

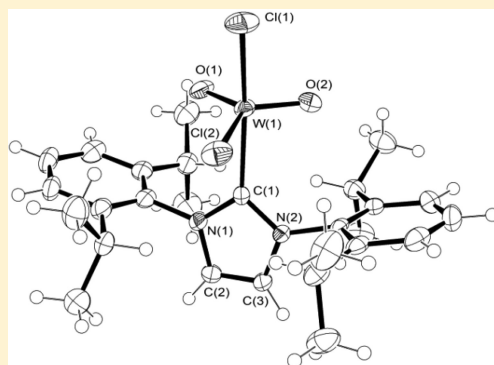
Tungsten(VI) N-Heterocyclic Carbene Complexes: Synthetic, Structural, and Computational Study

Christopher A. Dodds, Mark D. Spicer,* and Tell Tuttle

WestCHEM, Department of Pure & Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, U.K.

Supporting Information

ABSTRACT: The reaction of WOCl_4 with 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (Idipp) leads to an orange solid whose spectroscopic data are consistent with the 1:1 adduct $[\text{WOCl}_4(\text{Idipp})]$. Computational studies at the DFT level further support this formulation. Exposure of this compound to the atmosphere results in rapid hydrolysis to various imidazolium salts. If air diffuses very slowly into solutions of $[\text{WOCl}_4(\text{Idipp})]$, it also undergoes slow hydrolysis to form $[\text{WO}_2\text{Cl}_2(\text{Idipp})]$. This has been crystallographically characterized and is the first five-coordinate, 1:1 adduct of WO_2Cl_2 . This complex has also been subject to DFT calculations, and its metal–ligand bonding has been explored. The carbene–metal interaction is primarily σ -donor in nature. The mechanism of the hydrolysis has also been probed by computational methods, revealing a plausible, low-energy reaction pathway.



INTRODUCTION

Examples of N-heterocyclic carbene (NHC) complexes have been known for about 40 years, thanks to the pioneering work of Wanzlick,¹ Öfele,² Lappert,³ and Taube.⁴ However, it was not until the isolation and structural characterization of a free NHC by Arduengo in the early 1990s⁵ that the enormous potential of these species as ligands was widely recognized and began to be exploited. An explosion of research in this area has since occurred, resulting in an extensive array of metal NHC complexes, mostly with low- to medium-oxidation-state later d-block metals. This work has been driven primarily by the favorable properties of these ligands in catalytic applications.⁶

In contrast, the chemistry of these ligands with higher oxidation state metals, while beginning to receive more attention, remains relatively underdeveloped. The exceptionally strong σ -electron donor ability of NHCs, coupled with their steric profile,⁷ renders them ideal candidates for stabilizing high-oxidation-state metal centers. Furthermore, unlike phosphines, which readily form phosphine oxides, NHCs are not susceptible to facile oxidation, and thus complexes may be prepared by direct combination of the free NHC with high-oxidation-state oxide and halide precursors. Herrmann reported the first examples of high-oxidation-state complexes with NHCs as ligands. Using tetramethylimidazol-2-ylidene the compounds $[\text{CH}_3\text{ReO}_3(\text{NHC})_2]$ and $[\text{MCl}_4(\text{NHC})_2]$ ($\text{M} = \text{Nb}, \text{Ta}$) were obtained.⁸ This report was followed by a second⁹ detailing the syntheses of $[\text{W}^{\text{VI}}\text{O}_2\text{Cl}_2(\text{NHC})_2]$ and $[\text{MoO}_2\text{Cl}(\text{NHC})_3]\text{Cl}$ ($\text{NHC} = 1,3\text{-dimethylimidazol-2-ylidene}$). However, the first structurally characterized high-oxidation-state NHC complex, a 1:1 adduct with VOCl_3 , $[\text{VOCl}_3(\text{NHC})]$ ($\text{NHC} = 1,3\text{-dimesitylimidazol-2-ylidene}$), was not reported until some

years later.¹⁰ In contrast to other VOCl_3 adducts, which are highly moisture sensitive,¹¹ this complex is remarkably stable, being unchanged for extended periods of time even when exposed to the atmosphere. It is also of particular interest due to an unusual bonding arrangement in which back-bonding occurs from the d^0 metal to the carbene ligand mediated by the p orbitals on cis-halide ligands.

Subsequently, a number of reports detailing higher oxidation state NHC complexes have appeared. Abram¹² has prepared and structurally characterized a number of stable Ta^{V} , Tc^{V} , and Re^{V} complexes, and Royo et al.¹³ have also reported adducts of Re^{V} and a study of $[\text{Mo}^{\text{VI}}\text{O}_2\text{Cl}_2(\text{NHC})_2]$ complexes.¹⁴ Very recently Hor has described the synthesis of a comparatively stable molybdenum(VI) compound, $[\text{CpMo}(\text{O})_2(\text{NHC})]^+$, by reaction of $[\text{CpMo}(\text{CO})_2(\text{NHC})(\text{NCMe})]^+$ with $^t\text{BuOOH}$.¹⁵ In addition to these d-block complexes, a number of high-oxidation-state f-block complexes have also been noted. Arnold has reported the formation of cerium(IV) complexes with anionic alkoxy-NHC ligands,¹⁶ while both Costa and Arnold,¹⁷ have reported high-oxidation-state uranium NHC complexes.

Despite the growing interest in high-oxidation-state early-transition-metal NHC complexes, this area of chemistry remains poorly developed, with few complexes having been unambiguously characterized. For instance, the group 6 (Mo, W) complexes described above are exceptionally moisture sensitive materials and without definitive structural determinations remain the subject of considerable conjecture with regard to their structures. Some decomposition products have

