alkyl in the case of 1-hexene, but only for the branched one in the case of styrene.

These findings satisfactory explain the influence of reaction temperature on the regioselectivity. For both substrates an increase in temperature produces an increasing linear isomer, the effect being stronger in the case of styrene.[16,17]

Isomerization of metal-alkyl intermediates has been often invoked in rhodium- and cobalt-catalyzed hydroformylation of alkenes[10,14,20-23] in order to explain the influence of reaction parameters on the product distribution. However, experimental evidence for differing behavior of isomeric metal alkyls toward β-hydride elimination, during the hydroformylation of 1-alkenes is reported here for the first time.

Experimental Section

Benzene was dried over molecular sieves and distilled under nitrogen. $Rh_4(CO)_{12}$ was prepared as reported in the literature.[24] GC analysis of the deuterioformylation mixtures were performed on a Dani 6800 chromatograph equipped with 2 m × 0.4 cm columns of 10% SE30 on 60/80 mesh Chromosorb WAW DCMS or 5% UCON LB 550X on 60/80 Chromosorb WAW DCMS and a flame-ionization detector; nitrogen was used as carrier gas. The analysis of the olefinic products was also carried out by using a 8500 Perkin-Elmer gas chromatograph equipped with a 12 m × 0.22 mm BP1 capillary column, using helium as carrier gas.

Mass spectra were measured with a VG 70/70E spectrometer at 70 eV: the accelerating voltage was 6 kV, and the emission current was 100 μA. GC-MS analyses of olefinic mixtures were performed by use of the same spectrometer coupled with a DANI 3800 gas chromatograph equipped with a silica capillary column SE30 (50 m × 0.53 mm).

^2H NMR spectra were recorded in CCl_4 solutions on a Varian VXR 300 spectrometer, operating at 46 MHz for ^2H. $CDCl_3$ was used as external standard.

Deuterioformylation of 1-Hexene: General Procedure. Deuterioformylation of 1-hexene, at partial substrate conversion, was performed following a general procedure previously described for other substrates.[16] In a 50-mL evacuated stainless-steel autoclave, a solution of $Rh_4(CO)_{12}$ (0.5 mg, 6.7×10^{-4} mmol) and 1-hexene (2.0 g, 23.8 mmol) in benzene (10.0 g) was introduced by suction. Carbon monoxide was introduced to the desired pressure: the autoclave was then rocked and heated to the reaction temperature, and deuterium was rapidly introduced to the desired total pressure. When the reaction started, the drop in pressure was restored by injection of a carbon monoxide-deuterium mixture (1:1) from a high-pressure container. Progress in the reaction was followed by the pressure drop in the high-pressure gas reservoir. When the gas absorption reached the value corresponding to the desired conversion to aldehydes, the autoclave was rapidly cooled, the reaction mixture was siphoned out, and GC was used to determine the isomeric composition. The degree of 1-hexene conversion was measured by GC, using benzene as an internal standard.

Unreacted substrate and benzene were separated from aldehydic products by fractional distillation at atmospheric pressure.

Chemically pure samples of unconverted 1-hexene and samples enriched in 2-hexene were obtained by careful fractional distillation of the reaction mixture at atmospheric pressure through a spinning band column.

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A Heteroatom-Stabilized Neutral Imine Organoactinide Complex: X-ray Structure of Dichlorobis(pentamethylcyclopentadienyl)uranium(IV) Phosphine Imine

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$Cp^*_2UCl_2(HNPPh_3)$ is formed from the reaction between $Cp^*_2UCl_2$ and 1 equiv of $HNPPh_3$ in toluene. The complex is of the "Cp_2MX_2Y type" and has been characterized by the usual spectroscopic and chemical methods and by single-crystal X-ray diffraction. $Cp^*_2UCl_2(HNPPh_3)$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.387$ (4) Å, $b = 17.048$ (6) Å, $c = 10.116$ (2) Å, $\alpha = 102.15$ (3)°, $\beta = 110.28$ (3)°, $\gamma = 77.59$ (3)°, $Z = 2$, $R = 0.0554$, and $R_G = 0.0615$. The U-N bond distance of 2.43 (1) Å is short for the separation of U(IV) and a neutral nitrogen donor ligand. The position of H(1), located by using low-angle X-ray data, indicates an agostic interaction with the uranium and hydrogen bonding with one of the chlorines. Consistent with this model, the N-H stretch occurs at a low frequency.

