yield and identified as an isomer of f, the oxametallacyclobutane complex $[(C_8H_{12}O)Ir(P_3O_9)](TBA)_2$. An X-ray crystallographic study[5] of its tetrahydrofuran solvate, $[(C_8H_{12}O)Ir(P_3O_9)]$-$(TBA)_2{\cdot}C_4H_8O$ (e) revealed the presence of discrete anions having the structure shown at the center of Figure 1. Pseudooctahedral coordination geometry at the Ir(III) center in e is defined by three terminal $P_3O_9^{3-}$ oxygen atoms (O_1, O_2, and O_3), an olefinic $C{=}C$ bond (C_1—C_2), and the carbon (C_6) and oxygen (O_4) atoms of an oxametallacyclobutane ring. The structure of the anion of e is related to that of a by insertion of an oxygen atom into a metal–carbon bond. The anion structures of e and f are related by transfer of an allylic proton (H_{3a}) in e to the alkoxide oxygen (O_4), forming the η^3-allyl and hydroxy groups of f.[6]

In Scheme I, we propose a mechanism for the conversion of a to e. Oxygen initially binds to the 18-electron Ir center in a to form the η^1-O_2 complex b. A complex utilizing η^2-O_2 coordination of the type observed in species such as $[Ir(PPh_3)_2$-$(CO)Cl(O_2)]$[7] is disfavored since such a complex containing η^4-C_8H_{12} and κ^3O-P_3O_9 ligands would have a 20-electron valence configuration. This type of η^1-O_2 coordination has been proposed for O_2 adducts of the 18-electron d^8 Ir(I) complexes $[(C_8H_{12})$-$Ir(phen)Y]$ ($Y = I^-, SCN^-$; phen = phenanthroline).[8] The η^1-O_2 intermediate b reacts with a second Ir center to form the μ-η^2-O_2, κ^3O-P_3O_9 complex, c. Complex c then undergoes internal redox[9] to form an isomeric Ir(III) oxo complex, d, whose coordinated oxygen atoms are inserted into Ir–C bonds to complete the transformation into e. Analogous oxygen atom transfer from the Ir(III) oxo complex, $[(C_5Me_5)Ir(O)]_2$, to PPh_3 has been observed.[10] A plausible 18-electron structure for d containing η^4-C_8H_{12} and κ^2O-$P_3O_9^{3-}$ ligands is shown in Scheme I. This structure is supported by NMR data for the first reaction intermediate observed at −20 °C in CH_3CN.[5] The X part of the observed ABX ^{31}P multiplet is assigned to the phosphorus atom in the uncoordinated phosphate group of the κ^2O-P_3O_9 ligand since its chemical shift (−21.5 ppm) is similar to that for free $P_3O_9^{3-}$ in CH_3CN (−22.0 ppm[4b]). Eight distinct ^{13}C NMR resonances are observed for the η^4-C_8H_{12} ligand.

It is interesting to note that oxametallacyclobutane complexes are frequently invoked as reaction intermediates for olefin epoxidation.[11] Thermal activation of the oxametallacyclobutane complex e yields f, however, not an epoxide such as g shown in Scheme I. In this context it should be noted that the heterogeneous catalyst Ag/Al_2O_3 does not effectively catalyze selective epoxidation of olefins containing acidic allylic hydrogens.[2] We are therefore investigating the chemistry of olefin complexes analogous to a that contain no acidic allylic hydrogens.

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Supplementary Material Available: Analytical and spectroscopic data for compounds a, e, and f, crystal structure reports for $[(C_8H_{12})Ir(P_3O_9)][(n\text{-}C_4H_9)_4N]_2$ (compound a), $[(C_8H_{12}O)Ir$-$(P_3O_9)][(n\text{-}C_4H_9)_4N]_2{\cdot}C_4H_8O$ (compound e), and $[(C_8H_{11}OH)$-$Ir(P_3O_9)][(n\text{-}C_4H_9)_4N]_2{\cdot}1.5H_2O$ (compound f), Tables I (fractional atomic coordinates for non-hydrogen atoms in a), II (anisotropic thermal parameters for non-hydrogen atoms in the anion of a), III (bond lengths and angles in the anion of a), IV (bond lengths and angles in the cations of a), V (fractional atomic coordinates for non-hydrogen atoms in e), VI (anisotropic thermal parameters for non-hydrogen atoms in e), VII (fractional atomic coordinates for hydrogen atoms in the anion of e), VIII (bond lengths and angles in the anion of e), IX (bond lengths and angles in the cations of e), X (bond lengths and angles in the THF solvent molecule of crystallization of e), XI (fractional atomic coordinates for non-hydrogen atoms in f), XII (anisotropic thermal parameters for non-hydrogen atoms in f), XIII (fractional atomic coordinates for hydrogen atoms in the anion of f), XIV (bond lengths and angles in the anion of f), and XV (bond lengths and angles in the cations of f), and Figures 2 (perspective ORTEP drawings of the anions of a, e, and f), 3 (perspective drawings of the cations of a), 4 (perspective drawings of the cations of e), 5 (perspective drawings of the THF solvent molecule of crystallization of e), and 6 (perspective drawings of the cations of f) (53 pages); structure factor tables for the crystal structure analysis of a, e, and f (59 pages). Ordering information is given on any current masthead page.

