to occur at around 23 000 cm^{-1} in the $[Mo_2Cl_8]^{4-}$ ion.[10]

If the absorption at 13 700 cm^{-1} is assumed to be due to the pure metal-localized $\delta \rightarrow \delta^*$ excitation, then the sign of the associated Cotton effect may be related to the absolute configuration of the complex in the following way. In the fully eclipsed configuration the transition is electric-dipole allowed in a direction along the Mo–Mo bond (figure 3a). Twisting the rear MoP_2Cl_2 group (viewed along the Mo–Mo bond) counterclockwise through an angle of between 0° and 45° results in the $Mo_2P_4Cl_4$ unit taking a left-handed helical configuration (Figure 3b). In this absolute configuration the $\delta \rightarrow \delta^*$ transition gives rise to a left-handed helical charge displacement and so to a negative Cotton effect. In the fully staggered configuration there is no overlap between the d_{xy} orbitals on the two Mo atoms and the absorption and CD spectra have zero intensity for a pure $\delta \rightarrow \delta^*$ transition. When the twist angle is between 45° and 90° the $Mo_2P_4Cl_4$ unit takes a right-handed helical configuration (Figure 3c) and the CD of the $\delta \rightarrow \delta^*$ transition should be positive. Rotation of the rear MoP_2Cl_2 group in the clockwise direction produces the opposite absolute configurations and Cotton effects.[11]

In summary, we have shown that the optical activity of the $\delta \rightarrow \delta^*$ transition can be explained by a simple metal-localized model and have established CD as a useful method of predicting the absolute configuration of configurationally chiral dimolybdenum compounds.

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(11) Note that the absolute configuration *as defined by the helicity of the bridging phosphines* is Λ for a counterclockwise rotation irrespective of whether the twist angle is greater or less than 45°. The CD, however, is governed by the *helicity of the chromophore*, which does change with the magnitude of the torsion angle. A similar situation is found in tris-chelated diamine complexes: Λ-$[Co(en)_3]^{3+}$ and Λ-$[Co(tn)_3]^{3+}$ have d–d circular dichroism of opposite sign, despite having the same absolute configuration as defined by their chelate rings, because their ligating atoms have opposite signed trigonal twists. See, for example: Peacock, R. D.; Stuart, B. *Coord. Chem. Rev.* **1982**, *46*, 129.

Uranium–Carbon Multiple-Bond Chemistry. 3. Insertion of Acetonitrile and the Formation of a Uranium–Nitrogen Multiple Bond[1]

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Metal–carbon multiply bonded alkylidene, M=CR$_2$, and alkylidyne, M≡CR, complexes are isoelectronic to imido, M=NR, and nitrido complexes, M≡N, respectively.[2,3] The possibility of similar reactions at metal–carbon multiple bonds and at their metal–nitrogen counterparts has been raised in several recent studies.[4,5] While there are no reported imido actinide complexes, we have recently characterized compounds that contain uranium–carbon multiple bonds[6-8] and have uncovered an extensive chemistry for these species.[1,9] It thus seemed reasonable that uranium–nitrogen multiply bonded species might also be isolated.

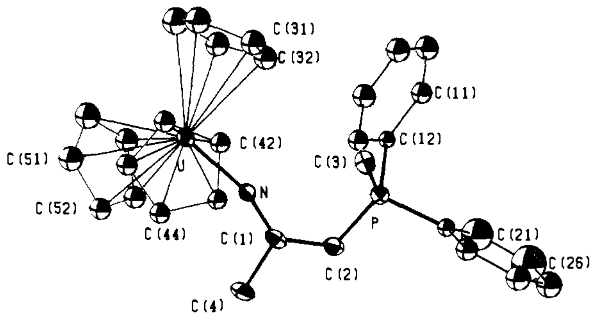

Figure 1. ORTEP representation of the $Cp_3UNC(Me)CHP(Ph)_2Me$ molecule.

