Table I. Mechanical and Thermal Properties of TPE Polypropylenes

sample	3	4
strength, MPa	3.97	12.1
strain to break, %	525	1260
recovery after break, %	86	94
G_{eq}, MPa	1.47	0.56
T_m,[a] °C	51.2, 66.0	53.1, 63.8
ΔH_f,[a] cal g^{-1}	3.26	2.93

[a] Samples annealed at 30 °C for 12 h before DSC scan.

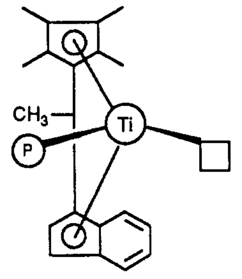
Table II. Elastomeric Properties of TPE Polypropylenes

sample	3			4		
strain, %	100	200	300	100	200	300
stress, MPa	3.13	3.39	3.53	3.07	3.30	3.59
recovery, %	93	91	83	97	96	92

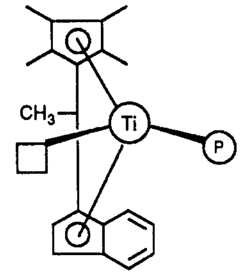
h gave 0.74 g of polypropylene (PP) **3**, which corresponds to a catalytic activity of 2.5 × 10^5 g of PP (mol of Ti)$^{-1}$ h^{-1} atm^{-1}. Polymerization at 25 °C also yielded polypropylene **4**. Polymers **3** and **4** were subjected to solvent fractionation.[10] Aside from a very small amount of acetone-soluble material, the polymers are completely soluble in refluxing ethyl ether, indicating uniformity of structure. They are also characterized by narrow molecular weight distributions. According to GPC using columns calibrated with polypropylenes of known $\bar{M}_w$, **3** has $\bar{M}_n$ = 66 600, $\bar{M}_w$ = 127 000, and $\bar{M}_w/\bar{M}_n$ = 1.9 and **4** has $\bar{M}_n$ = 98 400, $\bar{M}_w$ = 164 000, and $\bar{M}_w/\bar{M}_n$ = 1.7. The degree of crystallinity was found by Roland analysis of X-ray powder patterns obtained on samples annealed between 30 and 45 °C to be 28.6 ± 0.5% and 26.5 ± 0.4% for **3** and **4**, respectively. The polymers exhibit more than one melting endotherm; the transition temperature (T_m) and enthalpy (ΔH_f) obtained by DSC on samples annealed at 30 °C for 12 h are given in Table I. Annealing at lower temperatures resulted in lower T_m, which indicates a dependence of the size and order of crystalline domains on crystalline conditions.

The dynamic storage modulus (G') measured at 1 rad s^{-1} as a function of temperature showed a 3 orders of magnitude decrease between 60 and 80 °C due to the melting transition. G' increases only slightly with frequency at 50 °C but increases strongly with frequency at 100 °C, indicating an elastomeric state in the former but a single phase melt state in the latter. Stress–strain curves obtained on dogbone samples (molded at 100 °C, annealed at 60 °C for 2 h) showed very strong mechanical properties (Table I). In particular, **4** did not break until stretched beyond 1260%. The polymers exhibit excellent elastic recoveries (Table II); the strain recovery is better than 90% for **4** after elongation of 100–300%. These properties can be explained only by the presence of physical cross-links due to crystallization of stereoregular segments of the polypropylene chains. The molecular weight between cross-links ($\bar{M}_c$) was estimated from the equilibrium modulus (G_{eq}), which was measured at 50 °C, 0.5% strain, and stress relaxed for 10^4 s (Table I). The estimates for $\bar{M}_c$ [=(density)RT/G_{eq}] are 2.0 × 10^3 and 4.4 × 10^3 for **3** and **4**, respectively. Since the crystallizable segments in the polymer chains must be quite short as indicated by the low T_m, there are many alternating crystallizable and noncrystallizable segments, of the order of 20.[11] These polymers contain low homosteric pentad populations.[12] The detailed analysis of 500-MHz ^{13}C NMR spectra will be reported elsewhere.

Ewen pointed out that for syndiospecific propylene polymerization using (isopropylidenecyclopentadienyl-1-fluorenyl)dichlorohafnium, there is chain migration following each monomer insertion.[4] The bridging carbon in **1** is chiral and can have the polymer chain either syn (**1a**) or anti (**1b**) to the *ansa*-methyl group during polymerization.



1a



1b

The block structure of the present TPE polypropylene may be explained by postulating that during chain propagation on **1a** or **1b** they undergo occasional interconversion,

$$\text{stereoregular segment} \xleftarrow{k_{pi}} \mathbf{1b} \underset{k_{ba}}{\overset{k_{ab}}{\rightleftharpoons}} \mathbf{1a} \xrightarrow{k_{pa}} \text{amorphous segment}$$

where the k_p's are greater than k_{ab} and k_{ba}. The resulting polymer is microphase separated into crystalline and amorphous domains, and the former act as physical cross-links. Above T_m, the polymers are linear viscoelastic.

