The data in Table I reveal a number of interesting features regarding these systems: (1) For the substituted butadienes, **1a** and **1b**, significant electrocyclic ring closure can be induced *even when the isomerization reaction is significantly entropically and enthalpically disfavored*. (2) Either isomer of an isomeric pair can be converted into the other isomer. (3) Isomers are produced cleanly, and yields increase significantly with increasing fluence up to ~5 J/cm^2 where breakdown products begin to appear. (4) Yields decrease significantly as a function of added rare gas even at the lowest rare gas pressure used. (5) Yields increase for the substituted compounds vs. butadiene. We believe these features indicate a number of important properties about laser-induced isomerization in these systems. These will be discussed in more detail in a future publication but will be briefly considered here.

We believe that the selectivity of the isomerization process is principally due to the high contrast in absorption coefficient of the isomers at the chosen irradiation frequencies.[10] This then allows for selective "vibrational heating" of only one isomer and subsequent isomerization of that species. That this can be done even in the thermodynamically disfavored direction seemingly indicates that the deactivation rates for excited products compete with RRKM rates for the reverse isomerization reaction. Yields reported in Table I are yield/pulse cm^{-2} for samples typically irradiated for a few hundred pulses. Yields/pulse were linear as far as systematically tested which was up to a few thousand pulses. The isomerization of **1a** to **2a** was taken as far as 25% without significant decomposition and only slight diminution in the yield of product per pulse. A number of experimental studies have reported enhancement of yield and/or selectivity of a process as a function of added rare gas.[11] One postulated cause of increased yield is rotational hole filling. With **1a,b**, and for the reverse reactions we see a diminishment of yield as a function of added rare gas (see Table I). This may be due to the fact that for low fluence irradiation of a large molecule, a saturation effect like "hole burning" is not significant. Rather, rare gas deactivation may effectively compete with up pumping and/or reaction rate constants.

A recent theoretical treatment of laser-induced isomerization reactions indicates that rare gases may be used to enhance selectivity by making deactivation compete with isomer interconversion.[12] This treatment assumes that isomers interconvert rapidly on the time scale of deactivation in the absence of rare gas. Due to the low excitation conditions, the above assumption may not accurately describe isomerization in these diene systems. We are currently engaged in photoacoustic measurements and kinetic modeling to explain the substantially increased yields as a function of increasing fluence, measure actual energy deposited as a function of added rare gas, and obtain as much information as possible with regard to isomerization and quenching rates in these systems.

A variety of chemical and physical factors correlate with the degree of substitution in the butadienes. Srinivasan reported that the ultraviolet photochemical isomerization of 1,3-dienes follows roughly the same pattern as observed in laser isomerization experiments, with butadiene being the most difficult to isomerize.[9] This result was attributed to an increase with methyl substitution (**1a** > **1b** > **1c**) in the population of the ground-state s-cis conformer necessary for ring closure. Unfortunately, conformational populations are still not known with certainty. Conformational control of infrared-laser-induced ring closure would imply that ring closure is more facile than isomerization of *s-cis*-butadienes to s-trans or it is fast enough to statistically sample the s-cis and s-trans states and the density of s-cis states is greater than s-trans for the laser excited system. While either of these is possible, the first seems both entropically and energetically unlikely and an explanation may have to wait for further studies and detailed kinetic modeling of the system. Additionally a true comparison of yields should be done for equal energy deposition rather than equal fluence conditions. This is currently being worked on. It is interesting to note that the relative yields of the cyclobutenes **2a–c** correspond to their kinetic stabilities.[13]

Though the data we report is preliminary, taken into account with our previous work[3] and the work of others,[2] it is apparent that under appropriate conditions, clean selective isomerization can be induced in a variety of systems, even in a highly thermodynamically disfavored direction. With further study and refinement it may even be possible to use these procedures to effect the synthesis of specific isomers. In addition, we hope these systems will yield information about the dynamics of molecules in the excitation regime intermediate between the weak excitation case that usually occurs in infrared laser fluorescence studies and the higher degree of excitation necessary for dissociation. This region is one for which few experimental probes exist and is therefore not well understood with regard to energy-transfer phenomena. Thus isomer selective multiphoton excitation clearly offers potential both as a synthetic technique and as a probe of molecular dynamics.

