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Normal and Abnormal NHC Coordination in $[Os_4(\mu\text{-}H)_4(CO)_{11}(IMes)]$ and Exhaustive Dehydrogenation of an IMes Methyl Group

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*Summary: The osmium cluster $[Os_4(\mu\text{-}H)_4(CO)_{11}(IMes)]$ (**1**·nIMes) was prepared by treatment of IMesAgCl with $[Os_4(\mu\text{-}H)_4(CO)_{12}]$. The product of this reaction is believed to be the first tetranuclear NHC cluster compound. Thermolysis of this complex in benzene at reflux resulted in exhaustive dehydrogenation of an o-methyl group on IMes, partial dehydrogenation of benzene, and subsequent coupling of the two unsaturated fragments to produce **2**. The abnormal NHC complex (**1**·aIMes) was also isolated. All compounds were characterized by spectroscopic studies and confirmed by X-ray crystallography.*

In recent years[1] there has been much interest in N-heterocyclic carbenes (NHCs), both as free carbenes, where they behave as organocatalysts,[2] and as essential components of transition metal complexes, which have a wide range of reactivity in either stoichiometric or catalytic reactions.[3] NHCs play a role broadly similar to that of phosphines, but they are considered to be much more strongly bound to a metal center than phosphines and, hence, less likely to participate in coordination sphere rearrangements. Recent studies show that NHC−metal bonds are not inert, and NHCs participate in various inter- and intramolecular reactions.[4] Several reports illustrate that NHCs are susceptible to single C−H activation on the N-substituents.[5] Reductive eliminations have also been identified.[6] Our studies of the reactions of imidazolium ions and/or NHCs with simple reagents such as the electron, the proton, and the hydrogen atom[7]

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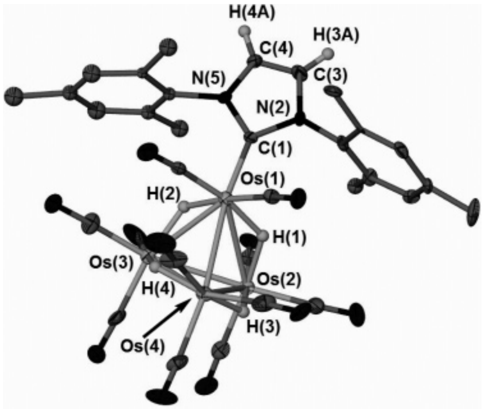

Figure 1. ORTEP view of **1**·nIMes. Ellipsoids are drawn at the 50% probability level. 2,4,6-Trimethylphenyl hydrogens have been omitted for clarity. Selected bond distances (Å): C(1)−Os(1) 2.05(3), C(1)−N(2) 1.44(3), C(1)−N(5) 1.43(3), Os(1)−Os(2) 2.988(2), Os(3)−Os(1) 2.938(2), Os(3)−Os(2) 2.8091(11), Os(4)−Os(2) 2.9524(11), Os(4)−Os(1) 2.826(3), Os(4)−Os(3) 2.9778 (13). Selected bond angles (deg): N(2)−C(1)−N(5) 97(3).

have led us to examine NHC complexes of structurally uncomplicated metal cluster compounds. A key feature of small clusters containing transition metals is the ability of the metal sites to react in concert, thus enhancing the reactivity that can be achieved with single-site metal complexes. Herein we report just such complex reactivity with the preparation of a normal NHC complex of a tetranuclear cluster, $[Os_4(\mu\text{-}H)_4(CO)_{11}(IMes)]$ (**1**·nIMes), its isomer, an abnormal NHC complex (**1**·aIMes), and its thermolysis reaction product **2**. Compound **2** results from a series of reactions including (a) exhaustive dehydrogenation of an *ortho*-methyl group on IMes; (b) partial dehydrogenation of a benzene molecule; and (c) C−C bond forming reaction between the two fragments.