We are interested in nitrogen donors that may be good coligands in organometallic complexes of electron-poor, high-valent actinides.[1,2] In this context, we have been drawn to phosphine imines, $[R_3PNH]$, which are isoelectronic with $[R_3PCH]^-$, a ligand we have studied a great deal.[3,4] There is very little known about the coordination chemistry of phosphine imines, $RNPR'_3$. In addition to a copper(II) chloride complex of *N*-phenyltriphenylphosphine imine[5] and a copper(I) chloride complex of

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N-(trimethylsilyl)triphenylphosphine imine,[6] which have been structurally characterized, only $Me_3M-N(SiMe_3)PPh_3$ (M = Al, Ga, In)[7-9] and $(OC)_nM[HNPPh_3]_2$ (M = Mo, W)[10] have been reported. Undoubtedly, the number of complexes of these ligands is limited because of the lability of the N–Si and N–H bonds. For example

$$M-X + Me_3SiNPPh_3 \rightarrow MNPPh_3 + Me_3SiX$$

has been observed for $MeWCl_5$,[11] $TiCl_4$,[12] $VOCl_3$,[12] WF_6,[13,14] and Mo_2Cl_{10}.[15]

In this paper we report $Cp*_2UCl_2(HNPPh_3)$, the first f-element or early-transition-metal complex with an intact $RNPR'_3$ ligand.

Experimental Section

All procedures were performed under a dry dinitrogen atmosphere by using normal Schlenk techniques and a Vacuum Atmospheres glovebox equipped with an HE 493 Dri-train or in a high vacuum line. Deuterated solvents were dried over sodium benzophenone ketyl and degassed by several freeze–thaw cycles on the high vacuum line. Infrared spectra (4000–600 cm^{-1}) were recorded on a Perkin-Elmer 1430 spectrometer. NMR spectra were recorded on a Nicolet NM-300 spectrometer. Chemical shifts were referenced to internal deuterated solvent and then recalculated to TMS = 0.0 ppm.

Uranium tetrachloride was purchased from Pfaltz and Bauer Research Chemicals. Reported procedures were used to prepare pentamethylcyclopentadiene (Cp*H),[16-18] (Mg[Cp*]Cl·thf),[19] $Cp*_2UCl_2$,[19] and $[HNPPh_3]$.[20] Elemental analysis was performed by Oneida Research Services, Inc., Whitesboro, NY 13492.

Synthesis of $Cp*_2UCl_2(HNPPh_3)$. $Cp*_2UCl_2$ (1.15 g, 1.98 mmol) and 0.55 g (1.99 mmol) of $HNPPh_3$ were dissolved in 50 mL of toluene under dinitrogen. The reaction mixture was heated to 60 °C and stirred for 72 h. During this time the color changed from deep red to dark orange. After filtration through a medium-porosity glass frit containing Celite filteraid, the solvent was evaporated leaving a dark oil that was redissolved in ca. 15 mL of diethyl ether. A dark red-brown microcrystalline product, which was insoluble in hexanes, was obtained after the ether was evaporated. The powder was slurried in about 10 mL of *n*-hexanes, and small amounts of diethyl ether were slowly added until all of the product dissolved to produce a red-orange solution. When the solution was left standing at −15 °C for 24 h, large red-orange crystals formed. These were isolated by filtration and washed with 2 × 0.5 mL hexane, giving an isolated yield of 1.09 g (64%) of crystalline solid $Cp*_2UCl_2(HNPPh_3)$: ^1H NMR (δ, C_7D_8, 21 °C) 1.9 (30 H, s, Cp*), 9.52 (3 H, m, J_{HH} = 7 Hz, Ph-*p*), 9.54 (6 H, t, J_{HH} = 7 Hz, Ph-*m*), 21 (6 H, br, Ph-*o*); IR (4000–600 cm^{-1}, thin film on NaCl) 3160 (w, br), 3065 (sh), 2900 (s), 1490 (s), 1440 (vs), 1380 (m), 1120 (s, br), 1025 (s, br), 1000 (w, sh), 910 (m), 750 (w), 725 (w), 700 (w). Anal. Calcd for $C_{38}H_{46}Cl_2UNP$: C, 53.28; H, 5.41; N, 1.63; Cl, 8.29. Found: C, 54.16; H, 5.09; N, 1.65; Cl, 7.91.

