

An *N*-heterocyclic carbene as a bidentate hemilabile ligand: a synchrotron X-ray diffraction and density functional theory study†

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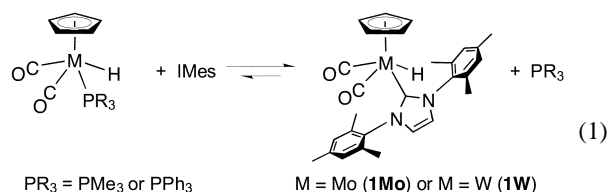
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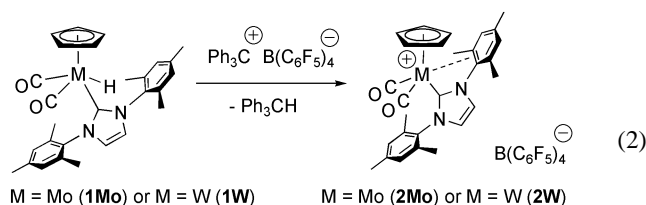
The *N*-heterocyclic carbene ligand IMes was shown by synchrotron crystallography and DFT computations to adopt a hemilabile bidentate coordination mode in CpM(CO)₂(IMes)⁺B(C₆F₅)₄⁻ (M = Mo, W), with a C=C bond of one mesityl weakly coordinated to the metal.

N-Heterocyclic carbene (NHC) ligands have recently become very popular as replacements for phosphines.¹ Most NHC ligands are designed and believed to be innocent spectator two-electron donors. There are a few examples, however, in which NHC ligands have been shown to adopt bidentate structures due to *ortho*-metallation,^{2–4} C–C activation,⁴ and dehydrogenation⁵ reactions — processes that involve breaking and formation of strong bonds and altering the backbone of the ligand. Furthermore, a non-destructive and readily reversible coordination mode — C–H agostic bonding or hydrogen bonding — has been previously reported for NHC ligands with aromatic substituents lacking adequate steric protection.³ The widely used IMes ligand (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), however, is sterically protected and has been so far regarded as a strictly monodentate ligand (as long as the backbone is intact). We now report the synthesis and structure of a series of formally 16e⁻ complexes, CpM(CO)₂(IMes)⁺B(C₆F₅)₄⁻ (**2Mo**, M = Mo; **2W**, M = W), in which IMes functions as a bidentate hemilabile⁶ ligand, stabilizing the electronically unsaturated complexes. §

Neutral molybdenum and tungsten complexes, CpM(CO)₂(IMes)H (M = Mo, **1Mo**; M = W, **1W**), were synthesized from CpM(CO)₂(PR₃)H (R = Me, Ph) and IMes through displacement of the phosphine ligand [eqn. (1)].



The stronger bonding of the carbene *vs.* the phosphine in this equilibrium is in accord with thermochemical studies.⁷ The cationic complexes, CpM(CO)₂(IMes)⁺B(C₆F₅)₄⁻ (**2Mo**, M = Mo, **2W**, M = W), were prepared by hydride transfer from **1** to Ph₃C⁺B(C₆F₅)₄⁻ [eqn. (2)].



The reaction is complete within minutes at 25 °C, and the analytically pure product precipitates from toluene in high yield (ν_{CO} IR in Nujol: **2Mo** 1999 and 1905 cm⁻¹; **2W** 1980 and 1890 cm⁻¹). In coordinating solvents, the metal carbonyl IR bands indicate adduct formation (**2Mo**-THF-d₈: 1977 and 1882 cm⁻¹; **2W**-THF-d₈: 1962 and 1859 cm⁻¹) with more electron density on the metal than in **2**, but less than in **1** (THF-d₈: **1Mo** 1918 and 1843 cm⁻¹; **1W** 1913 and 1822 cm⁻¹). The low solubility of **2** in non-coordinating solvents precludes direct NMR spectroscopic characterization, but the adducts **2Mo**-THF-d₈ and **2W**-THF-d₈ were fully characterized by ¹H, ¹³C, and ¹⁹F NMR spectroscopy (see ESI for complete characterization data). †