$[Os_4(\mu\text{-}H)_4(CO)_{11}(CO)]$ (**1**·CO) was activated toward substitution by the use of trimethylamine *N*-oxide, a convenient decarbonylation reagent.[8] Reaction of the activated complex with 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidenesilver(I) chloride ([(IMes)AgCl])[9] (eq 1) produced a crystalline solid characterized (*vide infra*) as $[Os_4(\mu\text{-}H)_4(CO)_{11}(IMes)]$ (**1**·nIMes). Previous work involving trinuclear osmium cluster species and [(IMes)AgCl] has resulted in the persistence of silver-containing species or undesired ligand subsititution.[10]

$$\mathbf{1}\cdot\mathrm{CO} + [(\mathrm{IMes})\mathrm{AgCl}] \rightarrow \mathbf{1}\cdot\mathrm{nIMes} + \mathrm{AgCl(s)} \qquad (1)$$

Solution ^1H NMR studies on the yellow crystalline product (**1**·nIMes) revealed the presence of the symmetrical IMes ligand in addition to four bridging hydride ligands (−20.1 ppm, broad). $^{13}C\{^1H\}$ solution NMR studies confirmed the presence of the IMes ligand. IR studies on a CH_2Cl_2 solution of **1**·nIMes exhibit seven ν(CO) bands. The structure of **1**·nIMes was further established using elemental analysis and LSIMS (M^+ 1377.9 *m*/*z*).

In order to determine the atom connectivity, we performed X-ray crystallographic studies.[11] Single yellow crystals of **1**·nIMes were grown from a mixture of CH_2Cl_2 and hexanes, and the results of the study are shown in Figure 1.

The crystallographic study revealed two crystallographically unique but chemically equivalent molecules in the unit cell. Compound **1**·nIMes contains an IMes ligand bound normally to the osmium cluster through a single carbon−osmium bond.[10] Within the cluster, the Os−Os distances are consistent with those containing bridging hydrides.

Surprising results were obtained from the thermolysis of **1**·nIMes in benzene solution (Scheme 1), although we note that similar results were obtained in toluene. Compound **1**·nIMes was dissolved in benzene and heated to 200 °C in a degassed Carius tube. After 72 h the solution was cooled and solvent removed *in vacuo*. The remaining solid was dissolved in a minimum of CH_2Cl_2 and applied to a silica gel column. IR