The above results demonstrate that **1** can produce polypropylene chains containing alternating crystallizable and noncrystallizable segments in any given chain. The polymers are quite homogeneous in structure as well as molecular weight. This is the first example of a thermoplastic elastomer comprising a single monomer.[13,14]

Acknowledgment is made to Fina Oil and Petroleum Company for support of this research. Helpful discussions with E. A. Mintz and GPC by D. He are also acknowledged.

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[10] Pasquon, I. *Pure Appl. Chem.* **1967**, *15*, 465.

[11] This *crude* estimate assumes that the crystallizable segments comprise about 20 monomer units. It is dependent upon the crystallization conditions.

[12] The average steric pentad distributions for **3** by the methyl ^{13}C NMR spectrum are as follows: [mmmm] = 0.40, [mmmr] = 0.16, [rmmr] = 0.043, [mmrr] = 0.15, [mrmm] + [rmrr] = 0.07, [rmrm] = 0.034, [rrrr] = 0.02, [rrrm] = 0.043, and [mrrm] = 0.07.

[13] Polypropylenes exhibiting elastomeric properties have been obtained by Tullock and co-workers[14] using alumina-supported bis(arene) Ti, Zr, and Hf catalysts. Their materials contain chains soluble in ethyl ether, hexane, heptane, and octane, as well as octane-insoluble ones. Hysteresis curves showed 110% permanent set after 300% elongation.

[14] (a) Tullock, C. W.; Tebbe, F. N.; Mulhaupt, R.; Overall, D. W.; Selterquist, R. A.; Ittel, S. D. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 3063. (b) Collette, J. C.; Tullock, C. W.; MacDonald, R. N.; Buck, W. H.; Su, A. C. L.; Harrell, J. R.; Mulhaupt, R.; Anderson, B. C. *Macromolecules* **1989**, *22*, 2851.

Oxygen Atom Transfer from O_2 to a Coordinated Olefin: A New Route to Oxametallacyclobutanes

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The selective oxidation of ethylene to ethylene oxide over Ag/Al_2O_3 is a process having major industrial importance due to its efficiency and simplicity.[2] Little is known about the detailed mechanism of O_2 to ethylene oxygen atom transfer in this system, however, except that ethylene reacts with adsorbed atomic oxygen as opposed to adsorbed molecular oxygen.[2] Given the fundamental significance of this process and oxygen activation processes in general,[3] we have synthesized a series of polyoxoanion-supported

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[1] (a) Crystalytics Company. (b) University of Illinois.

[2] (a) Van Santen, R. A.; Kuipers, H. P. C. E. *Adv. Catal.* **1987**, *35*, 265. (b) Roberts, J. T.; Madix, R. J. *J. Am. Chem. Soc.* **1988**, *110*, 8540.

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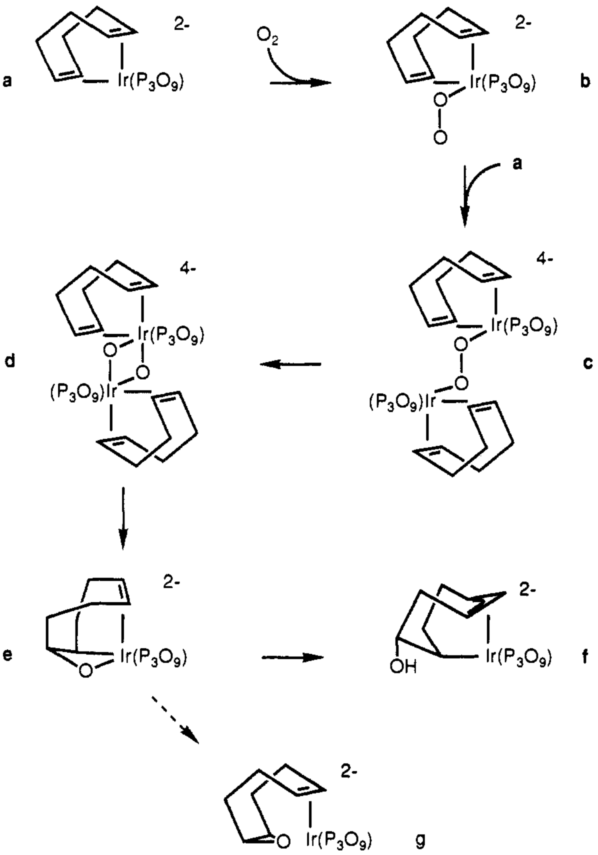
Scheme I



noble metal olefin complexes that might react with O_2 in a selective fashion and provide information concerning the mechanisms of oxygen activation and hydrocarbon oxidation.[4] We describe here the chemistry of one such species, $[(C_8H_{12})Ir(P_3O_9)](TBA)_2$, where C_8H_{12} = 1,5-cyclooctadiene and TBA = tetra-*n*-butylammonium.