The lack of suitable solvents for crystallization of **2** frustrated attempts to obtain single crystals suitable for conventional X-ray diffraction. Use of high intensity X-ray radiation at the National Synchrotron Light Source enabled a structural determination using a very small crystal (0.010 × 0.050 × 0.100 mm) furnished by slow diffusion of reactants. The carbene ligand in cationic **2W** is coordinated asymmetrically, with one of the mesityls closer to the metal (Fig. 1). A C=C bond of that mesityl exhibits a weak interaction with the tungsten. Complexes of W or Mo with η²-arene ligands constrained to the metal through chelation (as in **2W**) have been previously found to have M–C distances as long as 2.8 Å.⁸ The bonds in **2W** are even longer [W(1)–C(121) 2.901(13) Å and W(1)–C(122) 3.072(13) Å], and the interaction is weak, but is corroborated by other evidence. Thus, the N–C_{carbene}–W angles in **2W** are distorted [113.9(8) and 146.6(8)]⁹ to accommodate the chelating coordination mode. The methyl group of the interacting C=C fragment of **2W** is bent out of the plane of the mesityl ring by 13.4° and away from the metal, in accord with the change in hybridization. Comparison of the C–C distances within the interacting and non-interacting mesityl rings of **2W**, however, does not provide statistically significant evidence for localization of the η²-arene. The solid state structure of **2Mo** appears to be similar to that of **2W**, but the distances to the coordinated C=C are shorter (2.78 and 3.02 Å), suggesting a slightly

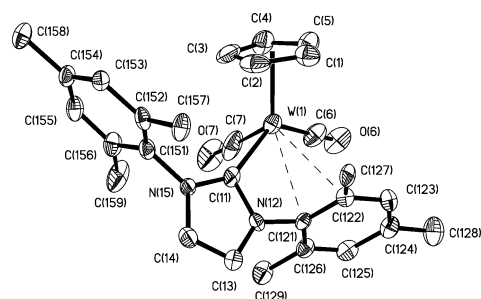


Fig. 1 ORTEP diagram of the cation of complex **2W** (30% probability ellipsoids). Selected bond lengths (Å) and angles (°): W(1)–C(6) 1.928(15), W(1)–C(7) 1.934(19), W(1)–C(11) 2.188(12), W(1)–C(121) 2.901(13), W(1)–C(122) 3.072(13); C(6)–W(1)–C(7) 77.9(6), C(6)–W(1)–C(11) 129.5(5), C(7)–W(1)–C(11) 84.1(5), N(12)–C(11)–W(1) 113.9(8), N(15)–C(11)–W(1) 146.6(8).

† Electronic supplementary information (ESI) available: experimental details and characterization data; table of results for hydrogenation of 3-pentanone; Gaussian 98 summary for the **W** and **Mo** models; ORTEP plot of **1W** and crystal data. See <http://www.rsc.org/suppdata/cc/b3/b303762b/>

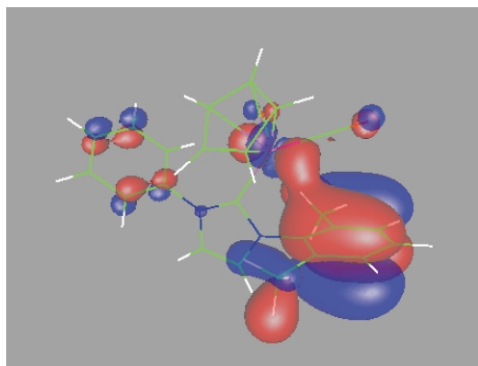
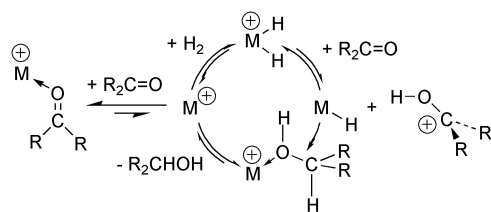


Fig. 2 An orbital (MO 102) showing bonding interaction of a C=C bond of the IMes carbene ligand with Mo.

stronger mesityl binding in **2Mo**. Unfortunately, structural refinement for **2Mo** is not yet satisfactory ($R_1 = 0.133$) and will not be reported in detail.