Table I. Crystal, Data Collection, and Reduction Parameters for $Cp*_2UCl_2(HNPPh_3)$

formula: $C_{38}H_{46}NPCl_2U$
fwt: 856.97
space group: $P\bar{1}$
crystal system: triclinic
a = 11.387 (4) Å
α = 102.15 (3)°
b = 17.048 (6) Å
β = 110.28 (3)°
c = 10.116 (2) Å
γ = 77.59 (3)°
Z = 2
V = 1779 (1) $Å^3$

cryst dimens: 0.59 × 0.41 × 0.29 mm
cryst shape: rectangular plate
cryst color: reddish orange
D(calcd): 1.60 g/cm^3
abs coeff (μ): 45.54 cm^{-1}
abs corr factor range: 1.00–2.18
radiatn (λ(Mo Kα)): = 0.71073 Å
scan rate: 4–24°/min
scan type: $2\theta-\theta$
2θ range: 3–60°
total observns: 10804
unique observns: 9814
unique data with $I > 3\sigma(I)$: 7480
no. of parameters: 179
over determinatn ratio: 41.8
R: 0.0554[a]
R_G: 0.0615[b]

[a] $R = \sum(|F_o - F_c|)/\sum(F_o)$. [b] $R_G = [\sum(|F_o - F_c|^2)/\sum(F_o^2)]^{1/2}$.

Collection and Reduction of X-ray Data. A single crystal of $Cp*_2UCl_2(HNPPh_3)$ from the preparation described above was selected, mounted, and sealed in a thin-walled glass capillary under dinitrogen. A Syntex P$\bar{1}$ four-circle computer-controlled diffractometer with graphite-monochromatized Mo Kα radiation ($K\alpha_1$ = 0.70930 and $K\alpha_2$ = 0.71359 Å) and a scintillation detector with pulse height analyzer was used for the measurement of diffraction intensities. During data collection, the intensities of three standard reflections, remeasured every 100 reflections, showed <4% variation. Corrections for Lorentz, polarization, and absorption effects were applied by using the program PROCESS,[21] with four psi scans (2θ = 13.70, 25.21, 35.60, 44.13°). Cell constants were determined by least-squares methods from the centered angular coordinates of 15 intense reflections with 2θ values between 30° and 40°. Atomic scattering factors for N^0, P^0, Cl^0, C^0, and H^0 were supplied by SHELX-76[22] and that for U^0 was taken from the literature.[23] Crystal data, data collection, and final refinement parameters are listed in Table I.

Structure Solution and Refinement. The structure was solved in the triclinic space group $P\bar{1}$. The position of the uranium atom was determined by Patterson methods, and the remaining atoms were located from a series of difference Fourier maps and least-squares refinements using SHELX-76. All non-hydrogen atoms were refined anisotropically except for the ring carbons of the pentamethylcyclopentadienide and phenyl groups which were refined isotropically as rigid bodies (C–C(Cp*) = 1.420 Å, C–C(Ph) = 1.395 Å). All non-hydrogen atoms were revealed in the first few difference Fourier syntheses. After several cycles of least-squares refinement R = 0.0679 and R_G = 0.0839 were obtained. Phenyl and methyl hydrogen atoms were then added at calculated positions and treated as rigid groups by using the parameters contained in SHELXTL. Several more cycles of least-squares refinements yielded R indices of R = 0.0557 and R_G = 0.0621.