Table I. Bond Lengths (Å) and Bond Angles (deg) with Their Standard Deviations for $Cp_3UNC(Me)CHP(Ph)_2Me$

atoms	distances	atoms	angles
U–N	2.06 (1)	U–N–C(1)	163 (1)
N–C(1)	1.34 (2)	N–C(1)–C(4)	118 (1)
C(1)–C(2)	1.39 (2)	C(2)–C(1)–C(4)	114 (1)
C(2)–P	1.74 (2)	C(1)–C(2)–P	123 (1)
C(3)–P	1.83 (2)		
C(12)–P	1.79 (1)		
C(22)–P	1.78 (1)		
C(1)–C(4)	1.54 (3)		

The synthesis of an (imido)uranium complex results from the reaction of $Cp_3U{=}CHP(Ph)_2Me$ with MeCN in equimolar quantities in toluene at 55 °C for 24 h.

$$\underset{\text{I}}{Cp_3U{=}CHP(Ph)_2Me} + MeCN \rightarrow \underset{\text{II}}{Cp_3UNC(Me)CHP(Ph)_2Me}$$

$$Cp = \eta^5\text{-}C_5H_5,\ Ph = C_6H_5,\ Me = CH_3$$

Evaporation of the volatile components of this mixture leaves a red solid which, after recrystallization, produces a 50% yield of II.[10] The ^1H NMR of this material can be assigned as follows: δ −20.6 (15 H, UCp_3), 4.83 (4 H, $P(Ph)_2$), 1.98 (4 H, $P(Ph)_2$), 3.12 (2 H, $P(Ph)_2$), 35.3 (J_{PCH} = 27 Hz, 1 H, P(CH)), −7.38 (3 H, P(Me)), 47.8 (3 H, $N(CH_3)$)). The IR spectrum exhibits peaks typical of the $CHP(Ph)_2Me$ moiety but does not contain any in the 2270 cm^{-1} region where coordinated nitriles show characteristic frequencies.[11] Since these data are insufficient to allow II to be adequately characterized, an X-ray crystal structure determination was undertaken.

Dark red crystals of $Cp_3UNC(Me)CHP(Ph)_2Me{\cdot}C_6H_5CH_3$ belonging to the triclinic space group $P\bar{1}$ with unit cell parameters a = 12.789 (2) Å, b = 14.479 (5) Å, c = 10.389 (3) Å, α = 94.39 (2)°, β = 110.7 (2)°, γ = 67.68 (2)°, V = 1661.2 (8) Å^3, and Z = 2 were grown from a 1:1 mixture of toluene and heptane. Data collection and reduction were carried out as described previously,[7,12] and the structure was routinely solved using Patterson and Fourier methods. Least-squares refinement using rigid group parameters for the Cp and Ph rings and anisotropic thermal parameters for the nongroup atoms converged at R_1 = 0.067 and R_2 = 0.082 using 5144 unique absorption corrected reflections for which $F_o^2 > 3\sigma(F_o^2)$. Each of the Cp groups is disordered over two positions related by rotation about the vector from the Cp centroid to the uranium atom. Each of the two orientations

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was refined as a rigid group with a variable occupancy constrained so that the total occupancy for each Cp ring was one. The refined occupancies for the major location of three rings are 0.54, 0.83, and 0.67, respectively. An ORTEP drawing of the molecule is shown in Figure 1. Selected bond lengths and angles are listed in Table I.

Clearly MeCN has inserted into the uranium–carbon bond of I forming an $NC(Me)CHP(Ph)_2Me$ ligand that coordinates through nitrogen. The uranium–nitrogen bond distance, 2.06 (1) Å, is the shortest reported and can be compared to 2.29 (1) Å found in $Cp_3UN(Ph)_2$,[13] which is a typical U–N bond distance for a uranium amide. Such a short U–N bond suggests multiple-bond character; in principle, nitrogen could donate as many as three electron pairs to uranium.

The U–N–C(1) angle of 163 (1)°, while consistent with considerable multiple-bond character, deviates significantly from 180° which would be expected for a sp hybridized nitrogen. Additionally the N–C(1) and C(1)–C(2) distances of 1.34 (2) and 1.39 (2) Å are shorter than normal single bonds. The C(2)–P distance of 1.74 (2) Å is shorter than the P–CH_3 distance, 1.83 (2) Å, but is somewhat longer than observed in simple unsubstituted ylides: 1.661 (8) Å in $H_2C{=}P(Ph)_3$[15] and 1.640 (6) Å in $H_2{=}P(Me)_3$.[16] Bond angles around C(1) and C(2) are consistent with predominant sp^2 hybridization for these atoms. In view of the bond angles and distances several resonance structures are probably important in describing the bonding in II. These include:

$$\mathrm{Cp_3U{\equiv}NC(Me){=}CHP(Ph)_2Me} \leftrightarrow$$

i

$$\mathrm{Cp_3U{=}\ddot{N}C(Me){=}CHP(Ph)_2Me} \leftrightarrow$$

ii

$$\mathrm{Cp_3U{=}N{=}C(Me)CH{=}P(Ph)_2Me}$$

iii

Their combination implies a highly delocalized π system and a uranium–nitrogen bond order between 2 and 3.