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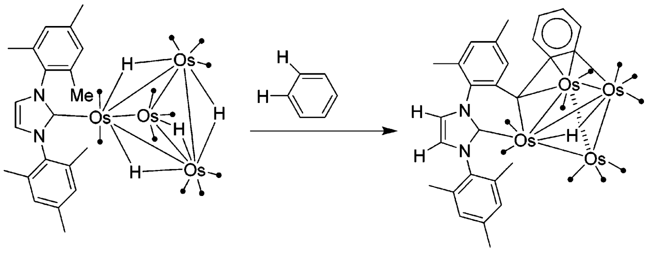
(8) General considerations: Care should be exercised when working with osmium carbonyls due to health and exposure risks. Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques. Solvents were thoroughly dried before use. Full experimental details are provided in the Supporting Information. **1**·nIMes: $[Os_4(\mu\text{-}H)_4(CO)_{11}(CO)]$ (**1**·CO) (110 mg, 0.1 mmol) in CH_2Cl_2 (50 mL) was stirred with 2 equiv of trimethylamine *N*-oxide (15 mg, 0.2mmol) in CH_2Cl_2 (20 mL) being added dropwise over 20 min at 0 °C. Subsequently, [(IMes)AgCl] (47.1 mg, 0.1mmol) was then added. After stirring for 2 h the solution had changed color from yellow to dark orange-brown. The appearance of gray AgCl(s) in the bottom of the reaction vessel was used to determine reaction completion. The solvent was removed *in vacuo* and the remaining solid dissolved in a minimum of CH_2Cl_2 and applied to a silica gel column. Elution under a 20% solution of CH_2Cl_2 to hexanes afforded a single orange-yellow band of **1**·nIMes (29 mg, 21%). Spectroscopic data and tentative assignments **1**·nIMes: IR(in CH_2Cl_2) ν(CO): 2094 sh, 2085 m, 2064 sh, 2053 vs, 2045 s ,2023 s, 2011 sh, 1996 m,br, 1979 m, 1951 w cm^{-1}. ^1H NMR (500 MHz, 295 K, CD_2Cl_2): δ −20.14 [s,br, μ-H], 2.12 [s, 12H, *ortho*-CH_3], 2.35 [s, 6H, *para*-CH_3], 7.05 [s, 4H, *meta*-H], 7.09 [d, 2H, *im*-H]. $^{13}C\{^1H\}$ NMR (100.61 MHz, 295 K, CD_2Cl_2): δ 19.4 [s, *o*-CH_3], 21.4 [s, *p*-CH_3], 124.9 [s, *NCC*], 130.5 [s, *Ar-C*-3,5], 135.9 [s, *Ar-C*-2,6], 137.1 [s, *Ar-C1*,], 141.0 [s, *Ar-C-4*]. MS (LSIMS): 1377.9 (P+). Anal. Calc for $C_{32}H_{28}N_2O_{11}Os_4$: C, 27.90, H 2.05, N 2.03. Found: C, 27.77, H, 2.10, N 1.93. **1**·aIMes: **1**·nIMes (184 mg, 0.133 mmol) was dissolved in benzene (15 mL) and heated to 200 °C in a Carius tube degassed three times by freeze−pump−thaw techniques. After 72 h the solution was cooled and solvent removed *in vacuo*. The remaining solid was dissolved in a minimum of CH_2Cl_2 and applied to a silica gel column. IR spectroscopic studies were performed on the reaction mixtures before and after column chromatography, and these studies indicated that no rearrangements occurred on the column. Compound **1**·aIMes was eluted in a 20% CH_2Cl_2 solution of hexanes as a yellow band (63 mg, 34%). **2** was eluted in a 20% CH_2Cl_2 solution of hexanes as a red-brown band (31 mg, 16%). IR spectroscopic evidence was found to support the existence of trace quantities of one other product tentatively assigned to an NHC−Os_6 cluster. Spectroscopic data and tentative assignments **1**·aIMes: IR (in CH_2Cl_2) ν(CO): 2084 m, 2052 vs, 2038 s, 2021 s, 