Received: September 7, 2011

Published: November 3, 2011

Scheme 1. Synthesis of Tungsten(VI) NHC Complexes

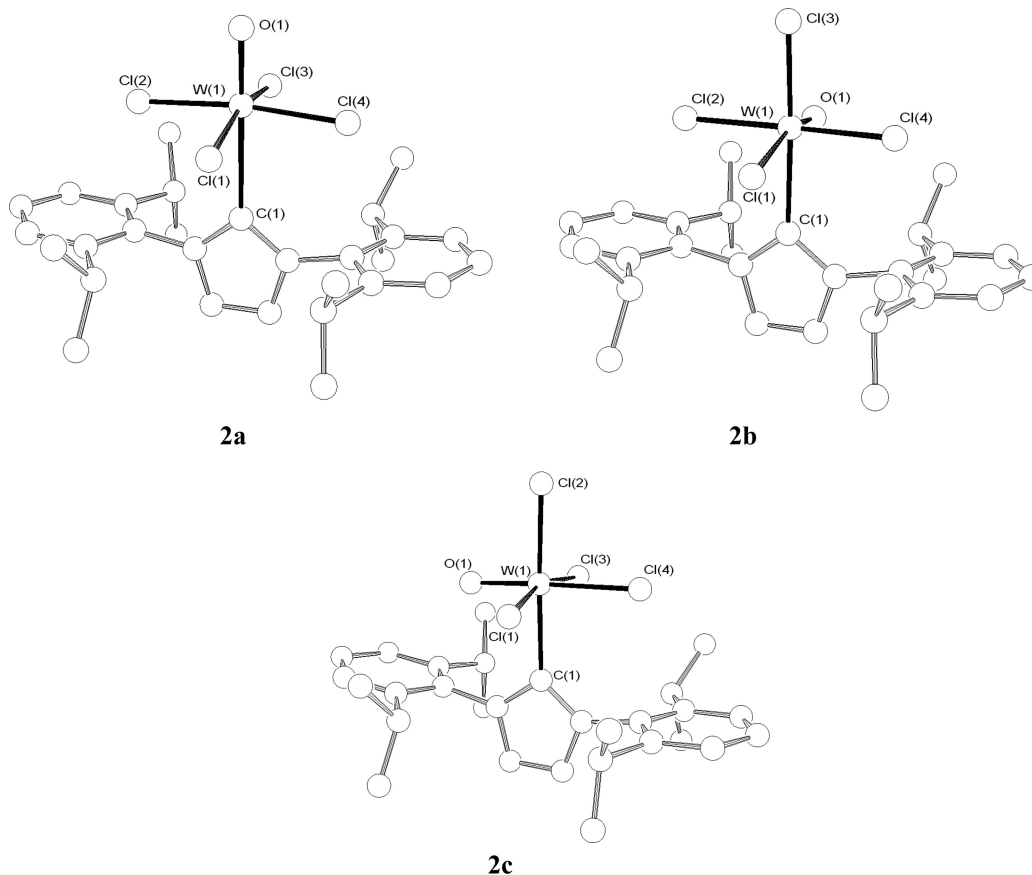
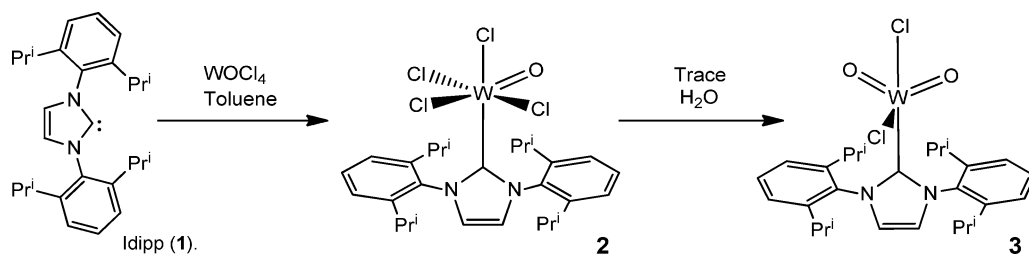


Figure 1. Calculated structures of isomers of $[\text{WOCl}_4(\text{Idipp})]$ (**2a**, top left; **2b**, top right; **2c**, bottom).

been isolated,¹³ hinting at hydrolytic decomposition, but no mechanistic information is available. Furthermore, most of the previous studies have utilized the least sterically demanding alkyl-substituted carbenes, presumably on the basis that these should be the strongest σ donors. In contrast, our surprisingly stable vanadium(V) complex¹⁰ utilized a mesityl-substituted NHC. The steric profiles of the N-aryl imidazol-2-ylidenes are such that they shield one face of the metal center efficiently and thus lower the rate of ligand displacement and/or hydrolysis. We reasoned that a similar approach may result in more tractable products with high-oxidation-state tungsten species. We report a contribution to this area of study, including the first structurally characterized W^{VI} NHC complex, which is also the first 1:1 adduct of WO_2Cl_2 , and evidence that it is formed as the result of adventitious hydrolysis. The structures of the complexes and the mechanism of hydrolysis are subjects of a computational investigation.

RESULTS AND DISCUSSION

Reaction of freshly prepared WOCl_4 with 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**Idipp**, **1**) in toluene results in the formation of a deep orange-brown solution, which on cooling overnight to -18°C yields an extremely moisture sensitive dark orange microcrystalline solid (Scheme 1).

^1H and ^{13}C NMR spectroscopy show the presence of a single NHC-containing species, whose chemical shifts are consistent with a coordinated NHC ligand. We believe this species to be the 1:1 adduct $[\text{W}(\text{O})\text{Cl}_4(\text{Idipp})]$ (**2**). The IR and Raman spectra of this material show a strong band at ca. 930 cm^{-1} and bands at 384 and 362 cm^{-1} which may be ascribed to modes with predominantly $\nu(\text{W}=\text{O})$ and $\nu(\text{W}-\text{Cl})$ character, respectively.¹⁸ The extreme moisture sensitivity of the material has precluded the collection of further reliable spectroscopic and analytical data. For instance, mass spectrometry shows only peaks due to the imidazolium ion. It has not proved possible to

grow crystals sufficiently large for X-ray diffraction in order to unequivocally establish its identity.

In the absence of conclusive structural data, a computational study was carried out to assess the stability of **2**. There are two primary isomers of **2**, one in which the NHC is disposed trans to the oxo ligand, and one in which it is trans to a chloro ligand. The geometry-optimized structures of both are shown in Figure 1.

The formation of both isomers is exothermic with respect to the starting materials (free carbene and WOCl_4). The least energetically favorable isomer **2a** ($\Delta H = -17.7 \text{ kcal mol}^{-1}$) has the NHC trans to the oxo ligand. A very long W–C distance (2.633 Å) is obtained, which may be rationalized in terms of the known trans effect of the π -bonding oxo ligand. The more stable isomer has the NHC ligand cis to the oxo ligand and trans to chloride. Two energy minima are obtained for this species which are related by a rotation around the W–C bond axis: that is, the plane of the imidazol-2-ylidene heterocycle lies either in the WCl_3 plane (**2b**, $\Delta H = -19.5 \text{ kcal mol}^{-1}$, $d(\text{W–C}) = 2.359 \text{ Å}$) or alternatively in the WOCl_2 plane (**2c**, $\Delta H = -22.6 \text{ kcal mol}^{-1}$, $d(\text{W–C}) = 2.317 \text{ Å}$). It is interesting to note that if the structures of **2b,c** are calculated using a N,N' -dimethyl-substituted NHC, although the minimized geometries obtained are essentially identical, they become equivalent in energy, implying that the steric contribution in the bulky Idipp ligand is significant in determining the nuances of conformation and structure. It is also notable that there is a parallel between the calculated stability of the complex and the tungsten to NHC carbon bond distance, confirming that it is this interaction which is primarily responsible for the stabilization of the complex with respect to the reactants. Finally, the calculated IR spectrum shows bands at 930, 334, and 328 cm^{-1} , consistent with the observed spectrum. Thus, the experimental and computational data strongly support our formulation as the 1:1 adduct of WOCl_4 with Idipp.