During the final cycles of least-squares a peak of 0.5 e/$Å^3$ about 0.7 Å from the nitrogen was added as the imino hydrogen, H(1). Since low-angle X-ray data is most sensitive to hydrogen scattering, the positional parameters and temperature factor of H(1)

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Table II. Bond Lengths (Å) and Selected Bond Angles (deg) for Cp*$_2$UCl$_2$(HNPPh$_3$)

Bond Lengths

U-Cl(1)	2.730 (4)	U-C(11)	2.79 (1)
U-Cl(2)	2.658 (4)	U-C(12)	2.81 (1)
U-N	2.43 (1)	U-C(13)	2.78 (1)
P-N	1.58 (1)	U-C(14)	2.75 (1)
U-H(1)	2.2 (2)	U-C(15)	2.75 (1)
N-H(1)	0.6 (2)	U-C(21)	2.75 (1)
N-P	1.58 (1)	U-C(22)	2.79 (1)
P-C(31)	1.82 (1)	U-C(23)	2.80 (1)
P-C(41)	1.80 (1)	U-C(24)	2.77 (1)
P-C(51)	1.80 (1)	U-C(25)	2.74 (1)
U-Cp(1)[a]	2.50 (4)	U-Cp(2)[a]	2.49 (4)

Bond Angles

Cl(2)-U-Cl(1)	151.0 (1)	N-P-C(31)	110.2 (5)
N-U-Cl(1)	72.5 (3)	N-P-C(41)	114.2 (6)
N-U-Cl(2)	78.5 (3)	N-P-C(51)	113.8 (6)
H(1)-U-Cl(1)	60 (6)	C(41)-P-C(31)	103.1 (5)
H(1)-U-Cl(2)	92 (6)	C(51)-P-C(31)	106.7 (5)
H(1)-U-N	14 (5)	C(51)-P-C(41)	108.1 (5)
H(1)-N-U	60 (16)	Cp(1)-U-Cp(2)[a]	134
P-N-U	155.8 (6)		
P-N-H(1)	137 (17)		

[a] Cp(1) and Cp(2) represent the centroids of the C(11)–C(15) and the C(21)–C(25) C$_5$ rings, respectively.

were refined by using only the data in which $2\theta \leq 15°$ (1365 reflections) to $R = 0.0337$ and $R_G = 0.0397$. While the problems of locating a hydrogen atom in such close proximity to the uranium should not be minimized, low-angle data has been successfully used to locate hydrogen atoms in the vicinity of other heavy atoms[24-27] and we have found agreement between the position of the α-hydrogen in Cp$_3$U=CHPMe$_3$ as determined by using low-angle X-ray data[28] and that obtained from a neutron structure.[29] Consequently, we feel that the position of H(1) determined in this structure is probably correct within the indicated uncertainties.

The H(1) positional parameters that were obtained in the restricted angle least-squares cycles were held constant in the final cycles of refinement which used all of the reflection data for which $I \geq 3\sigma(I)$. A final difference Fourier map showed no peaks greater than 0.5 e/Å^3 except for five peaks between 2.5 and 3.5 e/Å^3 located less than 1 Å from the uranium. The final cycle of refinement yielded parameter shifts no greater than 3% of their estimated standard deviation except for several of the Cp* methyl carbon atoms which ranged from 10 to 70% of their estimated standard deviation. Bond distances and angles are summarized in Table II, and final positional and temperature factors are listed in Tables III, IV, and V (supplementary material). Observed and calculated structure factors are in Table VI (supplementary material).

Discussion

The reaction between Cp*$_2$UCl$_2$ and HNPPh$_3$ forms Cp*$_2$UCl$_2$(HNPPh$_3$):

$$Cp^*_2UCl_2 + HNPPh_3 \rightarrow Cp^*_2UCl_2(HNPPh_3)$$

Interestingly, Cp*$_2$UCl$_2$(HNPPh$_3$) is stable even in the presence of excess HNPPh$_3$, and we were unable find any evidence for dehydrohalogenation which would produce Cp*$_2$U(Cl)(NPPh$_3$) and [H$_2$NPPh$_3$]$^+$Cl$^-$. Cp*$_2$UCl$_2$(HNPPh$_3$) has been characterized by IR, NMR, elemental analysis, and x-ray diffraction. While an NMR resonance was not observed for the NH proton between ±200 ppm, presumably because of broadening due to the quadrupolar nitrogen and the paramagnetic U(IV), an N–H stretch is observed at 3160 cm^{-1}. Consistent with the X-ray structure which indicates hydrogen bonding of the NH proton with a chloride and an agostic interaction with the uranium, this band is broad and substantially lower than the N–H frequency in HNPPh$_3$, 3380 cm^{-1},[10] Mo(CO)$_4$(HNPPh$_3$)$_2$, 3335 cm^{-1},[10] or [Mo(CO)$_3$(HNPPh$_3$)$_2$]$_2$, 3225 cm^{-1}.[10]