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(6) Reaction of 1,5-cyclooctadiene with $[(C_5Me_5)Ir(Me_2CO)_3](PF_6)_2$ in acetone yields the η^2,η^3-cyclooctadienyl complex $[(C_5Me_5)Ir(C_8H_{11})](PF_6)$, presumably by loss of an allylic proton from the 1,5-cyclooctadiene complex $[(C_5Me_5)Ir(C_8H_{12})(Me_2CO)](PF_6)_2$: White, C; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 1305.

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$XeCl_2$: A van der Waals Molecule

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Modern theories of chemical bonding have been quite successful in predicting the bonding characteristics of many small molecules. However, the bonding in some systems, such as the rare gas dihalides, is not so easily predicted. Although the XeF_2, XeF_4, and XeF_6 molecules have been known and characterized for nearly 30 years, evidence for the analogous chlorine-containing compounds is quite ambiguous. In this communication, we report that we have observed the $B \leftarrow X$ transition of the $XeCl_2$ van der Waals molecule by two-color, pump-probe spectroscopy. This observation shows that the van der Waals isomer is stable with respect to unimolecular isomerization in the ground electronic state and long-lived up to at least the $v = 11$ level (within 1.7 kJ of the Cl_2 ground-state dissociation limit) of the Cl_2 stretch in the excited electronic state.

The discovery of the xenon fluoride compounds prompted Waters and Gray[1] to attempt a theoretical approach to the prediction of the stabilities of several analogous compounds. Using a modified molecular orbital theory, they predicted that each Xe–Cl bond in linear $XeCl_2$ has a bond energy of 29.7 kJ/mol. Subsequently, Nelson and Pimentel[2] produced a new species by passing a mixture of Cl_2 and xenon through a microwave discharge and condensing upon a window maintained at 20 K. A vibrational mode at 313 cm^{-1} was tentatively assigned to the asymmetric stretch of ClXeCl. Further study has shown that this feature can also be produced by irradiation of Cl_2 in a xenon matrix with 501.7-nm laser light.[3] If this assignment is correct, it would imply that there is little or no barrier to the formation of the $XeCl_2$ molecule from xenon and two chlorine atoms since the reaction proceeds at 20 K. Also, the asymmetric stretching frequency would imply that the bonding is quite strong. For instance, in the B state of the XeCl excimer, the well depth is 437.2 kJ/mol and the stretching frequency is only 194.8 cm^{-1}.[4] Still, the $XeCl_2$

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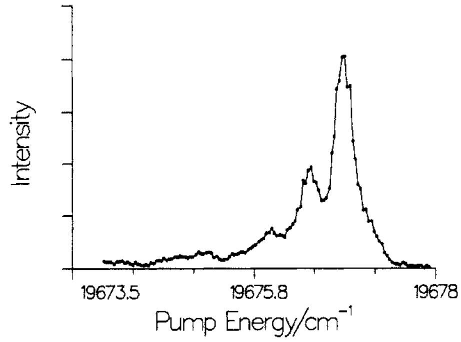

Figure 1. Excitation spectrum of the $XeCl_2$, B ← X, 10 ← 0 transition observed by detecting $Cl_2(B,v{=}8)$. The corresponding Cl_2, B ← X, 10 ← 0 transition occurs 9.5 cm^{-1} to the red of this peak.

molecule has never been isolated or even unambiguously identified.

