the orientations observed in the crystal must be ascribed to relatively weak intramolecular interactions and/or intermolecular crystal packing forces.

$Os(NAr)_3$ is soluble and stable in most common organic solvents and is stable to moist air in both the solid state and solution for days at 25 °C. It is insoluble and stable in water. It does not react at 25 °C with pyridine, tetrahydrofuran, tertiary amines, triphenylphosphine, gaseous HCl in ether, $Ph_3P{=}O$, propylene oxide, norbornene, cyclopentene, or styrene. However, **1** does react readily with PMe_2Ph in pentane to give violet, crystalline $Os(NAr)_2(PMe_2Ph)_2$ (**2**) and $Me_2PhP{=}NAr$ in high yield.[12] (Products that probably are related to **2** are obtained from analogous reactions between **1** and PMe_3, $P(OMe)_3$, or $P(OPh)_3$.) An X-ray study[13] showed **2** to be a square-planar complex in which there is a crystallographic inversion center (Figure 2). The bond lengths Os=N = 1.790 (6) Å and Os–P = 2.374 (2) Å are not unusual. The imido ligands are virtually linear (Os–N–C angle of 177.9 (5)°). Therefore **2** also might be called a "20-electron" complex, but again, an electron pair can be said to be in a nitrogen-based nonbonding MO (b_{3u} in D_{2h} symmetry) made up of the symmetric combination of the two in-plane p orbitals on the nitrogen atoms. (The b_{3u} orbital on osmium probably is used primarily for σ bonding to the phosphine ligands.)

Compound **1** reacts with Me_3NO to give red-black crystalline $OsO(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3$ (**3**),[14] an analogue of previously reported $OsO(N\text{-}t\text{-}Bu)_3$.[15] **3** readily transfers an oxygen atom to PPh_3 to generate Ph_3PO and **1** and reacts with norbornene, cyclopentene, and ethylene[16] to give orange, crystalline products that contain a plane of symmetry (by NMR) and therefore are postulated to be Os(VI) metallaimidazolidine complexes analogous to those postulated as intermediates in reactions between $OsO(N\text{-}t\text{-}Bu)_3$ and olefins.[15] The structure of $Os[(Ar)NCH_2CH_2N(Ar)](O)(NAr)$ has been confirmed by an X-ray study, details of which will be published later.

To our knowledge, **1** is the first example of a "pure" homoleptic imido complex[17] and a rare example of trigonal coordination.[18] The unusual square-planar geometry of **2** is reminiscent of square-planar complexes of the type $M(O\text{-}2,6\text{-}C_6H_3R_2)_4$ (M = W[19] or Re;[20] R = *i*-Pr or Me) where strong π bonding is believed to enforce the square-planar geometry. The structures of **1** and **2** challenge the notion that linearity or near linearity of an imido ligand implies donation of the electron pair on nitrogen to the metal.[5] The structure of a recently reported "20-electron" zirconium complex would justify a similar conclusion.[21]

Acknowledgment. R.R.S. thanks the National Science Foundation for research support (CHE 88-22508) and the U.S. Department of Energy, Division of University and Industry Programs, for funds to purchase the X-ray diffractometer (Grant DE-FG05-86ER75292). J.T.A. thanks the Deutscher Akademischer Austauschdienst for a NATO Postdoctoral Fellowship, and T.P.K. thanks the Science and Engineering Research Council for a NATO Postdoctoral Fellowship. We thank Dr. W. M. Davis for collecting the data set for **1** and Molecular Structure Corporation for collecting the data set for **2**.

Supplementary Material Available: Description of the X-ray study, an ORTEP drawing, and a fully labeled drawing and tables of final positional parameters and final thermal parameters for **1** and **2** (21 pages); tables of final observed and calculated structure factors for **1** and **2** (52 pages). Ordering information is given on any current masthead page.

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(12) Anal. Calcd for $C_{32}H_{45}N_2O_2Os$: C, 58.80; H, 6.91; N, 3.43. Found: C, 58.62; H, 7.14; N, 3.45. ^1H NMR (C_6D_6): δ 4.32 (C*H*Me₂), 1.53 (virtual t, PPh*Me*₂), 1.13 (CH*Me*₂); aryl proton resonances not listed.