This WOCl_4 adduct is highly reactive. Solutions exposed to the atmosphere instantaneously turn deep blue and then gradually fade to colorless. Imidazolium salts with various anions ($\text{IdippH}^+\text{X}^-$, $\text{X}^- = \text{Cl}^-$, $[\text{WOCl}_5]^-$, $[\text{WOCl}_4(\text{OH})]^-$) have been isolated from these mixtures. However, it was observed that NMR samples prepared in C_6D_6 , if left to stand in the tube overnight, deposited colorless crystals virtually quantitatively. Our expectation was that this would be the imidazolium salt arising from hydrolysis of **2**, but dissolution of this material in CDCl_3 gave a ^1H NMR spectrum whose chemical shifts were consistent with complexed Idipp. Concentrated toluene solutions of **2** were found, over a period of several days, to precipitate a colorless crystalline material (having an identical ^1H NMR spectrum). X-ray crystallography (Figure 2) of a sample thus obtained revealed this material to be the toluene solvate of the 1:1 complex $[\text{WO}_2\text{Cl}_2(\text{Idipp})]$ (**3**). This is the first structurally characterized tungsten(VI) NHC complex and the first 1:1 adduct of WO_2Cl_2 (all previously reported complexes are pseudo-octahedral 2:1 adducts).¹⁹ The steric profile of the NHC ligand is such that addition of a second ligand would not be possible, and the strong σ -donor ability is sufficient to stabilize the electron-poor tungsten(VI) center. Attempts to prepare this complex directly from WO_2Cl_2 yielded mixtures of NHC-containing species, including the desired complex as the major component (60–90% by NMR), but it could not be satisfactorily purified. Attempts to utilize $[\text{WO}_2\text{Cl}_2(\text{NCMe})_2]$ or $[\text{WO}_2\text{Cl}_2(\text{thf})_2]$ as starting materials also resulted in inseparable mixtures.

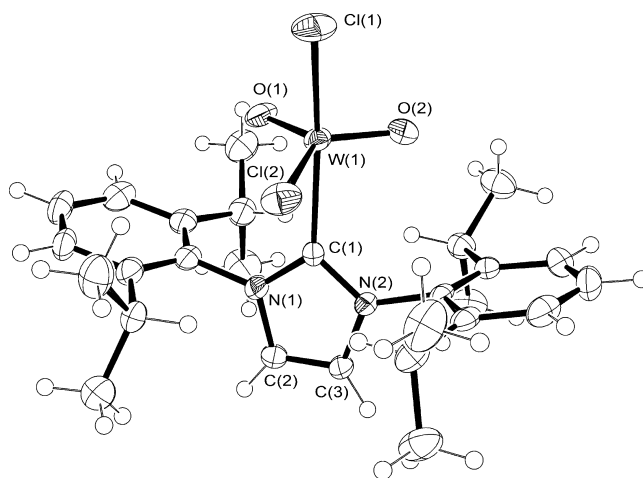


Figure 2. X-ray crystal structure of **3** with thermal ellipsoids shown at the 50% level.

The crystal structure shows the complex to have trigonal-bipyramidal geometry. The π -donor oxo ligands lie in the equatorial plane, as might be expected, while one chloride and the NHC ligand occupy the axial positions. The W=O (1.699(3) and 1.704(3) Å) and W–Cl (2.346(1) and 2.367(1) Å) distances are in the range of previously characterized WO_2Cl_2 adducts. Notably, the W–C distance, at 2.223(4) Å, is at the low end of reported W–C_{NHC} distances (range 2.18–2.31 Å, mean 2.26 Å),²⁰ although these distances do not seem to vary systematically with either oxidation state or coordination environment. The observed distance is somewhat shorter than that calculated for the most stable isomer of the WOCl_4 complex, and this is consistent with the less crowded metal center allowing a stronger metal–carbene interaction. The equatorial ligands are nearly coplanar (sum of in-plane angles 359.14°), although there is considerable variation of the angles within the plane from the ideal 120°. The axial ligands are tilted toward Cl(2). This results in a very acute Cl(2)–W(1)–C(1) angle (79.27(11)°) and a Cl(2)⋯C(1) distance (2.930 Å) that is substantially shorter than the sum of the van der Waals radii. This is reminiscent of the situation observed in $[\text{VOCl}_3(\text{IMes})]$ and led us to probe the structure and bonding by computational methods.

DFT calculations of the putative isomers of **3** were undertaken in an effort to understand the observed structural features. Four geometric isomers were considered (**3a–d**, Figure 3). The experimentally observed structure, **3a**, is found to be lowest in energy, followed by **3b** (+5.57 kcal/mol), the second isomer with oxo ligands in the equatorial plane. Isomer **3c**, in which one oxo ligand is axial, is some 16.54 kcal/mol less stable than **3a**, while **3d** spontaneously rearranges during structure optimization to give **3a**. The structural parameters from the crystal structure of **3a** and the calculated structures of **3a–c** are available in the Supporting Information. The calculated structure of **3a** reproduces the structural features of the crystallographic data well, although the bond distances to tungsten are overestimated by up to 0.05 Å. In all these minimized structures the W=O distances are essentially invariant (1.7287–1.7304 Å), while there is greater deviation in the W–Cl distances. In **3a** the W–Cl bond trans to the carbene is markedly longer (2.4125 Å) than the bond cis to the carbene (2.3084 Å), as might be expected on the basis of the ligand trans influence. The two other isomers are more