The structures and bond energies of the $HeCl_2$, $NeCl_2$, and $ArCl_2$ van der Waals molecules are well determined and show no signs of incipient chemical bonding in either the ground electronic state or the B excited electronic state that is reached upon excitation with green light.[5] In previous attempts to study $XeCl_2$ by laser-excited fluorescence, the B ← X transition could not be observed. Since the B state of Cl_2 is near the dissociation energy of the ground-state Cl_2 potential, it seemed possible that excitation of the $XeCl_2$ van der Waals ground state led to a chemical reaction rather than a detectable fluorescence signal. Indeed, such dynamics are observed in the vicinity of the $^1\Pi_u$ state.[6]

In the present study, the two-laser pump-probe method, described previously,[7] was used to observe the $XeCl_2$ B ← X spectrum and the Cl_2 products of vibrational predissociation. Briefly, ground-state $XeCl_2$ van der Waals clusters are formed in a free jet expansion of a 1700-kPa 2% Xe/helium mixture seeded with 10 Pa of Cl_2. The first laser "pumps" the cluster into an electronically and vibrationally excited state associated with the B state of free Cl_2. Vibrational energy is then transferred from the Cl_2 stretch into the van der Waals modes, and dissociation occurs. The second laser "probes" the production of free Cl_2 after dissociation via the E ← B electronic transition. Fluorescence from the Cl_2 E state gives the detected signal. Figure 1 shows a $XeCl_2$ excitation spectrum in which the probe laser is set to detect $Cl_2(B,v{=}8)$ while the pump laser is scanned across the $XeCl_2$ B, $v = 10$ ← X excitation. The signal-to-noise ratio for this spectrum is lower than that achieved for other rare gas-Cl_2 clusters. It is not presently known if this is due to lower production of the $XeCl_2$ ground state in the supersonic expansion or to other dynamics competing with vibrational predissociation of the electronic excited state.

A reasonable fit to the spectrum in Figure 1 can be made by assuming that the complex is T-shaped in both the X and B states, as for $HeCl_2$, $NeCl_2$, and $ArCl_2$.[5] The structure in the spectrum is mainly due to near-prolate K-type transitions that mainly involve rotation of the Cl_2 constituent about the Xe-Cl_2 axis. This assignment is further supported by parity selectivity in the dissociation process.[7] If the probe laser is positioned to detect the production of an even rotational state of the Cl_2 fragments, then only even values of the prolate K quantum number are observed in the excitation spectrum. The resolution of the spectrum is insufficient to resolve rotations which would determine the Xe-Cl bond lengths. From the bandwidths we can establish a lower limit for the excited-state lifetime of 50 ps. When probe spectra are used as described previously,[8] the bond energies for the Xe-Cl_2 van der Waals attraction are determined to be 3.69 ± 0.01 kJ/mol in the ground electronic state and 3.33 ± 0.01 kJ/mol in the excited electronic state. These values are 1.5 times greater than the bond energies in the $ArCl_2$ complex[9] and are as expected for van der Waals bonding; no signs of the formation of a chemical bond between the xenon and chlorines is observed.

In summary, two electronic states of the van der Waals isomer of $XeCl_2$ have been observed. Even with electronic and vibrational excitation to within 1.7 kJ of the Cl_2 dissociation energy, the van der Waals isomer is stable for at least 50 ps. If the linear Cl-Xe-Cl molecule is as stable as predicted, then there must be a large barrier in the bending mode that separates it from the van der Waals isomer.

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New Radical Chain Reaction of *S*-Alkoxycarbonyl Dithiocarbonates: A Useful Source of Alkyl Radicals from Alcohols

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The past few years have witnessed a dramatic growth in the development and use of radical reactions in organic synthesis.[1] One important requisite for radical-based methodology is the availability of a convenient source of carbon radicals from various functional groups. In this communication, we report a new method for generating alkyl radicals from alcohols through decarboxylation of the corresponding alkoxycarbonyl radical. This novel procedure follows from our recent work[2] on the radical chemistry of dithiocarbonates and xanthates in particular.

Alkoxycarbonyl radicals (ROCO) have seldom found use as precursors of the corresponding alkyl radicals (R•), mainly because release of carbon dioxide from these species is relatively slow in comparison with other possible competing processes usually inherent to the method of generation.[3,4] Limited kinetic studies[5] on *tert*-butoxycarbonyl radicals have yielded a rate constant of 10^5-10^6 s^{-1} at 60 °C for the unimolecular decarboxylation step. Ethoxycarbonyl radicals, which produce the higher energy ethyl radicals, are reported to extrude carbon dioxide much more

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