

A Highly Stable N-Heterocyclic Carbene Complex of Trichloro-oxo-vanadium(V) Displaying Novel Cl–C_{carbene} Bonding Interactions

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N-Heterocyclic carbenes are at the forefront of the revolution currently occurring in ligand design. As highly nucleophilic species, they are used extensively as ligands in systems that catalyze C–C bond formation.¹ Accordingly, transition-metal complexes of these carbenes have been subject to intense investigation in recent years.² However, this research has focused almost exclusively on systems in which the transition metal is in a low oxidation state. Only one study of high-oxidation-state transition-metal carbene complexes has been published to date, and X-ray diffraction data for the reported compounds are not available.³ Herein, we report an extremely stable carbene adduct of trichloro-oxo-vanadium(V), which exhibits a hitherto unobserved bonding interaction between the C_{carbene} atom and the neighboring chloride ligands.

The reaction of equimolar quantities of 1,3-dimesitylimidazol-2-ylidene and trichloro-oxo-vanadium(V) affords the deep red 1:1 adduct **1**.⁴ Both solid samples and dichloromethane solutions of **1** are stable in air and showed no decomposition on standing for over two months. The remarkable stability of **1** is in contrast to the other characterized adducts of trichloro-oxo-vanadium(V), which are all readily hydrolyzed in air.⁵ The stabilizing influence of the carbene ligand was further demonstrated electrochemically. In dichloromethane, **1** undergoes a 1-electron reversible reduction at a potential of +0.50 V,⁶ which is significantly lower than the standard potential of V(V)/V(IV) (+1.00 V).⁷

The molecular structure of **1**, determined by an X-ray analysis, reveals the interaction of the C_{carbene} with neighboring ligands (Figure 1).⁸ The chlorides cis to the carbene lie almost perpendicular to the plane of the heterocyclic ring of the carbene and are oriented toward this ligand (C(1)–V(1)–Cl(1) 81.04(6)^o and C(1)–V(1)–Cl(3) 82.20(6)^o). The distances of these cis chlorides, Cl(1) and Cl(3), to the C_{carbene} atom are 2.849(2) and 2.887(2) Å, well within the sum of the van der Waals radii for carbon and chlorine (3.45 Å),⁹ which suggests a strong interaction between chloride lone-pair electron density and the formally vacant molecular orbitals situated on the C_{carbene}. This is unexpected as the energy of the vacant p-orbital at the C_{carbene} of N-heterocyclic carbenes is considerably increased by strong N→C π-donation. Consequently, this orbital has been considered to play a very limited role in the reactivity of these species.² Indeed, photoelectron spectroscopy coupled with ab initio density functional theory (DFT) calculations has demonstrated that M–C_{carbene} π-back-bonding is negligible when N-heterocyclic carbenes are bound to group 10 metals.¹⁰

To gain further insights into this interaction DFT calculations (6-31+G(d,p) basis set, B3LYP method) were performed for a hypothetical VOCl₃ adduct of 1,3-dimethylimidazol-2-ylidene, **2**.¹¹ The optimized minimum-energy structure yielded bond distances and angles in good agreement with those obtained from the X-ray diffraction study of **1** (Figure 2). The close cis Cl–C_{carbene} distances obtained demonstrate that the observed interaction is independent of the steric bulk of the carbene employed and is unrelated to any