(13) A crystal was mounted in a glass capillary. Data were collected on a Rigaku AFC6R diffractometer at room temperature using graphite-monochromated Mo Kα radiation: space group $P2_1/c$ with a = 9.605 (2) Å, b = 9.314 (7) Å, c = 21.996 (3) Å, β = 96.56 (2)°, Z = 2, FW = 817.04, and ρ = 1.388 g/cm³. A total of 3914 reflections ($h,k,\pm l$) were collected in the range 0° < 2θ < 48° with the 2206 having $I > 3.00\sigma(I)$ being used in the structure refinement by full-matrix least-squares techniques (206 variables) using the TEXSAN crystallographic software package from Molecular Structure Corporation. Final R_1 = 0.029, R_2 = 0.044. Full details can be found in the supplementary material.

(14) A suspension of **1** (0.2 g, 0.24 mmol) and Me_3NO (0.063 g, 0.84 mmol) in toluene (20 mL) was stirred under dinitrogen at room temperature for 24 h. Solvents were removed in vacuo, and the residue was extracted and recrystallized from pentane to afford red-brown crystals of **2** in 63% yield: ^1H NMR (C_6D_6) δ 7.00 (H_m), 6.88 (H_p), 3.47 (Me_2CH), 1.08 (Me_2CH); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 153.77 (C_{ipso}), 141.33 (C_o), 128.59 (C_m), 122.51 (C_p), 29.31 (Me_2CH), 23.55 (Me_2CH). Anal. Calcd for $C_{36}H_{51}N_3OOs$: C, 59.07; H, 7.02; N, 5.74. Found: C, 58.75; H, 7.17; N, 5.65.

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(16) Anal. Calcd for $C_{38}H_{55}N_3OOs$: C, 60.05; H, 7.29; N, 5.53. Found: C, 60.18; H, 7.44; N, 5.70. ^1H NMR (C_6D_6): δ 7.15–6.80 (m, 9, aryl protons), 4.05 (AA′BB′ pattern, 4, C_2H_4), 3.79 (sept, 2, $CHMe_2$), 2.81 (sept, 2, $CHMe_2$), 2.41 (sept, 2, $CHMe_2$), 1.54 (d, 6, $CHMe_2$), 1.20 (d, 6, $CHMe_2$), 1.14 (d, 6, $CHMe_2$), 0.93 (d, 6, $CHMe_2$), 0.90 (d, 12, $CHMe_2$). ^{13}C NMR (C_6D_6): δ 70.48 (C_β); ν(Os=O) 896 cm⁻¹.

(17) (a) Closely related complexes that contain lithium–nitrogen bonds are $Li_2W(N\text{-}t\text{-}Bu)_4$ and $Li(tmeda)Re(N\text{-}t\text{-}Bu)_4$.[17b] "$Re(N\text{-}t\text{-}Bu)_3$" is actually a dimer, $[Re(N\text{-}t\text{-}Bu)_2(\mu\text{-}N\text{-}t\text{-}Bu)]_2$.[17c] $Os(N\text{-}t\text{-}Bu)_3(NSO_2aryl)$ was characterized by elemental analysis and by its reactions with olefins,[17d] but not crystallographically characterized. (b) Danopoulos, A. A.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1989**, 896. (c) Danopoulos, A. A.; Longley, C. J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Polyhedron*, in press. (d) Hentges, S. G.; Sharpless, K. B., unpublished results.

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X-ray Absorption Edge Spectroscopy of Ligands Bound to Open-Shell Metal Ions: Chlorine K-Edge Studies of Covalency in $CuCl_4^{2-}$

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Received July 20, 1989

Information on electronic structure can be obtained from analysis of X-ray absorption edge spectra.[1] This approach has been used to obtain information from edges of transition metals like Cu, Fe, Ni, and Mo.[2] It is also possible to directly study the absorption edge of ligands such as Cl and S bound to the metal.[2e,3] These edges fall in the 2–3-keV energy region where edge features are very well resolved.[4] We report here the observation of an intense preedge transition associated with ligands bound to open-shell central atoms. We further show that the