To further address the intriguing issue of the bidentate bonding mode of IMes a computational study was performed using the B3LYP implementation with the LANL2DZ basis set.¹⁰ To reduce computing time, the non-interacting mesityl group in **2** was replaced with phenyl, and the *para*-methyl group of the interacting mesityl group was replaced with H. Ground states were verified with analytical frequency calculations. The calculated structures of W and Mo model complexes exhibit an interaction between the metal and one of the mesityl C=C bonds (closest distances: 3.025 and 3.407 Å for W; 3.014 and 3.402 Å for Mo). The π -orbital associated with the interacting C=C fragment is distorted and elongated toward the metal (Fig. 2), and the methyl substituent of this C=C fragment is displaced out of the plane of the mesityl ring (8.2° for W and 7.2° for Mo), providing convincing evidence of bonding. While the strong W–C and Mo–C bonds are reasonably well computationally described by this method, with errors of 1–2%, bond lengths for the weakly interacting C=C bond and W or Mo centers exhibit more substantial errors, suggesting that the modeling of weak interactions will be sensitive to the basis set. The weak bonding may also be sensitive to the presence of counterion and crystal neighbors, which is not taken into account in the B3LYP/LANL2DZ calculations of the gas phase cation.

Complexes **2W** and **2Mo** exhibit modest catalytic activity for the hydrogenation of $\text{Et}_2\text{C}=\text{O}$. These reactions are proposed (Scheme 1) to proceed by an ionic hydrogenation, in which proton transfer from a cationic metal dihydride is followed by hydride transfer from a neutral metal hydride.¹¹ Hydrogenation of neat $\text{Et}_2\text{C}=\text{O}$ by **2W** (0.34 mol%) gives 2 turnovers in one day (23 °C, <4 atm H_2); higher activity is observed at 50 °C (15 turnovers in 1 day) but some decomposition is observed at the higher temperature. The catalytic activity of **2Mo** (~1 turnover in 1 day at 23 °C, <4 atm H_2) is lower than that of **2W**, in contrast to the trend observed for the previously reported phosphine-containing ionic hydrogenation catalysts $\text{CpM}(\text{CO})_2(\text{PR}_3)(\text{Et}_2\text{C}=\text{O})^+$.¹¹ It is tempting to speculate that the coordination of the C=C bond in **2** provides additional stabilization of the ground state and decreases catalytic activity by increasing the kinetic barrier for the transformation of **2** into the $18e^-$ dihydride species, $\text{CpM}(\text{CO})_2(\text{IMes})(\text{H})_2^+\text{B}(\text{C}_6\text{F}_5)_4^-$



Scheme 1

(perhaps more so in the molybdenum case if it is more strongly stabilized in **2Mo** than in **2W**). Further experimental and computational studies to address this issue are currently underway.

In summary, the bidentate hemilabile coordination mode of the IMes ligand of **2** is demonstrated experimentally and computationally. These results illustrate that even intact IMes is not an innocent spectator ligand, but is an active participant which possesses significant degrees of structural freedom and is capable of inflicting strong steric and electronic perturbations on the metal. This observation raises more general questions about the possible role of such NHC ligands in catalysis, particularly when high equilibrium concentrations of “ $16e^-$ ” species are required.

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Notes and references

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§ *Crystal data* for **2W**: 0.100 × 0.050 × 0.010 mm; monoclinic; $P2_1/c$; $a = 18.262(4)$, $b = 17.725(4)$, $c = 17.657(4)$ Å, $\beta = 113.87(3)^\circ$; $V = 5226.6(18)$ Å³, $Z = 4$ and $\rho_{\text{calc}} = 1.696$ g cm⁻³; $2\theta_{\text{max}} = 56.50^\circ$; National Synchrotron Light Source ($\lambda = 0.90350$ Å); psi scan; $T = 150(2)$ K; 4972 reflections, all 4800 unique reflections were used in the refinement; no polarization or absorption correction; direct method (SHELXL-97); refinement by full-matrix least squares based on F^2 (SHELXL-97); 749 parameters; hydrogens unrefined; $R_1 = 0.0573$ and $wR_2 = 0.1528$ for 4654 reflections for which $I > 2\sigma(I)$; residual electron density +2.775 and -0.998 e Å⁻³. CCDC 203786. See <http://www.rsc.org/suppdata/cc/b3/b303762b/> for crystallographic data in CIF or other electronic format.

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- For comparison, the N–C_{carbene}–W angles of 128.8(3) and 129.3(3)° in **1W** are essentially equivalent. The closest W...C_{mesityl} non-bonding distance in **1W** is 3.637(5) Å. The structure of **1W** is an unremarkable four-legged piano stool with a *cis* orientation of the carbonyls; details are given in the ESI. CCDC 203785.
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