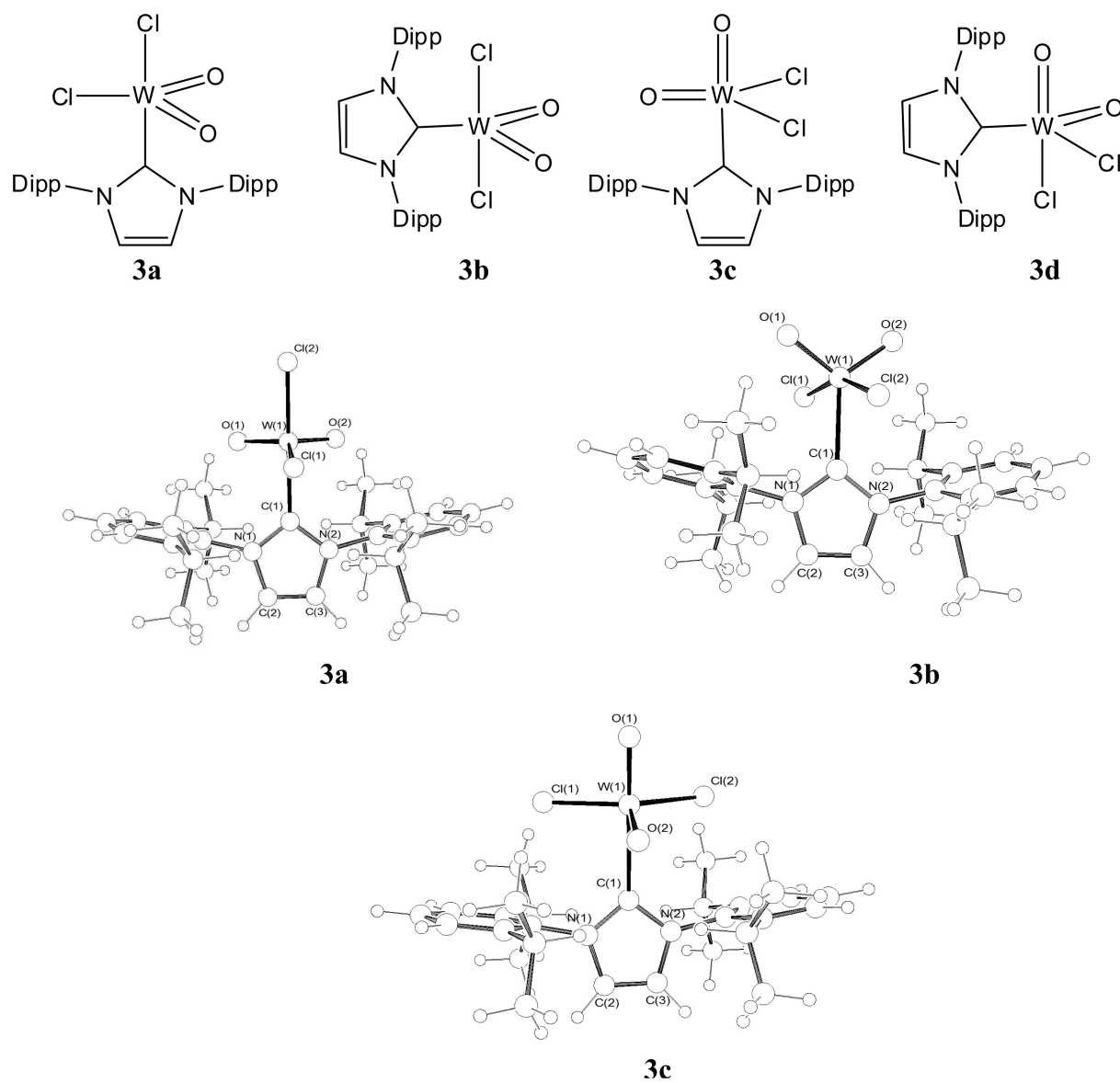


Figure 3. Calculated structures for the geometric isomers of 3.

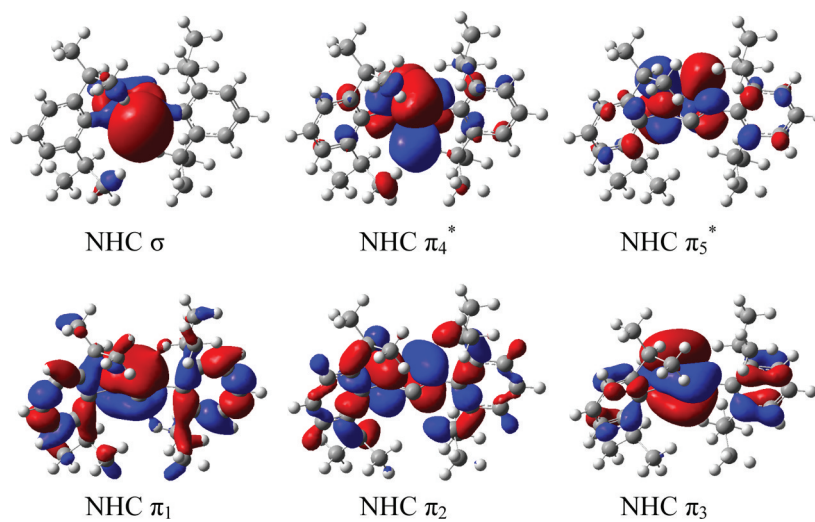


Figure 4. Calculated NHC orbitals potentially able to be involved in metal–NHC bonding.