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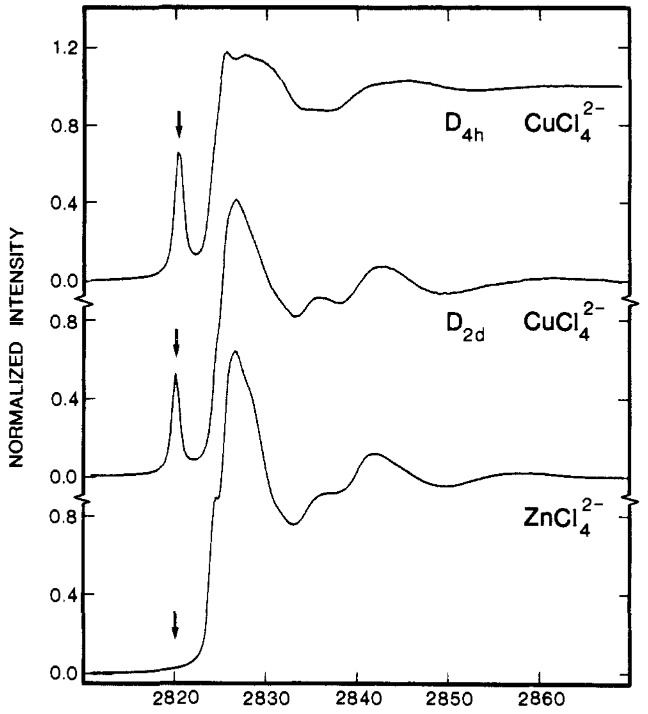

Figure 1. Cl K-edge XAS spectra of, from top, D_{4h} $CuCl_4^{2-}$, D_{2d} $CuCl_4^{2-}$, and $ZnCl_4^{2-}$. The intensity of the ~2820-eV feature reflects the amount of ligand character in the $(1 - \alpha^2)^{1/2}$(Cu $3d_{x^2-y^2}$) $- \alpha$(Cl 3p) antibonding molecular orbital, as seen in the decrease for D_{2d} relative to D_{4h}, and in the absence of this feature for $ZnCl_4^{2-}$, which has a closed 3d shell.

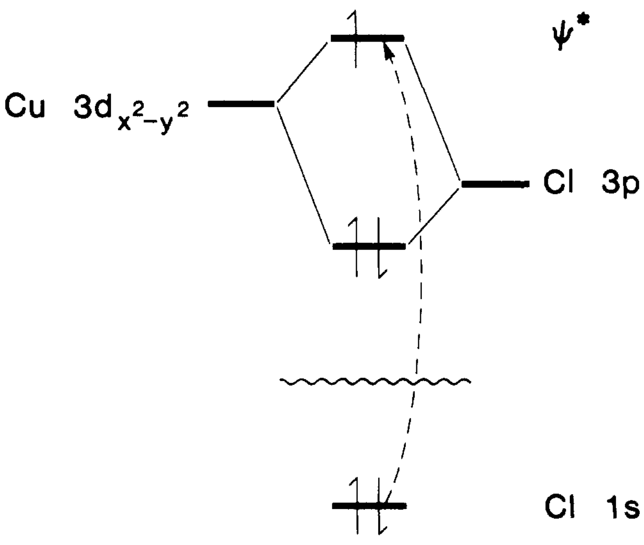

Figure 2. Orbital energy diagram showing the transition of the Cl 1s electron to the antibonding $(1 - \alpha^2)^{1/2}$(Cu $3d_{x^2-y^2}$) $- \alpha$(Cl 3p) molecular orbital.

properties of these preedge features can be used to probe covalency in metal–ligand bonding.

We have studied the ligand K edge of chlorine complexes of Cu and Zn: Cs_2CuCl_4,[5] bis(creatininium)$CuCl_4$,[6] and Cs_2ZnCl_4.[7] The Cu site in Cs_2CuCl_4 is distorted tetrahedral (D_{2d}),[8] and the Zn site in Cs_2ZnCl_4 is isostructural.[9] Bis(creatininium)$CuCl_4$ has a square-planar (D_{4h}) geometry.[6] X-ray absorption spectroscopy (XAS) edge data were measured at the Stanford Synchrotron Radiation Laboratory by using methodology that has been previously described.[10]