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A Uranium–Carbon Multiple Bond. Crystal and Molecular Structure of $(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$

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We have recently begun an investigation of actinide–phosphoylide chemistry.[1-4] We have prepared a green complex, formulated as $(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$ (I) on the basis of elemental analysis and spectroscopic characterization, in good yield from the reaction of $(\eta^5\text{-}C_5H_5)_3UCl$ with an equimolar amount of $Li(CH_2)(CH_2)P(CH_3)(C_6H_5)$. The mode of ylide–metal attachment suggested by this formulation is unusual, having been reported only for $(OC)_5MCHPR_3$ (M = Mn, Re),[5] $(CH_3)_3SiCHPR_3$,[6] and $(CH_3)_3SbCHPR_3$[7] at the time of isolation of I. This complex also differs from other uranium–phosphoylide complexes which we have structurally characterized[1-4] in that the carbon atom attached to the uranium is three- rather than four-coordinate. Since no structural data were available for compounds containing a M–CH–P unit and since the bonding between these atoms may be unusual, we have determined the crystal and molecular structure of I by X-ray diffraction. This determination not only confirms the proposed formulation of I

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Table I. Positional and Thermal Parameters[a] with Standard Deviations for Nongroup Atoms of $(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	0.8267 (1)	0.3680 (1)	0.09479 (4)	0.0073 (1)	0.0104 (1)	0.00152 (2)	0.0002 (2)	0.00153 (3)	0.00015 (8)
P	0.5701 (7)	0.2032 (9)	0.1470 (3)	0.0091 (8)	0.014 (1)	0.0016 (1)	−0.0010 (9)	0.0020 (3)	−0.0007 (3)
C(1)	0.647 (3)	0.337 (3)	0.120 (1)	0.010 (3)	0.011 (5)	0.0029 (7)	−0.001 (3)	0.003 (1)	0.0000 (1)
C(2)	0.608 (3)	−0.003 (3)	0.136 (1)	0.020 (5)	0.006 (4)	0.0033 (8)	−0.001 (4)	0.004 (2)	−0.002 (1)
C(3)	0.388 (3)	0.211 (4)	0.117 (1)	0.009 (4)	0.024 (6)	0.0032 (8)	−0.003 (4)	0.002 (1)	0.003 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table II. Some Bond Lengths (Å) with Their Standard Deviations for $(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$

U–C(1)	2.29 (3)
P–C(1)	1.69 (3)
P–C(2)	1.83 (3)
P–C(3)	1.83 (3)
P–C(11)	1.80 (2)
U–Cp[a]	2.79 (3)

[a] Average U–C distances for the 15 carbons of the C_5H_5 rings.

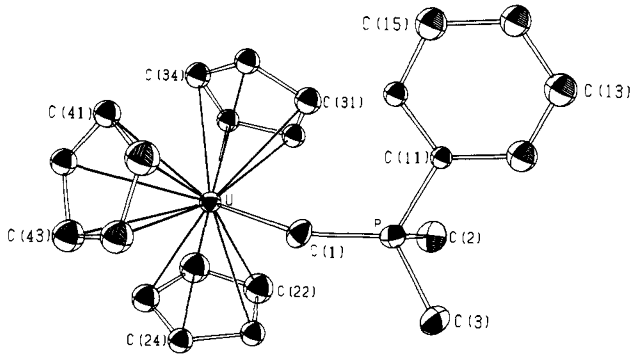

Figure 1. ORTEP perspective drawing of $(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$.

but also indicates that multiple bond character may be ascribed to the U–C bond. While this communication was in preparation, the synthesis and structure of the closely related $(\eta^5\text{-}C_5H_5)_2ClZrCHP(C_6H_5)_3$ (II) was published.[8]

Dark green crystals of $(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$ belong to the monoclinic space group $P2_1/c$ with a = 10.835 (2), b = 8.481 (2), c = 25.566 (13) Å; β = 111.77 (3)°; V = 2182 (1) Å^3; Z = 4, ρ_{calcd} = 1.78 g/cm^3. Intensity data were collected on a Syntex P$\bar{1}$ computer-controlled diffractometer using monochromatized Mo Kα radiation. Data reduction was carried out as previously described,[9,10] and the structure was solved with little difficulty by Patterson and Fourier techniques. Least-squares refinement using rigid groups for the C_5H_5 and C_6H_5 rings[11] converged at R_1 = 0.071, R_2 = 0.078 for the 1985 data for which $F_o^2 > 3\sigma(F_o^2)$.[12] An ORTEP drawing of the molecule is shown in Figure 1, positional and anisotropic thermal parameters for the nongroup atoms are reproduced in Table I, and bond lengths are shown in Table II. The positional and isotropic thermal parameters for the carbon atoms refined in rigid groups are listed in Table III, deposited as supplementary material.