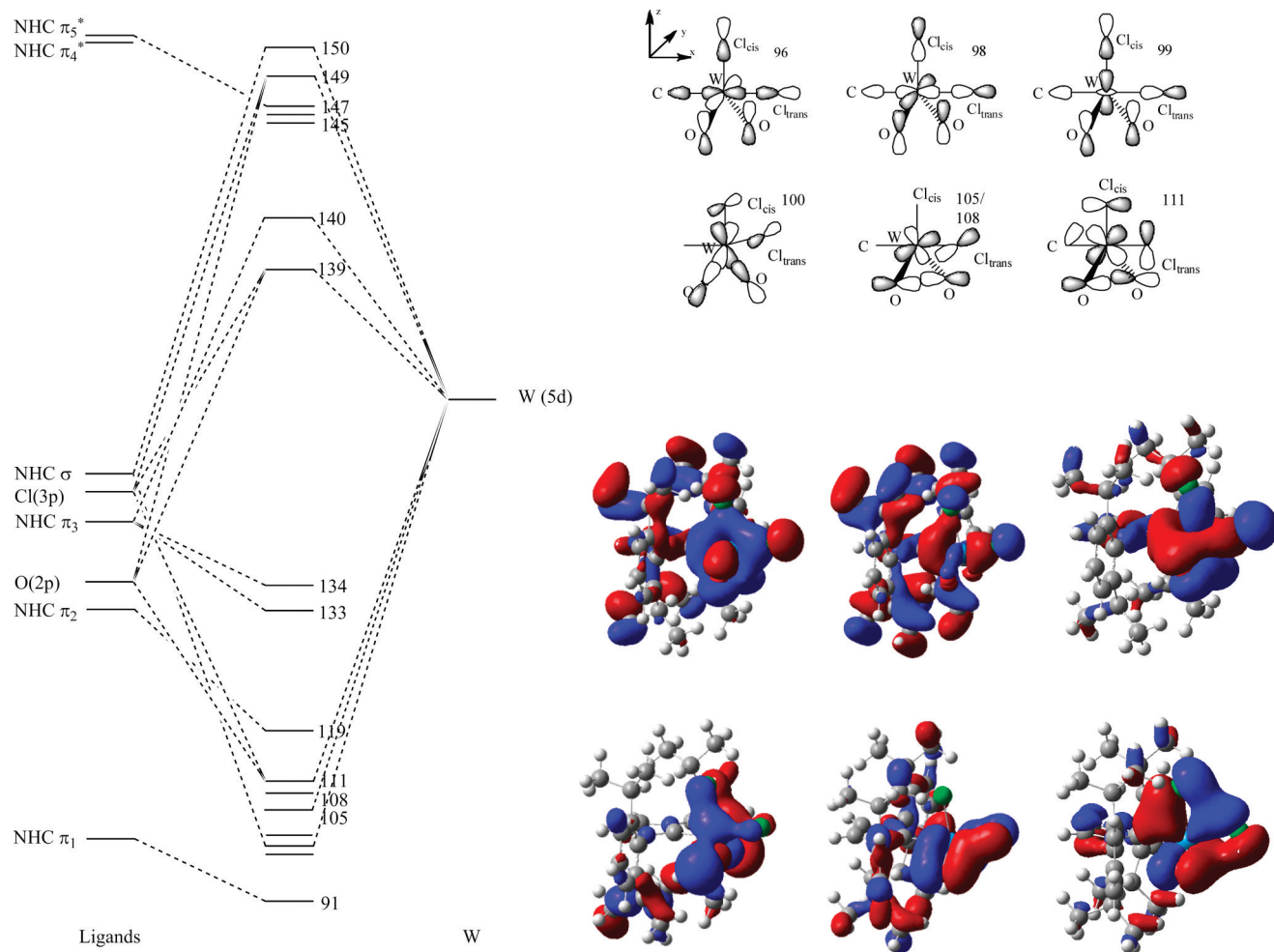


Figure 5. Semiquantitative MO scheme for $[\text{WO}_2\text{Cl}_2(\text{Idipp})]$ and associated bonding molecular orbitals (left), isosurfaces obtained from DFT calculations (top right), and cartoon representations of the isosurfaces (bottom right).

symmetric, presenting two very similar W–Cl distances; **3b** has $d(\text{W–Cl}) = 2.3654$ and 2.3662 Å, while **3c** has $d(\text{W–Cl}) = 2.3079$ and 2.3084 Å. In concert with this decrease in W–Cl bond distance (and hence increased W–Cl bond strength) the calculated W–C_{carbene} distance increases (**3a**, 2.2758 Å; **3b**, 2.3238 Å; **3c**, 2.5928 Å). This trend, in turn, parallels the relative energies of the three isomers, the longest W–C_{carbene} bond occurring in the least stable isomer, indicating again that the metal–carbene bond is a decisive factor in the stability of these species.

We were also interested in probing the electronic structure of **3a**.²¹ The bonding of NHCs with low- and medium-oxidation-state metal centers has been explored by computational means, but metals in high oxidation states have received less attention. Of particular interest is the degree of π back-bonding from the metal to the carbene π^* orbitals. For low oxidation states Meyer²² and others have shown a significant contribution of such an interaction to the bond strength. However, for medium oxidation states it would seem that such an interaction is largely absent.²³ We reported previously¹⁰ limited details of a computational study on $[\text{V}(\text{O})\text{Cl}_3(\text{IMes})]$, which showed an unusual, alternative π interaction of the Cl ligands cis to the NHC with the carbenic carbon atom. This suggested that in high-oxidation-state complexes there is still the possibility of back-bonding via the coligands, despite the formal absence of electrons at the metal center. Analysis of a range of d^0 metal

carbene complexes, including $[\{\text{Ti}(\text{NHC})\text{Cl}_3\}_2(\mu_2\text{-O})]$, $[\text{Ti}(\text{NHC})(\text{NMe}_2)_2\text{Cl}_2]$, and $[\text{TiCl}_4(\text{NHC})]$, suggests this interaction is widespread in its occurrence.²⁴ Finally, in a low-valent but electron-deficient (14e) compound analysis has shown a degree of NHC ligand to metal π -donation to offset the electron deficiency.²⁵

DFT calculations on both the free carbene, Idipp, and the tungsten carbene complex **3a** using B3LYP functionals and 6-31G(p,d) basis sets gave a helpful insight into the bonding in these species. The free carbene (Figure 4), as might be expected, has a carbon-based lone pair as the HOMO. Furthermore, there are five π orbitals which are potentially able to interact with the metal d orbitals. The totally symmetric orbital (NHC π_1) is at lowest energy and two further orbitals (NHC π_2 and NHC π_3) are overall bonding in character. These three orbitals are all occupied. Finally, two unoccupied high-energy orbitals (NHC π_4 and NHC π_5) with overall antibonding character are also observed.

The metal complex has approximate C_s symmetry, and therefore the d orbital degeneracies observed in a pure trigonal-bipyramidal geometry are lifted. The calculations confirm that the formal x axis lies along the M–NHC bond and the z axis along the M–Cl_{cis} bond and symmetry descent results in the d orbital representation becoming $3A'$ ($d_{x^2-y^2}$, d_z^2 , d_{xy}) + $2A''$ (d_{xz} , d_{yz}). Inevitably the metal–ligand bonding picture is rather complex, and the interaction between the metal and the NHC

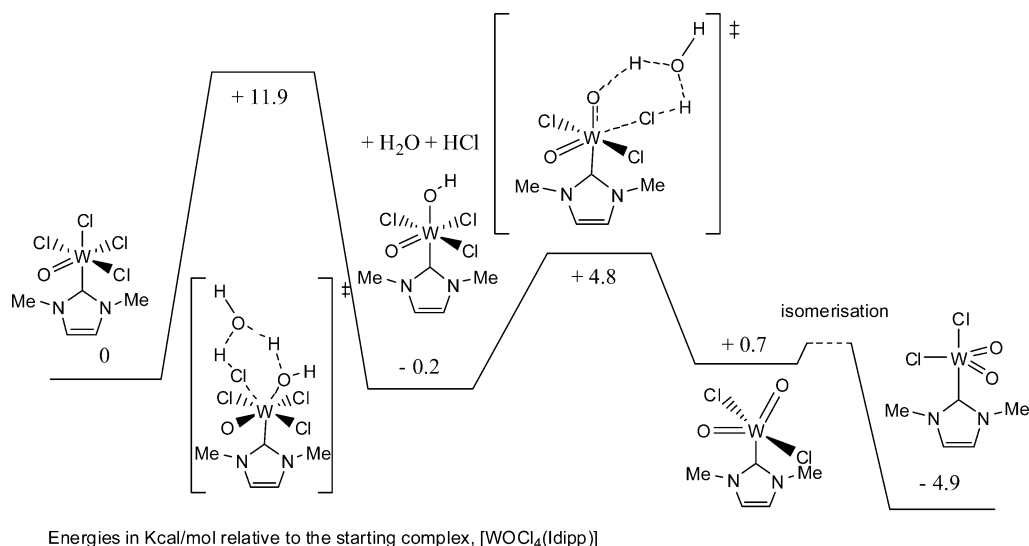


Figure 6. Calculated reaction pathway for the conversion of 2 to 3.