The 1,5-cyclooctadiene complex $[(C_8H_{12})Ir(P_3O_9)](TBA)_2$ (a) is prepared from $(P_3O_9)(TBA)_3$[4b] and $[(C_8H_{12})Ir(CH_3CN)_2](PF_6)$ in CH_2Cl_2 and has the anion structure shown at the top of Figure 1 according to a single-crystal X-ray diffraction study.[5] Square-pyramidal coordination geometry at the 18-electron Ir(I) center in a is established by two olefinic C=C bonds and two terminal $P_3O_9^{3-}$ oxygens (O_2 and O_3) defining the "square" base and a third terminal $P_3O_9^{3-}$ oxygen (O_1) forming the apex.

Volumetric gas buret measurements indicate that compound a in 1,2-dichloroethane is consumed by $^1/_2$ equiv of O_2 at ambient temperature to form $[(C_8H_{11}OH)Ir(P_3O_9)](TBA)_2$ in >75% yield according to ^{31}P NMR spectroscopy. The structure of the product anion shown at the bottom of Figure 1 was determined by single-crystal X-ray diffraction analysis of its hydrated TBA salt, $[(C_8H_{11}OH)Ir(P_3O_9)](TBA)_2 \cdot 1.5H_2O$ (f).[5] Two of the six pseudooctahedral coordination sites about the Ir(III) atom in f are occupied by a π-bonded allyl group (C_1, C_2, C_3) and the remaining four sites by three $P_3O_9^{3-}$ oxygens (O_1, O_2, O_3) and a σ-bonded carbon (C_6).