We have already discussed the relationship between I and other metal–carbon multiply bonded species[7,8] and pointed out similarities in carbon monoxide insertion chemistry.[9] This comparison can now be extended since products similar to (II), $R_3MNC(Me)CHCMe_3$, have been reported for the insertion of MeCN into metal–carbon double bonds of the alkylidene complexes $R_3MCHCMe_3$ (M = Ta and Nb; R = $(CH_3)_3CCH_2$).[14] Schrock draws these compounds with metal–nitrogen double bonds[14] but reports no structural data. In contrast to the reaction of I with MeCN, which requires 24 h at elevated temperature, the reaction of $R_3TaCHCMe_3$ with MeCN is described[14] as "quite vigorous".

Uranium (IV) is a very electron-deficient ion. "In the actinide series ... the energies of the 5f, 6d, 7s, and 7p orbitals are about comparable over a range of atomic numbers (especially U–Am), and since the orbitals also overlap spatially, bonding can involve any or all of them".[17] Thus, a closed-shell configuration would consist of 32 electrons. In Cp_3UCH_3 there are 22 electrons in the uranium valence shell while for $Cp_3U{=}CHP(Ph)_2Me$ the electron count rises to 24, still far short of 32. Steric crowding among the ligands is considerable for $Cp_3U{=}CHP(Ph)_2Me$[7] so that addition of another ligand to increase the electron count is not feasible. However, in II the electron count is as high as 26 for the resonance form i, identical with that of Cp_4U. Organouranium compounds are sterically saturated but electronically unsaturated.[18] *As such uranium has a high affinity for small ligands with several available electron pairs.* Oxygen ligands fall into this category, and the affinity of uranium for oxygen is well-known. The U–X multiple bonds, as in $Cp_3U{=}CHP(Ph)_2Me$ and $Cp_3U{\equiv}NC(Me)CHP(Ph)_2Me$, also fulfill this role. Their discovery confirms the ability of U(IV) and, presumably, other actinide ions to form multiple bonds with multiple electron pair donor ligands.

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Registry No. I, 77357-86-9; II, 88780-83-0.

Supplementary Material Available: Summary of crystal data (Table II), a listing of observed and calculated structure factors (Table III), and positional and thermal parameters for group and nongroup atoms (Tables IV–VI) for $Cp_3UNC(Me)CHP(Ph)_2Me{\cdot}C_6H_5CH_3$ (26 pages). Ordering information is given on any current masthead page.

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Dimerization Energy Decomposition of Lithium First-Row Hydrides

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Currently there is wide interest in molecules containing lithium and organic fragments. The reason stems largely from their use as synthetic reagents and their novel bonding properties.[1,2] These molecules can form multicenter electron-deficient, coordinate, ionic, and covalent bonds.[3] Streitwieser et al.[4] have anticipated that the driving force for oligomerization is largely that of ionic aggregation. On the basis of projection functions and Mulliken population[5] analyses, they proposed that the C–Li bond in the $(CH_3Li)_2$ dimer has essentially no shared covalent character. On the other hand,[6] charge distributions of dimers of first-row metal hydrides invoking more than one bridging hydrogen were found difficult to generalize. In order to investigate the degree of nonionic character in lithium dimers of the first-row atoms, we have performed energy decomposition analyses, which proved especially fruitful in the calculation of the properties of hydrogen-bonded[7] and electron donor–acceptor[8] complexes. Our purpose is to provide some insight into the origin of the dimerization of monomeric $LiXH_n$[9] molecules, where XH_n is a first-row atom hydride, and total dimerization energy

$$\Delta E = E(\mathrm{LiXH}_n)_2 - 2E(\mathrm{LiXH}_n) \quad (n = 0, 1, 2, 3)$$

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