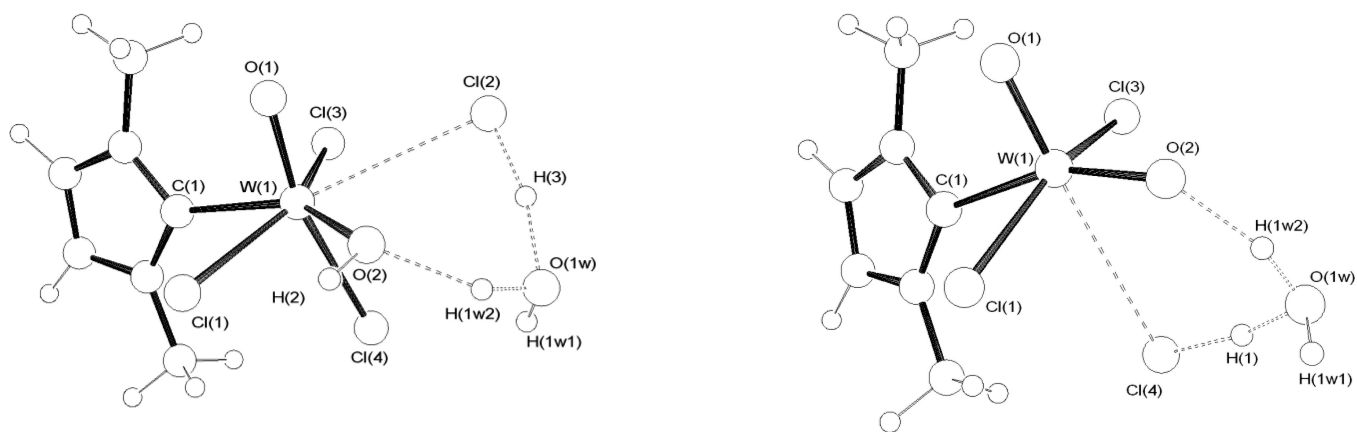


Figure 7. Calculated transition states in the hydrolytic conversion of 2 to 3.

is not independent of the other coligands. The MO surfaces generated show significant contributions from both NHC and the oxo and chloro ligands.

Of the NHC molecular orbitals potentially capable of bonding to the metal, NHC π_1 , NHC π_2 and NHC π_3 remain, to all intents and purposes, nonbonding in nature in the complex 3a. NHC π_3 interacts very weakly with the d_{xz} orbital, but the major interaction, as expected, is between NHC σ and the $d_{x^2-y^2}$ and d_{z^2} orbitals. The metal–ligand bonding orbital sets are summarized in Figure 5, which shows the calculated MO surfaces and cartoon representations. Equivalent antibonding orbitals are seen in each case. The lowest energy orbitals are those involving NHC σ , $2 \times \text{Cl}(\sigma)$ and $2 \times \text{O}(\pi)$ interactions with the metal $5d_{x^2-y^2}$ and $5d_{z^2}$ orbitals. The remaining bonding orbitals have no carbene character but rather arise from various combinations of metal 5d and O and Cl orbitals alone. In ascending energy these may be summarized as follows: $2 \times \text{O}(\text{p}\sigma) + 2 \times \text{Cl}(\text{p}\pi)$ interacting with $5d_{yz}$; $2 \times \text{O}(\text{p}\pi) + \text{Cl}_{\text{trans}}(\text{p}\pi)$ interacting with $5d_{xy}$; and $2 \times \text{O}(\text{p}\pi) + \text{Cl}(\text{p}\pi)$ interacting with $5d_{xz}$. The last example also shows a degree of π interaction of this composite orbital with the carbene carbon of the NHC, similar to those seen in [VOCl₃(IMes)] and [TiCl₂(NMe₂)₂(IMes)].

The full MO bonding picture is summarized in the semiquantitative orbital energy diagram in Figure 5. It is

interesting to note that the M–L bonding orbitals are substantially lower in energy than the HOMO, which is a ligand-based aryl π orbital. However, the LUMO, and several of those orbitals immediately higher in energy are M–L antibonding orbitals and thus have substantial metal 5d character. This is consistent with the formal d^0 valence electron configuration and confirms that any reduction process is likely to be predominantly metal based, in contrast to some low-valent macrocyclic NHCs recently reported, in which reduction is ligand based.²⁶

It is clear that in the formation of 3a adventitious hydrolysis has occurred, transforming the WOCl₄ fragment into WO₂Cl₂. While exposure of 2 to the atmosphere results in rapid and complete decomposition of the WOCl₄ adduct, it would seem that the slow diffusion of moisture into the solution allows a controlled hydrolysis to take place. Such efficient hydrolytic transformations are rarely observed in high oxidation state complexes, complete decomposition being more usual, and we were interested in probing this reaction further by computational methods.

Initial attempts to model this reaction using a single molecule of water resulted in a highly strained transition state of improbably high energy. Introduction of a second molecule of water, however, resulted in a plausible reaction pathway summarized in Figure 6.

The first step is nucleophilic attack by water at the tungsten center, resulting in a weakening of one of the W–Cl bonds. This may be considered an associative interchange mechanistic pathway. A second molecule of water mediates the concerted loss of HCl, accepting a proton from the coordinating water (generating a coordinated hydroxide) and simultaneously transferring a proton to the ejected chloride anion. The second step is the transfer of H⁺ to the chloride anion leading to elimination of HCl, and this process is again mediated by a single water molecule, which accepts a proton from the bound OH and donates a proton to the emergent Cl[−] anion. The calculated transition states are shown in Figure 7.