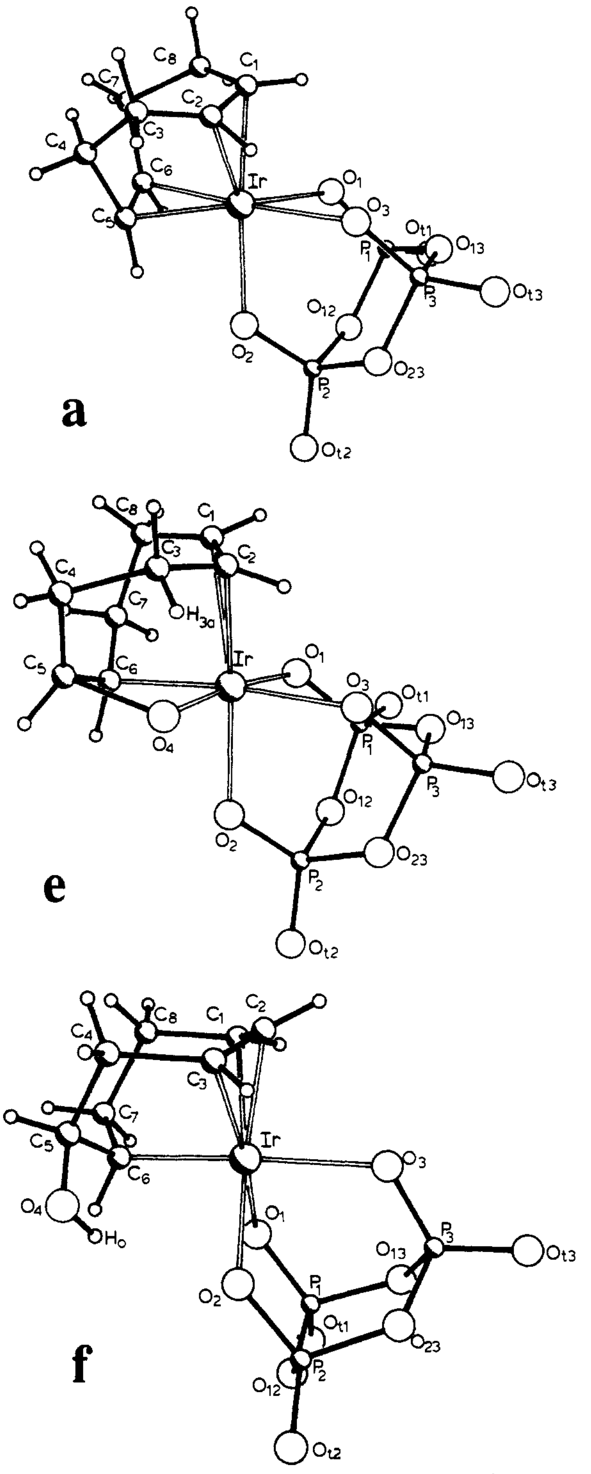


Figure 1. Perspective drawings of the $[(C_8H_{12})Ir(P_3O_9)]^{2-}$ anion in a (top), the $[(C_8H_{12}O)Ir(P_3O_9)]^{2-}$ anion in e (middle), and the $[(C_8H_{11}OH)Ir(P_3O_9)]^{2-}$ anion in f (bottom). Iridium atoms are represented by large shaded spheres, carbon atoms by medium-sized shaded spheres, and phosphorus atoms by small shaded spheres; oxygen and hydrogen atoms are represented by large and small unshaded spheres, respectively. Hydrogen atoms bonded to carbon, except as noted below, are at idealized sp^2- or sp^3-hybridized positions with C–H bond lengths of 0.96 Å. Hydrogen atoms on C_5 and C_6 of e were refined as independent isotropic atoms. The hydroxyl group in f was refined as a rigid group with an O–H bond length of 0.85 Å.

The transformation of a to f proceeds via several intermediates that can be detected by ^{31}P NMR spectroscopy. One of these compounds has been isolated from an CH_3CN solution in 75%

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[3] (a) Jørgensen, K. A. *Chem. Rev.* **1989**, *89*, 431. (b) *Oxygen Complexes and Oxygen Activation by Transition Metals*; Martell, A. E., Sawyer, D. T., Eds.; Proceedings of the Fifth Annual IUCCP Symposium; Plenum Press: New York, 1988. (c) van Asselt, A.; Trimmer, M. S.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 8254. (d) Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1987**, *109*, 424. (e) Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790. (f) Guengerich, F. P.; Macdonald, T. L. *Acc. Chem. Res.* **1984**, *17*, 9. (g) Atlay, M. T.; Preece, M.; Strukul, G.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1982**, 406. (h) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. (i) Mimoun, H.; Machirant, M. M. P.; de Roch, I. S. *J. Am. Chem. Soc.* **1978**, *100*, 5437.

[4] (a) Besecker, C. J.; Klemperer; W. G.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 6158. (b) Besecker, C. J.; Day, V. W.; Klemperer, W. G. *Organometallics* **1985**, *4*, 564. (c) Klemperer, W. G.; Yagasaki, A. *Chem. Lett.* **1989**, 2041. (d) Day, V. W.; Klemperer, W. G; Main, D. J. *Inorg. Chem.*, in press.

[5] For analytical, spectroscopic, and X-ray crystallographic data, see paragraph at end of paper regarding supplementary material.

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.

Acknowledgment. We acknowledge the National Science Foundation for support of this work and Professor Thomas Rauchfuss for useful discussions.

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.

(7) Vaska, L. *Science* **1963**, *140*, 809.

(8) (a) de Waal, D. J. A.; Gerber, T. I. A.; Louw, W. J.; van Eldik, R. *Inorg. Chem.* **1982**, *21*, 2002. (b) Louw, W. J.; Gerber, T. I. A.; de Waal, D. J. A. *J. Chem. Soc., Chem. Commun.* **1980**, 760.

(9) (a) Taube, H. *J. Gen. Physiol.* **1965**, *46*, 29. (b) Yarino, T.; Matsushita, T.; Masuda, I.; Shinra, K. *J. Chem. Soc., Chem. Commun.* **1970**, 1317.

(10) McGhee, W. D.; Foo, T.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8543.

(11) See, for example: (a) Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120. (b) Rappé, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 3287. (c) Walba, D. M.; DePuy, C. H.; Grabowski, J. J.; Bierbaum, V. M. *Organometallics* **1984**, *3*, 498. (d) Collman, J. P.; Brauman, J. I.; Meunier, B.; Raybuck, S. A.; Kodadek, T. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 3245. (e) Collman, J. P.; Kodadek, T.; Raybuck, S. A.; Brauman, J. I.; Papazian, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 4343. (f) Groves, J. T.; Avaria-Neisser, G. E.; Fish, K. M.; Imachi, M.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 3837. (g) Girardet, M.; Meunier, B. *Tetrahedron Lett.* **1987**, *28*, 2955.

$XeCl_2$: 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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(1) Waters, J. H.; Gray, H. B. *J. Am. Chem. Soc.* **1963**, *85*, 825-826.

(2) Nelson, L. Y.; Pimentel, G. C. *Inorg. Chem.* **1967**, *6*, 1758-1759.

(3) Howard, W. F., Jr.; Andrews, L. *J. Am. Chem. Soc.* **1974**, *96*, 7864-7868.

0002-7863/90/1512-2033$02.50/0