1995 m, 1985 m, 1977 m, 1942 br,sh,w cm^{-1}. ^1H NMR (600 MHz, 295 K, CD_2Cl_2): δ −20.50 [s, 1H,], −19.85 [s, 2H, μ-H], −19.85 [s, 1H, μ-H], 2.07 [s, 3H, *o*-CH_3], 2.09 [s, 3H, *o*-CH_3], 2.11 [s, 3H, *o*-CH_3], 2.2 [s,br, 3H, *o*-CH_3], 2.2 [s,br, 6H, *p*-CH_3], 6.63 [s, 1H, *meta*-H], 6.68 [s, 2H, *meta*-H], 7.04 [s, 1H, im-H], 7.07 [s, 1H, im-H], 7.09 [s, 2H, im-H], 7.95 [s, 2H, C(1)-H], 7.99 [s, 1H, C(1)-H]. $^{13}C\{^1H\}$ NMR (150.92 MHz, 295 K, CD_2Cl_2): δ 17.3 [s, *o*-CH_3], 17.4 [s, *o*-CH_3], 18.3 [s, *o*-CH_3], 21.4 [s, *p*-CH_3], 21.5 [s, *p*-CH_3], 126.0 [s, *NCa·NHC·C*], 129.9 [s, *Ar-C*-3,5], 130.1 [s, *Ar-C*-3,5], 130.2 [s, *Ar-C*-3,5], 131.4 [s, *Ar-C*-3,5], 134.1 [s, *Ar-C*-2,6], 134.2 [s, *Ar-C*-2,6], 134.4 [s, *Ar-C*-2,6], 134.7 [s, *Ar-C*-2,6] 135.0 [s, *Ar-C1*],136.0 [s, *Ar-C1*,], 141.4 [s, *Ar-C-4*], 141.9 [s, *Ar-C-4*], 177.4 [s, NCa·*NHC·C*]. MS (LSIMS): 1377.9 (P^+). Anal. Calc for $C_{32}H_{28}N_2O_{11}Os_4$: C, 27.90, H 2.05, N 2.03. Found: C, 27.41, H, 2.04, N 2.24. **2**: IR (in CH_2Cl_2) ν(CO): 2076 s, 2044 vs, 2013 s, 1996 s, 1980 m, 1969 m, 1916 br,w cm^{-1}. ^1H NMR (600 MHz, 295 K, CD_2Cl_2): δ −9.95 [s, μ-H], 1.32 [s, 3H, H57], 2.20 [s, 3H, H59], 2.30 [s, 3H, H58], 2.33 [s, 3H, H67], 2.59 [s, 3H, H68], 6.86 [m, 1H, H75A], 6.88 [s, 1H, H53A], 6.92 [s, 1H, H55A], 7.03 [s, 1H, H63A], 7.11 [s, 1H, H63A], 7.17 [d, J_{HH} = 2.3 Hz, 1H, H4A], 7.18 [m, 1H, H74A], 7.57 [d, J_{HH} = 8.7 Hz, 1H, H76A], 7.71 [d, J_{HH} = 2.3 Hz, 1H, H3A], 7.84 [d, J_{HH} = 7.8 Hz, 1H, H73A]. $^{13}C\{^1H\}$ NMR spectroscopic data and tentative assignments (150.91 MHz, 295 K, CD_2Cl_2): δ 18.5 [s, C57], 19.7 [s, C59], 20.5 [s, C67], 21.0 [s, C68], 21.3 [s, C58], 120.6 [s, C53], 123.8 [s, C4], 123.9 [s, C3], 128.1 [s, C55], 129.3 [s, C75], 129.5 [s, C63], 130.0 [s, C76], 130.8 [s, C74], 131.1 [s, C73], 132.4 [s, C65], 134.3 [s, C52], 135.8 [s, C56], 135.9 [s, C62], 136.9 [s, C51], 137.0 [s, C61], 140.8 [s, C66], 147.0 [s, C54], 148.0 [s, C64], 155.2 [s, C69], 162.9 [s, C71], 166.6 [s, C72], 181.0 [s, C1]. MS (LSIMS) 1419.7 (P+). Anal. Calc for $C_{37}H_{26}N_2O_{10}Os_4$: C, 31.31, H 1.85, N 1.97. Found: C 31.32, H 1.99, N 1.72. Solution studies: **1**·aNHC (45 mg, 0.033 mmol) was dissolved in benzene (20 mL) and heated to 200 °C in a Carius tube degassed three times by freeze−pump−thaw techniques. After 48 h the reaction mixture was subjected to column chromatography and the isolated materials corresponded to **2** (23 mg, 0.016 mmol) and a *trace* of **1**·aIMes. Infrared spectroscopic evidence for the generation of a small amount of $Os_4H_4(CO)_{12}$ was also observed, as indicated by diagnostic bands at 2067 and 2019 cm^{-1}. Some insoluble black material was noted at the top of the column.

