Hakansson, M. *Organometallics* **1997**, *16*, 4243–4244. (c) He, X.; Ruhlandt-Senge, K.; Power, P. P. *J. Am. Chem. Soc.* **1994**, *116*, 6963–6964. (d) Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067–1079.

(6) (a) Bradford, C. W.; Nyholm, R. S.; Gainsford, G. J.; Guss, J. M.; Ireland, P. R.; Mason, R. *J. Chem. Soc., Chem. Commun.* **1972**, 87–89. (b) Arce, A. J.; Arrojo, P.; Deeming, A. J.; De Sanctis, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 1491–1492. (c) Adams, R. D.; Captain, B.; Zhu, L. *Inorg. Chem.* **2007**, *46*, 4605–4611. (d) Deng, M.; Leong, W. K. *Dalton Trans.* **2002**, 1020–1023. (e) Adams, R. D.; Pearl, W. C., Jr *J. Organomet. Chem.* **2011**, *696*, 1198–1210. (f) Garcia, M. E.; Ramos, A.; Ruiz, M. A.; Lanfranchi, M.; Marchio, L. *Organometallics* **2007**, *26*, 6197–6212. (g) Briard, P.; Cabeza, J. A.; Llamazares, A.; Ouahab, L.; Riera, V. *Organometallics* **1993**, *12*, 1006–1008. (h) Cabeza, J. A.; Franco, R. J.; Llamazares, A.; Riera, V. *Organometallics* **1994**, *13*, 55–59.

(7) Adams, R. D.; Rassolov, V.; Zhang, Q. *Organometallics* **2012**, *31*, 2961–2964.

(8) (a) te Velde, G.; Bickelhaupt, F. M.; van Gisbergen, S. J. A.; Fonseca Guerra, C.; Baerends, E. J.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931. (b) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391. (c) *ADF2012*; SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, 2012; http://www.scm.com. (d) Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E. *Phys. Rev. Lett.* **2008**, *100*, 136406.

(9) (a) Brookhart, M.; Green, M. H. L.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1. (b) Crabtree, R. H. *Angew. Chem., Int. Ed.* **1993**, *32*, 789–805.

(10) See the Supporting Information.