The XAS edges for the three compounds are shown in Figure 1. All three spectra show a primary edge onset at around 2822 eV and a maximum at about 2827 eV. The two D_{2d} complexes show very similar edge structure, with an unresolved transition as a shoulder on the main edge rise, and also very similar features in the region above the edge. The edge of the D_{4h} Cu complex is very different both at its maximum and above the main edge. The features above the edge arise primarily from continuum shape resonance effects.[11] These will be different for the D_{2d} and D_{4h} complexes because of the difference in the repulsive potentials expected in the more open D_{4h} geometry compared to those for the tetrahedral case. A striking feature in the spectra is the appearance of an intense low-energy transition at ~2820 eV for both Cu(II) complexes but which is absent for the Zn(II) complex. Further, it is important to note that the intensity of the 2820-eV transition is different for the D_{2d} vs D_{4h} Cu(II) complexes.

$ZnCl_4^{2-}$ contains a d^{10} closed-shell Zn(II) metal ion. The lowest energy transition available in this complex for the Cl 1s K edge is to the unoccupied Cl 4s and 4p orbital levels. The 1s → 4p transition is electric dipole allowed and is primarily responsible for the edge transition at 2827 eV and for the similarly intense edge transitions in the spectra of both the Cu(II) complexes. For both of the Cu(II) spectra, the appearance of a new feature at lower energy than the primary edge peak requires the presence of a transition from Cl to a new lower energy unfilled orbital. Cu(II) in the $CuCl_4^{2-}$ complexes is a d^9 open-shell ion, which from EPR studies has been shown to contain a hole in the $3d_{x^2-y^2}$ orbital on the Cu atom.[12]

The appearance of the additional low-energy 2820-eV transition must then correspond to a Cl 1s → Cu $3d_{x^2-y^2}$ transition. However, due to the localized nature of the Cl 1s orbital, this transition can only have absorption intensity if the $3d_{x^2-y^2}$ orbital contains a significant contribution of Cl p character, which must result from covalency.

As shown in Figure 2, a bonding interaction between the Cu $3d_{x^2-y^2}$ and the valence Cl 3p results in the antibonding wave function $\psi^* = (1 - \alpha^2)^{1/2}(\text{Cu } 3d_{x^2-y^2}) - \alpha(\text{Cl 3p})$, where α^2 represents the Cl 3p character, contained in a normalized, symmetry-adapted molecular orbital encompassing the four Cl ligands. The lowest energy Cl K-edge transition is thus the Cl 1s → ψ^* transition. The electric dipole intensity for this transition is given by eq 1a, where c is a constant. Substitution of ψ^* as given above, combined with the localized nature of the Cl 1s orbital, results in eq 1b, where $c|\langle \text{Cl 1s}|\mathbf{r}|\text{Cl 3p}\rangle|^2$ is simply the intensity of the pure Cl 1s → 3p transition. Thus the intensity observed in the 2820-eV transition is the intensity of a 1s → 3p transition weighted by α^2, the covalent character contained in the antibonding orbital.

$$I(\text{Cl 1s}\rightarrow\psi^*) = c|\langle \text{Cl 1s}|\mathbf{r}|\psi^*\rangle|^2 \tag{1a}$$

$$= \alpha^2 c|\langle \text{Cl 1s}|\mathbf{r}|\text{Cl 3p}\rangle|^2 \tag{1b}$$

$$= \alpha^2 I(\text{Cl 1s}\rightarrow\text{Cl 3p}) \tag{1c}$$

It is now important to note that the differences in intensity for the 2820-eV transition between the D_{2d} and D_{4h} $CuCl_4^{2-}$ spectra must reflect the difference in covalency of ψ^* in these complexes. The fact that the 1s → ψ^* transition is more intense for the D_{4h}

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complex indicates that α^2 is larger, and hence the $3d_{x^2-y^2}$ orbital is more covalent in character in this complex relative to the D_{2d} complex. From a variety of more traditional spectroscopy methods (EPR superhyperfine analysis, etc.), it is established that ψ^* in D_{4h} $CuCl_4^{2-}$ contains ~61% Cu $3d_{x^2-y^2}$ and ~39% Cl 3p character.[12] On the basis of the experimental intensity ratios for the 2820-eV transition and calibrating it for D_{4h} $CuCl_4^{2-}$ to the $\alpha^2 = 0.39$ value, the intensity of the 2820-eV feature gives a corresponding value for D_{2d} $CuCl_4^{2-}$ of $\alpha^2 \simeq 0.29$ and thus approximately 71% Cu character. While traditional spectroscopic approaches are not as accessible for D_{2d} $CuCl_4^{2-}$, $X\alpha$ calculations predict a decrease of ~6% in the $3d_{x^2-y^2}$ orbital on going to the D_{2d} distorted tetrahedral structure, which is consistent with our XAS experimental findings.[13]