Scheme 1



1·nIMes **2**

spectroscopic studies were performed on the reaction mixtures before and after column chromatography, and these indicated that no rearrangements occurred on the column. Three compounds were eluted, the first an isomer of **1**·nIMes, namely, an abnormally[5h,12] bound NHC complex (**1**·aIMes) (yield 34%), the second a red compound **2** (yield 16%), and the third compound (trace) that appears to be a NHC−Os_6 cluster. Crystals of **1**·aIMes were grown from a CH_2Cl_2 solution. Mass spectral data and elemental analysis indicated that the solid was an isomer of **1**·nIMes. Spectroscopic studies on this crystalline material were performed and the spectral data are dramatically different from those of **1**·nIMes. For instance, the symmetry of the osmium hydride cluster has been reduced, as indicated by the observation of three distinct signals in the anticipated region for osmium hydrides. Also, there are five signals with an overall integration corresponding to 18H for the 2,4,6-trimethylphenyl CH_3 groups, indicating a significant lowering of symmetry for the IMes ligand. The result of the crystallographic study, which is shown in Figure 2, clearly indicates that **1**·aIMes is bound in the abnormal fashion with a Os−C bond that is 2.121(12) Å long. The metrical parameters for the cluster are comparable to those of **1**·nIMes. We note that perhaps the conversion of **1**·nIMes to **1**·aIMes is not entirely unexpected since the steric constraints (steric pressure) are dramatically decreased upon isomerization from the cramped pocket around C_2 to the more spacious pocket around C_4−C_5.[12]

Crystals of **2** were grown in CH_2Cl_2 and hexanes by slow evaporation. ^1H solution studies on the solid revealed the presence of five distinct signals in the region anticipated for methyl groups with an integration of 15H. These signals are indicative of a significant lowering of the symmetry of the cluster. Furthermore, in the metal hydride region, a single resonance at −19.9 ppm indicated the presence of one unique bridging hydride ligand. Curiously, new peaks were evident in the aryl region of the ^1H spectrum with a ABCD spin system, consistent with the incorporation of a 1,2-disubstituted benzene ring into the unit. The result of a crystallographic study is shown in Figure 3.

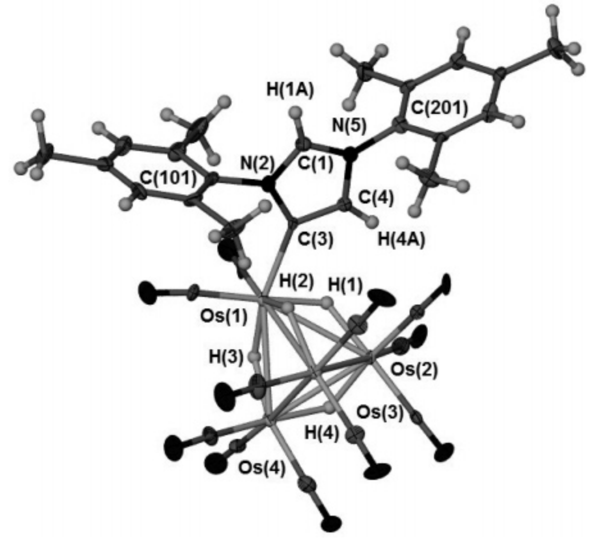


Figure 2. ORTEP view of **1**·aIMes. Ellipsoids are drawn at 50% probability. Selected bond distances (Å): Os(1)−C(3) 2.121(9), C(3)−C(4) 1.366(17), C(3)−N(2) 1.380(16), C(4)−N(5) 1,397(16), C(1)−N(2) 1.332(17), C(1)−N(5) 1.315(17). Selected bond angles (deg): N(2)−C(3)−C(4) 104.0(11), N(5)−C(1)−N(2) 110.0(11).

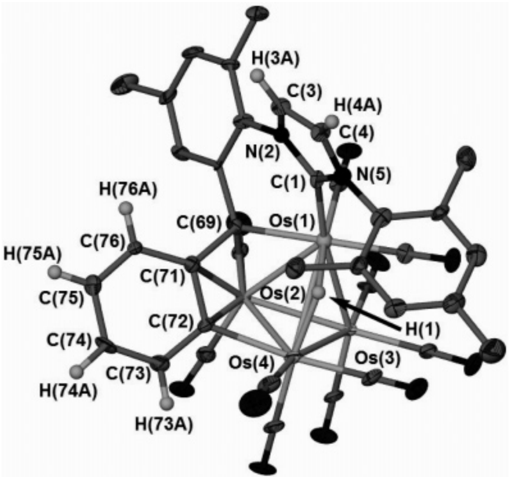


Figure 3. ORTEP view of **2**. Ellipsoids are drawn at 50% probability. Selected bond distances (Å): Os(1)−C(1) 2.090(9), Os(1)−C(69) 2.093(10), Os(2)−C(69) 2.199(10) Os(2)−C(72) 2.241(10) Os(2)−C(71) 2.365(10) C(71)−C(76) 1.409(14), C(71)−C(72) 1.460(13), C(72)−C(73) 1.428(15), C(73)−C(74) 1.348(16), C(74)−C(75) 1.441(15), C(75)−C(76) 1.337(15). Selected bond angles (deg): N(2)−C(1)−N(5) 104.3(8).