CONCLUSIONS

The reaction of WOCl₄ with Idipp yields an extremely moisture sensitive adduct, which on the basis of NMR spectroscopy and computational analysis is a six-coordinate species with the NHC cis to the oxo ligand. Slow hydrolysis of this complex leads to a high yield of the complex [WO₂Cl₂(Idipp)], which is the first five-coordinate 1:1 adduct of WO₂Cl₂ and the first structurally characterized tungsten(VI) NHC complex. The metal–NHC bonding, as revealed by DFT calculations, is primarily σ donor in character, with a modest contribution from back-donation originating from a composite MO involving the 5d_{xz} and Cl p orbitals, similar to interactions observed in other d⁰ metal carbene complexes. A plausible hydrolysis mechanism, obtained from DFT calculations, is also reported.

EXPERIMENTAL DETAILS

General Considerations. All manipulations were performed under an atmosphere of dry argon gas on a Schlenk line. Glassware was dried overnight in an oven at 120 °C and prior to use was evacuated, heated with a heat gun, and filled with dry argon. All solvents were dried and distilled prior to use: toluene (Na/benzophenone); dichloromethane (CaH₂). 1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride and its corresponding carbene (Idipp) were prepared by the method of Arduengo.²⁷ WOCl₄ and WO₂Cl₂ were prepared by the method of Gibson²⁸ and used immediately. All other chemicals were purchased from Aldrich and used as received, except for hexamethyldisiloxane, which was distilled prior to use. NMR spectra were obtained at room temperature in d₆-benzene or CDCl₃ on a Bruker DPX 400 spectrometer operating at 400 MHz (¹H) and 100 MHz (¹³C).

Syntheses. *Preparation of [WOCl₄(Idipp)].* Freshly prepared WOCl₄ (0.342 g, 1 mmol) was dissolved in toluene (12 mL) and cooled to −78 °C. To this stirred solution was added via cannula 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (0.388 g, 1 mmol) in toluene (12 mL), also cooled to −78 °C. The reaction mixture was stirred for 1 h and slowly warmed to room temperature. The mixture was filtered, removing a small quantity of brown solid and yielding a deep red-brown solution. An orange-brown microcrystalline product was isolated by concentration the toluene solution and storing at −18 °C. Yield: ca. 0.4 g; 55%. ¹H NMR (400 MHz, C₆D₆; δ /ppm): 0.92 (d, 12H, CH(CH₃)₂, ³J_{HH} = 6.8 Hz); 1.41 (d, 12H, CH(CH₃)₂, ³J_{HH} = 6.8 Hz); 2.71 (sept, 4H, CH(CH₃)₂, ³J_{HH} = 6.8 Hz); 6.58 (s, 2H, im-H^{4,5}); 7.03 (d, 4H, meta-CH, ³J_{HH} = 7.9 Hz); 7.20 (t, 2H, para-CH, ³J_{HH} = 7.9 Hz). ¹³C{¹H} NMR (100 MHz, C₆D₆; δ /ppm): 23.15 (s, CH(CH₃)₂); 26.44 (s, CH(CH₃)₂); 29.68 (s, CH(CH₃)₂); 124.88 (s, im-C^{4,5}); 129.67 (s, Ar-C); 131.88 (s, Ar-C); 134.51 (s, Ar-C); 146.44 (s, Ar-C).

Preparation of [WO₂Cl₂(Idipp)]. An isolated sample of [WOCl₄(Idipp)] prepared as detailed above was dissolved in a minimum quantity of dry toluene. Standing in the refrigerator (5 °C) for an extended period (typically about 1 week) resulted in the formation of a colorless crystalline material in essentially quantitative yield. ¹H NMR (400 MHz, CDCl₃; δ /ppm): 1.13 (d, 12H, CH(CH₃)₂, ³J_{HH} = 6.88

Hz); 1.43 (d, 12H, CH(CH₃)₂, ³J_{HH} = 6.8 Hz); 2.61 (sept, 4H, CH(CH₃)₂, ³J_{HH} = 6.8 Hz); 7.26 (s, 2H, im-H^{4,5}); 7.32 (d, 4H, meta-CH, ³J_{HH} = 7.8 Hz); 7.53 (t, 2H, para-CH, ³J_{HH} = 7.8 Hz). ¹³C{¹H} NMR (100 MHz, CDCl₃; δ /ppm): 22.82 (s, C(CH₃)₂); 26.30 (s, C(CH₃)₂); 29.33 (s, C(CH₃)₂); 124.50 (s, im-C^{4,5}); 125.31 (s, Ar-C); 131.53 (s, Ar-C); 137.36 (s, Ar-C); 146.81 (s, Ar-C).

Attempted Direct Preparation of [WO₂Cl₂(Idipp)] from WO₂Cl₂. WO₂Cl₂ was prepared in a modification to the procedure outlined by Gibson et al. A dichloromethane solution of freshly prepared WOCl₄ was reacted in situ with a further 1 equiv of hexamethyldisiloxane. The product was isolated rapidly to prevent formation of undesirable siloxane species. The WO₂Cl₂ thus prepared (0.287 g, 1 mmol) was suspended in toluene (12 mL) and cooled to −78 °C. To this stirred solution was added via cannula 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (0.388 g, 1 mmol) in toluene (12 mL), also cooled to −78 °C. The reaction mixture was stirred for 1 h and slowly warmed to room temperature. The mixture was filtered, yielding a small quantity of pale green solid and a colorless solution. Microcrystalline material was isolated by concentration of the toluene solution and storing at −10 °C. Yield: 0.3 g; ca. 45%. The desired product (60–90%) was also contaminated with varying amounts of at least two other NHC complexes which could not be separated.

X-ray Crystallography. Crystals were coated in mineral oil under an N₂ atmosphere and mounted on a glass fiber. X-ray diffraction data were obtained at 123(2) K on a Nonius Kappa CCD diffractometer equipped with graphite-monochromated Mo K α radiation.

Data reduction and correction for absorption were performed using the Denzo/Scalepack program.²⁹ The heavy atoms (tungsten and chlorine) were located in the Patterson map and the light atoms identified in the Fourier difference map, and the model was refined on F². All non-H atoms were refined with anisotropic displacement parameters and, although many of the hydrogen atoms could be identified in the difference electron density maps, they were placed in calculated positions, riding on the parent atom. The structure solution and refinement used the programs Shelxs-86³⁰ and Shelxl-97³¹ and the WingX utility.³²

Theoretical Calculations. All structures were optimized at the density functional level of theory,^{33–35} where the B3LYP functional^{36–39} was used in conjunction with the 6-31G(d,p)^{40–43} basis set and the MWB60 pseudopotential and associated basis set for W.⁴⁴ Frequency calculations were performed to characterize the optimized structures as minima or transition states, where the transition states were found to each have a single imaginary frequency. In addition, the vibrational frequencies were used to obtain temperature-corrected energies, enthalpies, entropies, and free energies. The Gaussian03 program⁴⁵ was used for all calculations. The structures of the NHC complexes were all calculated using the complete 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene (Idipp) ligand, whereas the mechanism was probed by using the 1,3-dimethylimidazol-2-ylidene to save computational time.