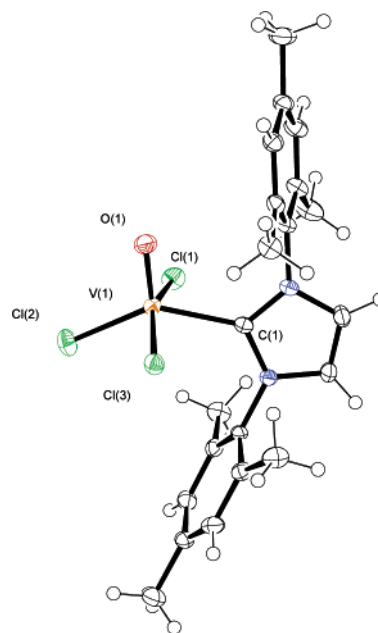


Figure 1. Molecular structure of **1**. Selected bond lengths (Å) and angles (deg): V(1)–C(1) 2.137(2), V(1)–O(1) 1.5749(16), V(1)–Cl(1) 2.2462(7), V(1)–Cl(2) 2.2232(7), V(1)–Cl(3) 2.2537(6), C(1)–V(1)–Cl(1) 81.04(6), C(1)–V(1)–Cl(2) 142.08(6), C(1)–V(1)–Cl(3) 82.20(6), O(1)–V(1)–C(1) 105.83(8), O(1)–V(1)–Cl(1) 99.77(6), O(1)–V(1)–Cl(2) 112.09(7), O(1)–V(1)–Cl(3) 98.42(6), Cl(1)–V(1)–Cl(2) 92.22(3), Cl(1)–V(1)–Cl(3) 158.01(3), Cl(2)–V(1)–Cl(3) 92.28(3).

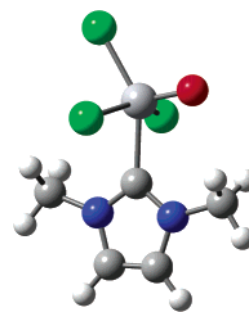


Figure 2. Calculated molecular structure of **2**. Selected calculated interatomic lengths (Å) and angles (deg): V–C(1) 2.14, V(1)–O(1) 1.55, V(1)–Cl(1) 2.27, V(1)–Cl(2) 2.21, V(1)–Cl(3) 2.28, Cl(1)–C(1) 2.81, Cl(3)–C(1) 2.81, C(1)–V(1)–Cl(1) 78.86, C(1)–V(1)–Cl(3) 79.01, Cl(1)–V(1)–Cl(2) 93.258.

crystal-packing forces. Analysis of the molecular orbitals given by the DFT calculations indicates that substantial bonding overlap does indeed occur between the lone pairs of the cis chloride ligands and the formally vacant p-orbital of the C_{carbene} atom. Figure 3b shows

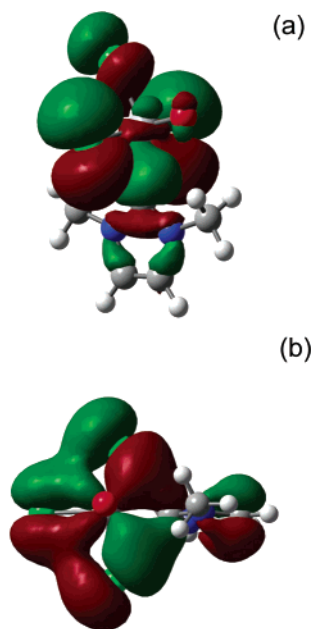


Figure 3. Isosurfaces of (a) carbene–vanadium σ bonding orbital (b) one of the carbene–chloride bonding orbitals (generated at $0.02 \text{ e}^{0.5} \text{ \AA}^{-1.5}$ using GaussView2.1).

the calculated HOMO-8 orbital, which illustrates this. It is noteworthy that these interligand bonding interactions involve significant vanadium d-orbital contributions and can, therefore, be considered to be a form of back-bonding to the carbene with the electron density originating from the chloride ligands' lone pairs rather than the metal.

The occurrence of these interactions may be due to the high Lewis acidity of the vanadium center, which gives rise to a more polar $\text{C} \rightarrow \text{M}$ σ -donation than in the low-valent late transition metal cases previously studied. This, in turn, results in a partial positive charge on the $\text{C}_{\text{carbene}}$, which is stabilized by the bonding interactions with the chlorides' lone pairs.