The structure of **2** was unanticipated; however, the elemental analysis and LSIMS (P^+ 1419.7 *m/z*) are consistent with the formulation. The complex exhibits an $Os_4(CO)_{10}$ core with an NHC ligand coordinated to one osmium site with a Os(1)−C(1) bond interaction that is 2.090(9) Å long. During the thermolysis reaction, one of the methyl groups of the NHC was activated such that all three C−H bonds were cleaved. The formerly methyl carbon center now bridges two osmium sites, forming two distinct Os−C interactions: Os(1)−C(69) and Os(2)−C(69). The activation of three C−H bonds on an NHC-supported complex is unprecedented and indicates that the anticipated enhanced reactivity can be achieved using metal cluster compounds.[13]

The complex exhibits notable features including the formation of a new interaction with a fragment derived from the benzene molecule. Three new osmium−carbon interactions result from this coupling: Os(2)−C(71) 2.365(10) Å, Os(2)−C(72) 2.241-

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(11) Crystal data for **1**·nNHC: $C_{32}H_{28}N_2O_{11}Os_4$, orthorhombic, space group *Pca*2(1), $a = 27.9147(5)$ Å, $b = 16.5133(3)$ Å, $c = 15.2219(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 7016.7(2)$ Å^3, $Z = 8$, $D_c = 2.608$ Mg/m^3, absorption coefficient = 14.500 mm^{-1}, R1 = 0.0839, wR2 = 0.1011 GOF = 0.969. Crystal data for **1**·aNHC: $C_{32}H_{28}N_2O_{11}Os_4$, triclinic, space group $P\bar{1}$, $a = 14.0263(5)$ Å, $b = 15.9043(6)$ Å, $c = 16.2287(6)$ Å, $\alpha = 96.672(2)°$, $\beta = 96.046(2)°$, $\gamma = 90.049(2)°$, $V = 3575.4(2)$ Å^3, $Z = 4$, $D_c = 2.599$ Mg/m^3, absorption coefficient = 14.299 mm^{-1}, R1 = 0.0672, wR2 = 0.1781 GOF = 1.020. Crystal data for **2**: $C_{40}H_{33}N_2O_{10}Os_4$, triclinic, space group $P\bar{1}$, $a = 12.3074(4)$ Å, $b = 12.6819(4)$ Å, $c = 14.7598(5)$ Å, $\alpha = 74.792(2)°$, $\beta = 87.235(2)°$, $\gamma = 62.317(2)°$, $V = 1961.26(11)$ Å^3, $Z = 2$, $D_c = 2.476$ Mg/m^3, absorption coefficient = 12.976 mm^{-1}, R1 = 0.0552, wR2 = 0.1448 GOF = 1.040.

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(10) Å, and Os(4)−C(72) 2.185(10) Å. Formation of this coupling could result from a systematic CH bond activation of the benzene ring followed by complexation of the aromatic double bond or via a double dehydrogenation to produce a benzyne-type intermediate. However, no mechanistic pathway is apparent from the product. The ring derived from benzene exhibits bond alternation, but strong shielding of one of the methyl groups on the IMes fragment indicates that the moiety exhibits a shielding cone, suggestive of aromaticity within the deformed C_6 ring. Finally, a C−C bond formation reaction has occurred between the dehydrogenated methyl group of IMes and the dehydrogenated benzene fragment [C(69)−C(71) 1.428(14) Å]. The result of the dehydrogenation and subsequent coupling of the NHC-methyl group and the benzene fragment is formal conversion of C(69) from a methyl group to a bridging carbene. It is possible that the alternation of bond unsaturation along C(69)−C(71)−C(76)−(C75)−C(74)−C(73)−C(72) is oriented such that the π-system above the planar ring is responsible for the shielding experienced by the IMes methyl group.