ASSOCIATED CONTENT

Supporting Information

Tables giving structural data (both calculated and experimental), CIF files giving the crystallographic data for [Idipp]⁺[WOCl₅][−] and [WO₂Cl₂(Idipp)], and xyz files giving the Cartesian coordinates of the calculated structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: m.d.spicer@strath.ac.uk.

ACKNOWLEDGMENTS

We thank the EPSRC for funding (C.A.D.).

REFERENCES

- (1) Öfele, K. *J. Organomet. Chem.* **1968**, *12*, P42.
- (2) Wanzlick, H.-W.; Schönherr, H.-J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 141.
- (3) Hitchcock, P. B.; Lappert, M. F.; Terreros, P. *J. Organomet. Chem.* **1982**, *239*, C26.
- (4) Sundberg, R. J.; Bryan, R. F.; Taylor, I. F. Jr.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 381.
- (5) Arduengo, A. J. III *J. Am. Chem. Soc.* **1991**, *113*, 361.
- (6) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.
- (7) Clavier, H.; Nolan, S. P. *Chem. Commun.* **2010**, 841.
- (8) Herrmann, W. A.; Öfele, K.; Elison, M.; Kühn, F. E.; Roesky, P. *W. J. Organomet. Chem.* **1994**, *480*, C7.
- (9) Herrmann, W. A.; Lobmaier, G. M.; Elison, M. *J. Organomet. Chem.* **1996**, *520*, 231.
- (10) Abernethy, C. D.; Codd, G.; Taylor, M. K.; Spicer, M. D. *J. Am. Chem. Soc.* **2003**, *125*, 1128.
- (11) Beard, C. D.; Barrie, R. J.; Evans, J.; Levason, W.; Reid, G.; Spicer, M. D. *Eur. J. Inorg. Chem.* **2006**, 4391.
- (12) (a) Braband, H.; Abram, U. *Chem. Commun.* **2003**, 2436. (b) Braband, H.; Zahn, T. I.; Abram, U. *Inorg. Chem.* **2003**, *42*, 6160.
- (13) Royo, B.; Herdtweck, E.; Romão, C. C. *Eur. J. Inorg. Chem.* **2004**, 3305.
- (14) Mas-Marzá, E.; Reis, P. M.; Peris, E.; Royo, B. *J. Organomet. Chem.* **2006**, *691*, 2708.
- (15) Li, S.; Kee, C. W.; Huang, K.-W.; Hor, T. S. A.; Zhao, J. *Organometallics* **2010**, *29*, 1924.
- (16) (a) Casely, I. J.; Liddle, S. T.; Blake, A. J.; Wilson, C.; Arnold, P. *L. Chem. Commun* **2007**, 5037. (b) Arnold, P. L.; Casely, I. J. *Chem. Rev.* **2009**, *109*, 3599.
- (17) (a) Oldham, W. J. Jr.; Oldham, S. M.; Scott, B. L.; Abney, K. D.; Smith, W. H.; Costa, D. A. *Chem. Commun.* **2001**, 1348. (b) Arnold, P. L.; Liddle, S. T. *Chem. Commun.* **2006**, 3947.
- (18) Fowles, G. W. A.; Frost, J. L. *J. Chem. Soc. A* **1967**, 671.
- (19) (a) Davis, M. F.; Levason, W.; Light, M. E.; Ratnani, R.; Reid, G.; Saraswat, K.; Webster, M. *Eur. J. Inorg. Chem.* **2007**, 1903. (b) Davis, M. F.; Levason, W.; Ratnani, R.; Reid, G.; Rose, T.; Webster, M. *Eur. J. Inorg. Chem.* **2007**, 306. (c) Jimtaisong, A.; Luck, R. L. *Inorg. Chem.* **2006**, *45*, 10391. (d) Herrmann, W. A.; Thiel, W. R.; Herdtweck, E. *Chem. Ber.* **1990**, *123*, 271.
- (20) (a) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380. (b) CCDC (1994). *Vista - A Program for the Analysis and Display of Data Retrieved from the CSD*; Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.
- (21) Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. *Coord. Chem. Rev.* **2009**, *253*, 687.
- (22) Hu, X.; Castro-Rodriguez, I.; Olsen, K.; Meyer, K. *Organometallics* **2004**, *23*, 755.
- (23) Green, J. C.; Herbert, B. J. *Dalton Trans.* **2005**, 1214.
- (24) Spicer, M. D.; Dodds, C. A.; Culver, J. P.; Abernethy, C. D. *ACS Symp. Ser.* **2006**, *917*, 252.
- (25) (a) Dorta, R.; Stevens, E. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5054. (b) Scott, N. M.; Dorta, R.; Stevens, E. D.; Correa, A.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 3516.
- (26) Findlay, N. J.; Park, S. R.; Schoenebeck, F.; Cahard, E.; Zhou, S. Z.; Berlouis, L. E. A.; Spicer, M. D.; Tuttle, T.; Murphy, J. A. *J. Am. Chem. Soc.* **2010**, *132*, 15462.
- (27) Arduengo, A. J. III; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523.
- (28) Gibson, V. C.; Kee, T. P.; Shaw, A. *Polyhedron* **1990**, *9*, 2293.
- (29) Otwinowski, Z.; Minor, W. *Processing of X-ray Diffraction Data Collected in Oscillation Mode. Methods in Enzymology*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol. 276 (Macromolecular Crystallography, part A), p 307.
- (30) Sheldrick, G. M. *SHELXS-86, Program for Crystal Structure Solution*; Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1986.
- (31) Sheldrick, G. M. *SHELX97, Programs for Crystal Structure Analysis (Release 97-2)*; Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
- (32) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.
- (33) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, 1133.
- (34) Parr, R. G.; Yang, W. T. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
- (35) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- (36) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (37) Hertwig, R. H.; Koch, W. *Chem. Phys. Lett.* **1997**, *268*, 345.
- (38) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (39) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
- (40) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
- (41) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
- (42) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
- (43) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.
- (44) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.
- (45) Frisch, M. J. et al. *Gaussian 03, V. C.01*; Gaussian, Inc., Wallingford, CT, 2004.