Ligand XAS spectroscopy thus provides a powerful new approach for probing covalent character in valence orbitals of transition-metal complexes.[14] This method, while having clear parallels with superhyperfine analysis in EPR, can in many cases be an advantageous alternative approach, in that obtaining a resolvable superhyperfine signal is often not possible, as is the case with D_{2d} $CuCl_4^{2-}$. This XAS method will be most powerful in the 2-3-keV energy region, based on the high-energy resolution, which allows it to be applied to P, S, and Cl ligands. Other ligands such as Br, which have much higher K-edge energies, can also be studied,[15] but the lower energy resolution will make interpretation less straightforward.

Acknowledgment. This research was supported by NSF CHE-8817702 and NIH RR-01209 (to K.O.H.) and NSF CHE-8613376 (to E.I.S.). Experimental data were recorded at the Stanford Synchrotron Radiation Laboratory, which is supported for operation by the Department of Energy's Office of Basic Energy Sciences, Division of Chemical Sciences, using instrumentation and resources provided by the National Institutes of Health, Division of Research Resources.

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Efficient Entry to Bicyclic Lactones via van Halban-White Cyclizations

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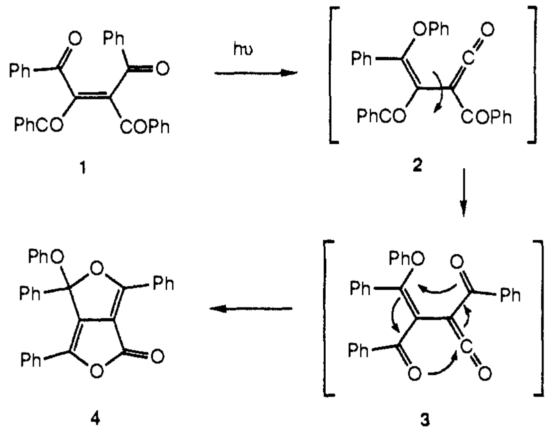
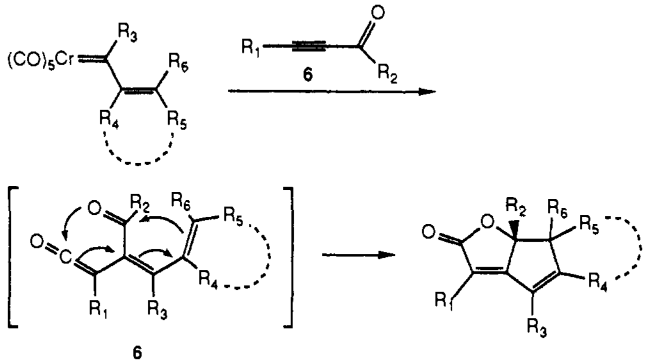
The photochemistry of tetrabenzoylethylene was first examined by van Halban 78 years ago;[1] however, the structure of the photoproduct was finally determined to be **4** by White only 11 years ago.[2] This reaction involves migration of a phenyl group from carbon to oxygen to generate the cross-conjugated ketene **2**,[3] which undergoes rotation about the center bond to generate the conformer **3** necessary for the double cyclization that gives rise to the dilactone **4**. Although no other examples of cyclizations of this type are known, it is nonetheless a prototype for a class of reactions that in their fullest scope could have value in organic synthesis for carbocyclic as well as heterocyclic systems. We report here that the reactions of ketoalkynes with group 6 alkenylcarbene complexes[4] give bicyclic lactones whose formation can be interpreted to be the result of a van Halban-White type double-cyclization of cross-conjugated ketenes of the type **6**.





As indicated in Table I, bicyclic lactones **15**-**19** can be obtained in moderate to excellent yields from the reactions of various alkenylcarbene complexes[4a,5a,14] with acetylenic ketones, aldehydes,

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