In order to study the reactivity of **1**·aIMes, the thermolysis of **1**·aIMes (45 mg, 0.033 mmol) was allowed to proceed for 48 h at 200 °C in benzene (20 mL). After 48 h the reaction mixture was subjected to column chromatography and the isolated materials corresponded to **2** (23 mg, 0.016 mmol) and a trace of **1**·aIMes. Infrared spectroscopic evidence for the generation of a small amount of $Os_4H_4(CO)_{12}$ was also observed, as indicated by diagnostic bands at 2067 and 2019 cm^{-1}. Some insoluble black material was noted at the top of the column. The ability of both the normal and abnormal osmium−carbene species to form **2** suggests rearrangement is prevalent at high temperatures.

In the realm of NHC chemistry the reaction observed for the conversion of **1**·nIMes to **2** is unprecedented, and analogous reactivity in PR_3 chemistry is, to our knowledge, unknown. Exhaustive dehydrogenation of a methyl group is extremely rare, although not unprecedented. For example, for ruthenium, $[Ru_6(\mu_3\text{-H})(\mu_5\text{-CbipyMe})(\mu\text{-CO})_3(CO)_{13}]$ (**3**) and $[Ru_7(\mu_3\text{-H})(\mu_5\text{-CbipyMe})(\mu\text{-CO})_2(CO)_{16}]$ (**4**) have been isolated from the reaction of 6,6′-dimethyl-2,2′-bipyridine and $[Ru_3(CO)_{12}]$ in chlorobenzene at reflux. It is clear that the production of **3** and **4** is a complex reaction, since the metal clusters in the products are of higher nuclearity than those of the starting materials. Discrete single-site osmium carbyne complexes have been reported,[14] and these were formed from a triple benzylic dehydrogenation of cymene by an osmium amide complex. Finally, metal-bound methyl groups have also been exhaustively dehydrogenated[15] to give carbide complexes.

In summary we have described the preparation of two osmium NHC clusters exhibiting both normal and abnormal NHC binding.[16] These two compounds represent rare examples[12] of osmium NHC complexes. The ability of the abnormal carbene complex to form **2** suggests they may play a broader role in metal−NHC complexes than previously thought. We have also shown the unprecedented activation of three C−H bonds on the IMes ligand at a metal site. The dehydrogenated material reacts, through an unknown mechanism, with a dehydrogenated fragment derived from benzene, and a novel C−C bond formation reaction occurs between the dehydrogenated NHC ligand and the benzene fragment. The results indicate fascinating chemistry for NHC complexes of late-metal carbonyl clusters[17] and hydrogen-rich metal surfaces/clusters and also suggest that ligands such as IMes may not be suitable for metal hydride-rich reaction media.

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Supporting Information Available: Synthetic procedures and selected characterization data and CIF files for **1**·nIMes, **1**·aIMes, and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) IMes is isosteric to *m*-terphenyl 1,3-bis(2,4,6-trimethylphenyl), a popular ligand design for stabization of reactive organometallic fragments. *Single* C−H bond activations have been reported for *m*-terphenyls; exhaustive dehydrogenation has, to our knowledge, not been observed. See: Grigsby, W. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 7981.

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(16) For other abnormal IMes bonding see: Lebel, H.; Janes, M. K.; Charette, A. B.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5046. A closely related complex, $(aIPr)(nIPr)PdCl_2$, has also been reported. See: Campeau, L. C.; Thansandote, P.; Fagnou, K. *Org. Lett.* **2005**, *7*, 1857.

(17) While this paper was in review a report was published describing unusual reactivity of NHC cluster compounds. See: Ellul, C. E.; Mahon, M. F.; Saker, O.; Whittlesey, M. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 6343.