In previous studies carbene complexes have been classified as Fischer-type (electrophilic, singlet $\text{C}_{\text{carbene}}$) or Schrock-type (nucleophilic, triplet $\text{C}_{\text{carbene}}$), depending on the oxidation state of the metal.¹³ In this case, complexation of an N-heterocyclic carbene to vanadium(V) results in an electrophilic singlet $\text{C}_{\text{carbene}}$, which is typical of Fischer-type systems, but is unusually supported by a high-oxidation-state metal center. N-Heterocyclic carbenes may, therefore, be used to extend Fischer-type carbene properties to high-oxidation-state metal complexes and thus complement their established Schrock-type carbene chemistry.

In conclusion, coordination of a N-heterocyclic carbene to trichloro-oxo-vandium(V) results in a highly stable vanadium(V) complex. The stability of this compound to air makes it an excellent entry point into vanadium-oxo chemistry and demonstrates the utility of N-heterocyclic carbenes to stabilize high-oxidation-state transition-metal complexes.

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Supporting Information Available: CIF file for **1**. Input coordinates for **2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (4) Synthesis and spectroscopic and analytical data for **1**: $\text{V}(\text{O})\text{Cl}_3$ (0.5 g, 2.88 mmol) was added dropwise to a solution of $:\text{CN}(\text{Mes})\text{C}_2\text{H}_2\text{N}(\text{Mes})$, prepared according to Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361, (0.88 g, 2.88 mmol) in 100 cm^3 of toluene. Deep-red crystals of **1** formed on standing for 3 weeks at 25°C , which were collected by filtration and washed with hexane. A second crop of crystals formed when the filtrate was set aside for a further 3 weeks at -30°C . Total yield: 1.05 g, 76%. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 2.23 [s, 12H, *o*- CH_3], 2.35 [s, 6H, *p*- CH_3], 7.01 [s, 4H, *Ar-H*], 7.12 [s, 2H, C_2H_2]. ^{13}C NMR (100.6 MHz, CDCl_3 , 298 K): δ 18.8 [s, *o*- CH_3], 21.0 [s, *p*- CH_3], 129.5 [s, NCC], 130.0 [s, *m*-CH], 134.0 [s, *p*- CCH_3], 135.6 [s, *o*- CCH_3], 140.2 [s, *ipso*-C], V-C not observed. ^{51}V NMR (105.3 MHz, CDCl_3 , 298 K): δ -77.1 [s, $\Delta\nu_{1/2} = 32 \text{ Hz}$]. IR (KBr disc): $\nu_{\text{V=O}}$ 1020, 972 cm^{-1} . Raman: $\nu_{\text{V=O}}$ 1017, 972 cm^{-1} . Mp: 65°C . Anal. for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{Cl}_3\text{OV}$: calcd C 52.80, H 5.06, N 5.86, Cl 22.26. Found: C 49.44, H 4.96, N 5.32, Cl 21.85.
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- (6) Cyclic voltammetry was conducted on $4 \times 10^{-3} \text{ M}$ solutions of **1** in dichloromethane with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte.
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- (8) Crystal data for **1**: red needle (0.6 mm \times 0.15 mm \times 0.04 mm) $\text{C}_{21}\text{H}_{22}\text{Cl}_3\text{N}_2\text{O}_1\text{V}$, $M = 477.74$, triclinic, space group $P-1$ (No. 2), $a = 7.8641(2) \text{ \AA}$, $b = 8.2857(2) \text{ \AA}$, $c = 18.2282(5) \text{ \AA}$, $\alpha = 102.388(1)^\circ$, $\beta = 91.132(1)^\circ$, $\gamma = 108.175(1)^\circ$, $V = 1097.39(5) \text{ \AA}^3$, $Z = 2$, $D_c = 1.446 \text{ g cm}^{-3}$, $T = 123 \text{ K}$, $\mu(\text{Mo K}\alpha) = 0.831 \text{ mm}^{-1}$, 8549 reflections measured, 4972 unique reflections ($R_{\text{int}} = 0.026$), refinement with 258 parameters converged with agreement factors R_1 (all data) = 0.056, wR_2 (all data) = 0.087, S (all data) = 1.003. The structure was solved by standard direct methods techniques (SHELXS-97)¹² and refined using full matrix least squares based on F^2 (SHELXL-97).¹² All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions riding on the atoms to which they were attached.
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