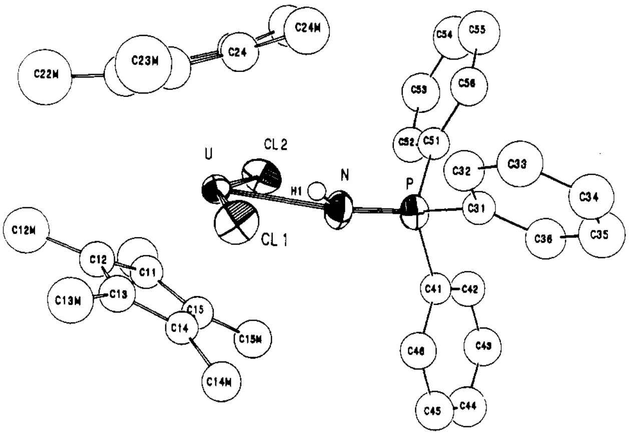

Figure 1. A perspective drawing of Cp*$_2$UCl$_2$(HNPPh$_3$).

A perspective drawing of Cp*$_2$UCl$_2$[HNPPh$_3$] is shown in Figure 1. The molecule is of the Cp$_2$MX$_2$Y type with uranium being bound by two pentamethylcyclopentadienide rings, two chlorides, and the nitrogen of the phosphine imine ligand. If each Cp* is considered to occupy three coordination sites, each Cl one and the N one, the U(IV) is nine-coordinate. This is not a common coordination geometry for Cp*$_2$U compounds; the most similar are Cp*$_2$U(Cl)$_2$(pz) (pz = C$_3$H$_4$N$_2$)[30] and Cp*$_2$U(AA)Cl (AA = chelating (CH$_2$)PR$_2$(CH$_2$)$^-$).[31]

The average U–C(Cp*) distance, 2.773 (1) Å, and Cp*(centroid)–U–Cp*(centroid) angle, 134°, are similar to other Cp*$_2$An (An = U or Th) complexes. The Cp* rings adopt the less sterically hindered, staggered arrangement. Consistent with the near planarity of the atoms in the equatorial positions, the sum of the N–U–Cl(1) and N–U–Cl(2) angles, 72.5 (3)° and 78.5 (3)°, respectively, equals the 151.0 (1)° Cl(1)–U–Cl(2) angle. The U–N–P atoms form a 155.8 (6)° angle, and the bond lengths and angles about P are similar to those found in other phosphine imide complexes[1] and in [H$_2$NPPh$_3$]$^+$.[32]

There are two different U–Cl distances in Cp*$_2$UCl$_2$(HNPPh$_3$), 2.658 (5) and 2.730 (4) Å, and both are longer than the U–Cl distances of about 2.56–2.60 Å found in Cp$_3$UCl, 2.56 (2) Å,[33] [UCl$_2$(DMSO)$_6$][UCl$_6$], 2.60 (2) Å (anion),[34] UCl$_4$·2(hmpa), 2.58 (1) and 2.60 (1) Å,[35] and UCl$_4$·2(TPPO), 2.609 (4) and 2.626 (3) Å,[36] but are about the same as that in Cp*$_2$U(Cl)$_2$(pz), 2.696 (2) Å,[30] and in [UCl$_2$(DMSO)$_6$]$^{2+}$, 2.70 (2) Å. In Cp*$_2$UCl$_2$(HNPPh$_3$) the longer U–Cl(1) bond is to the chlorine which is hydrogen bonded to H(1). The Cl(1)–U–Cl(2) angle of 151.0 (1)° is similar to the corresponding angle of 148.29 (8)° in UCp*$_2$Cl$_2$(pz)[30] but is greater than about 96° in Cp*$_2$U-