The uranium–carbon bond is the shortest yet observed, the range for other uranium–carbon bonds being from 2.33 (2) Å in $(\eta^5\text{-}C_5H_5)_3UC{\equiv}C(C_6H_5)$[13] to 2.66 (3) Å in $(\eta^5\text{-}C_5H_5)U[(CH_2)(CH_2)P(C_6H_5)_2]_3$.[14] Atom C(1) is three-coordinate. Considering it to be sp^2 hybridized, and after applying a correction of 0.03 Å for the difference between sp^2 and sp^3 carbon atom hybridization, the U–CH(PR$_3$) bond in I is still 0.11 Å (or 3σ) shorter than the uranium–carbon bond in $(\eta^5\text{-}C_5H_5)_3U(n\text{-}C_4H_9)$, 2.43 (2) Å.[15] The uranium–carbon bonds in $(\eta^5\text{-}C_5H_5)_3UCH_2C(CH_3){=}CH_2$, 2.48 (3) Å,[16] and $(\eta^5\text{-}C_5H_5)_3U[CH_2(p\text{-}CH_3C_6H_4)]$, 2.54 (2) Å,[15] are even longer so that the shortening of the uranium–carbon bond in I is even more significant.

Structurally the M–CH–P units in I and II[8] are very similar. In both the M–C distance is short, the ylide C–P distance somewhat longer than observed for simple unsubstituted ylides [1.69 (3) Å in I, 1.708 (6) Å in II, 1.661 (8) Å in $H_2CP(C_6H_5)_3$[17]], and the M–C–P angle is large [142. (1)° in I, 135.9 (3)° in II]. Both molecules bear a structural relationship to alkylidene–metal complexes where metal–carbon distances are also very short and the M–C–X angles are large [e.g., Ta–C–C is 150.4 (5)° in $(\eta^5\text{-}C_5H_5)_2ClTa{=}CHC(CH_3)_3$[18,19]]. It has already been pointed out that the metal–carbon bonds in the alkylidenes[18] and II[8] should be considered to contain multiple bond character on structural, chemical, and spectroscopic grounds. While the nature of the bonding in organoactinides is not firmly established and the question of ionic vs. covalent bonding has attracted continuing attention for over 20 years,[19–21] structural comparisons clearly indicate similarities between I, II, and alkylidene complexes. In this respect it seems appropriate to formulate I as the first example of an actinide alkylidene and ascribe multiple bond character to its U–C bond.

There are also very interesting chemical similarities between I and the transition-metal alkylidenes. The formation of I occurs via the abstraction of a proton from one of the methylene groups in the starting ylide by the second methylene group. This bears a striking resemblance to the intramolecular proton transfer by which many of the alkylidene complexes reported by Schrock[18] are formed. Similarities also exist in the reaction chemistry of these complexes. I, II, and $(\eta^5\text{-}C_5H_5)_2ClTa{=}CHC(CH_3)_3$ all insert[8,18] CO into their respective M=C bonds. The structure of the product of such a reaction, $(\eta^5\text{-}C_5H_5)_3U(OCCH)P(CH_3)(C_6H_5)_2$, has been determined by our group and is reported in a separate communication.[22]

Supplementary Material Available: A listing of the positional and thermal parameters of the group atoms (1 page). Ordering information is given on any current masthead page.

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(12) The final difference Fourier map was carefully examined. The largest peaks, with the exception of ripples as large as 2.0 e/Å^3 near the uranium atom, were 1.0 e/Å^3 and were associated with the C_5H_5 rings. The crystal, when originally sealed in a capillary tube in the summer of 1979, was reported to be green. In Jan 1980 before data was collected the crystals appeared red and after data collection were black. This suggests some decomposition of the material. Check reflections monitored after every 100 reflections during data collection showed no significant change in intensity, so decomposition of the crystal during data collection was negligible. However, the change in the crystal color over long periods of time may indicate a process which slowly degrades the crystal quality, leading to relatively high error indices.

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