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Table III. Positional and Thermal Parameters of Anisotropically Refined Atoms for $Cp^*_2UCl_2(HNPPh_3)$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
U	0.14970 (5)	0.23484 (3)	0.47647 (6)	N	−0.060 (1)	0.2893 (7)	0.334 (1)
Cl(1)	0.0506 (4)	0.3563 (2)	0.6492 (4)	P	−0.1814 (4)	0.2927 (2)	0.1978 (4)
Cl(2)	0.1353 (5)	0.1476 (3)	0.2221 (5)				

atom	*U*(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
U	0.0318 (2)	0.0300 (2)	0.0343 (3)	0.0045 (2)	0.0097 (2)	−0.0044 (2)
Cl(1)	0.065 (2)	0.048 (2)	0.049 (2)	−0.003 (2)	0.027 (2)	−0.001 (2)
Cl(2)	0.064 (3)	0.052 (2)	0.050 (3)	−0.008 (2)	0.028 (2)	−0.019 (2)
N	0.037 (6)	0.051 (6)	0.037 (5)	0.007 (5)	−0.008 (4)	−0.005 (5)
P	0.034 (2)	0.041 (2)	0.034 (2)	0.000 (1)	0.010 (2)	−0.003 (1)

Table IV. Positional and Thermal Parameters for Isotropically Refined Non-Hydrogen Atoms and H(1) for $Cp^*_2UCl_2(HNPPh_3)$

atom	*x*	*y*	*z*	*U*, Å²
C(11)	0.359 (1)	0.2458 (5)	0.401 (1)	0.047 (3)
C(12)	0.404 (1)	0.2565 (5)	0.552 (1)	0.050 (4)
C(13)	0.339 (1)	0.3314 (5)	0.603 (1)	0.050 (3)
C(14)	0.254 (1)	0.3670 (5)	0.483 (1)	0.042 (3)
C(15)	0.266 (1)	0.3141 (5)	0.358 (1)	0.044 (3)
C(11M)	0.419 (2)	0.184 (1)	0.306 (2)	0.072 (5)
C(12M)	0.522 (2)	0.207 (1)	0.639 (2)	0.080 (6)
C(13M)	0.370 (2)	0.370 (1)	0.758 (2)	0.074 (5)
C(14M)	0.178 (2)	0.451 (1)	0.484 (2)	0.059 (4)
C(15M)	0.201 (2)	0.330 (1)	0.210 (2)	0.062 (4)
C(21)	0.2131 (9)	0.0781 (6)	0.536 (1)	0.051 (3)
C(22)	0.2491 (9)	0.1255 (6)	0.673 (1)	0.063 (4)
C(23)	0.1371 (9)	0.1686 (6)	0.701 (1)	0.061 (4)
C(24)	0.0318 (9)	0.1478 (6)	0.582 (1)	0.053 (4)
C(25)	0.0788 (9)	0.0919 (6)	0.480 (1)	0.043 (3)
C(21M)	0.302 (2)	0.017 (1)	0.470 (2)	0.077 (6)
C(22M)	0.377 (2)	0.117 (2)	0.785 (3)	0.097 (8)
C(23M)	0.132 (3)	0.215 (2)	0.845 (3)	0.095 (8)
C(24M)	−0.106 (2)	0.173 (1)	0.571 (2)	0.070 (5)
C(25M)	−0.004 (2)	0.048 (1)	0.348 (2)	0.061 (5)
C(31)	−0.3191 (9)	0.3481 (6)	0.2466 (9)	0.040 (3)
C(32)	−0.3263 (9)	0.3477 (6)	0.3813 (9)	0.057 (4)
C(33)	−0.4339 (9)	0.3881 (6)	0.4172 (9)	0.068 (4)
C(34)	−0.5342 (9)	0.4288 (6)	0.3184 (9)	0.065 (4)
C(35)	−0.5269 (9)	0.4293 (6)	0.1837 (9)	0.076 (6)
C(36)	−0.4193 (9)	0.3889 (6)	0.1478 (9)	0.060 (4)
C(41)	−0.174 (1)	0.3486 (5)	0.069 (1)	0.040 (3)
C(42)	−0.211 (1)	0.3221 (5)	−0.078 (1)	0.055 (4)
C(43)	−0.206 (1)	0.3706 (5)	−0.170 (1)	0.067 (5)
C(44)	−0.164 (1)	0.4455 (5)	−0.116 (1)	0.068 (4)
C(45)	−0.127 (1)	0.4720 (5)	0.030 (1)	0.062 (4)
C(46)	−0.132 (1)	0.4235 (5)	0.123 (1)	0.054 (4)
C(51)	−0.2202 (9)	0.1945 (6)	0.107 (1)	0.044 (3)
C(52)	−0.1520 (9)	0.1453 (6)	0.021 (1)	0.057 (4)
C(53)	−0.1781 (9)	0.0669 (6)	−0.039 (1)	0.070 (5)
C(54)	−0.2725 (9)	0.0378 (6)	−0.013 (1)	0.081 (5)
C(55)	−0.3407 (9)	0.0871 (6)	0.073 (1)	0.079 (5)
C(56)	−0.3145 (9)	0.1655 (6)	0.133 (1)	0.058 (4)
H(1)	−0.05 (2)	0.30 (1)	0.40 (2)	0.2 (1)

$(Me)_2$[37] and 135° between the outer equatorial positions in $Cp^*_2U(AA)Cl$.[31] The wide angle and long U–Cl bonds in $Cp^*_2UCl_2(HNPPh_3)$ probably reflect crowding in the equatorial girdle.

In view of the long U–Cl distances, the 2.43 (1) Å U–N bond distance in $Cp^*_2UCl_2(HNPPh_3)$, which is the shortest yet found in a complex of uranium with an uncharged nitrogen donor ligand, is notable. For comparison the U–N distance is 2.607 (8) Å in $Cp^*_2UCl_2(pz)$,[30] 2.61 (2) and 2.58 (2) Å in $Cp_3U(NCMe)_2{}^+$,[38] and 2.68 (2) Å for the U–NCMe distance in $Cp_3U(NCS)(NCMe)$.[39] The $HNPPh_3$ ligand consequently appears to be tightly bound to the metal. We have previously noted that U–N bond distances, which range between 2.02 and 2.68 Å, appear to reflect both the ligand charge and the number of donor electrons on the ligand.[1,2] For $HNPPh_3$ semiempirical calculations and experimental data have been interpreted in terms of resonance form A being more important than B.[40]

$$\underset{A}{Ph_3P^+{-}\ddot{N}^-H} \leftrightarrow \underset{B}{Ph_3P{=}\ddot{N}H}$$

This indicates that the P–N bond is highly polar and that $HNPPh_3$ could function as a two-electron pair donor, both of which would tend to shorten the U–N bond in $Cp^*_2UCl_2(HNPPh_3)$.

Bonding between the $Cp^*_2UCl_2$ and $HNPPh_3$ fragments also may involve interactions of both Cl(1) and U with H(1). We have discussed the accuracy of the H(1) position above. Within the resulting large uncertainties, the U–H(1) distance, 2.2 (2) Å, is short, similar to the terminal Th–H distance, 2.29 (3) Å, in $(Cp^*ThH_2)_2$,[41] and is consistent with an interaction of the N–H bond with the electron-deficient uranium center. Such an interaction would weaken the N–H bond, make the hydrogen more positive, and enhance hydrogen bonding. The N–H(1) vector points in the general direction of Cl(1), which, combined with the Cl(1)–H(1), 2.3 (2) Å, and Cl(1)–N, 3.06 (1) Å, distances, both considerably shorter than the sum of the van der Waals radii of Cl (1.8 Å), H (1.2 Å), and N (1.5 Å), together with the U–Cl(1) distance, 2.730 (4) Å, which is longer than U–Cl(2), 2.658 (4) Å, and the low N–H IR frequency, is consistent with hydrogen bonding of H(1) with Cl(1).

Interactions of electropositive metals with C–H bonds have been documented in numerous examples, and these interactions are thought to influence the chemistry of these species.[42] In this light, the structure of $Cp^*_2UCl_2(HNPPh_3)$ may model an intermediate stage in a hydrogen-transfer reaction and may indicate that reactions such as the recently documented[43] hydrogen exchange in $Cp^*_2Ce[N(H)^tBu][N(H)_2{}^tBu]$ are metal-mediated.

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Supplementary Material Available: Table V, positional and thermal parameters for hydrogen atoms of $Cp^*_2UCl_2(HNPPh_3)$ (1 page); Table VI, observed and calculated structure factors for $Cp^*_2UCl_2(HNPPh_3)$ (38 pages). Ordering information is given on any current masthead page.

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