Stable Analogs of the Uranyl Ion Containing the −N=U=N− Group

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A series of compounds containing the −N=U=N− group has been prepared. Their physical and chemical properties are reported. They adopt a *trans* configuration, and are thermally robust. The chemistry of some recently-prepared O=U=N− compounds is also described. These are the first examples of stable analogs of the uranyl ion $UO_2{}^{2+}$. The factors that determine their stability are discussed.

Introduction

The uranyl ion $UO_2{}^{2+}$ is well-known for its chemical stability, being resistant to reactions which modify the dioxo unit. This property is of particular importance in the nuclear fuel cycle and has stimulated detailed interest in its electronic structure.[1] However, only a few compounds of uranium containing the analogous imido and iminato ligands are known, and these bear little resemblance to the uranyl ion.[2] Syntheses of compounds containing these ligands have relied on the presence of bulky organometallic groups in compounds such as $(Me_5Cp)_2U(O)$-NC_6H_3-2,6-*i*-Pr_2[3] or $(Me_5Cp)_2U(NPh)_2$,[4] both of which approximate to tetrahedral geometry, and on trimethylsilyl-imido and amido compounds, such as $Me_3SiN=U[N(SiMe_3)_2]_3$.[5] By contrast, imido and iminato analogs of oxo compounds of the transition metals are common, and methods for their interconversion have been established.[6,7]

Until our recent report[2] of the preparation and crystal structure of the phosphorane-iminato compound $[Ph_4P][OUCl_4(NPTol_3)]$ containing a linear O=U=N− group, no stable structural analogs of the uranyl ion had been isolated. However, unstable analogs, such as UN_2 in an N_2 matrix, have been identified,[8] and the OUN^+ ion has been characterized in a mass spectrometer.[9] Recent theoretical studies of OUO^{2+}, NUO^+, and NUN, as well as other isoelectronic species, suggest that many of these triatomic units could have significant stability.[10]

We now describe the synthesis of a series of compounds containing the linear −N=U=N− group, and report their physical and chemical properties together with those of related compounds containing the O=U=N− group by way of comparison. Both classes of compound resemble the dioxo species in being thermally robust; the solids remain unchanged in air, and their solutions are stable at high temperatures in the absence of moisture.

Results and Discussion

Preparation and Properties. Deep red $[Ph_4P][OUCl_4$-$(NPR_3)]$ salts **1** are formed by the reaction of the oxopentachlorouranate(VI) salt $[Ph_4P][UOCl_5]$ with trimethylsilylphosphoranimines $R_3PNSiMe_3$ (eq 1). The phosphorane substituents can either be aryl groups, or a mixture of aryl and alkyl groups.

(1)
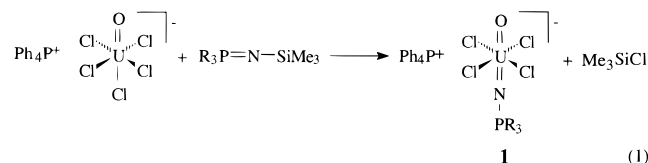
When R = *m*-Tolyl, the crystal structure[2] shows the O=U=N− unit to be nearly linear (179°) with a short U−N distance (1.90 Å), indicative of a multiple bond between U and N. Bis(iminato) compounds **2** (eq 2) can be isolated from the same reaction mixture by controlling the conditions of workup.

(2)
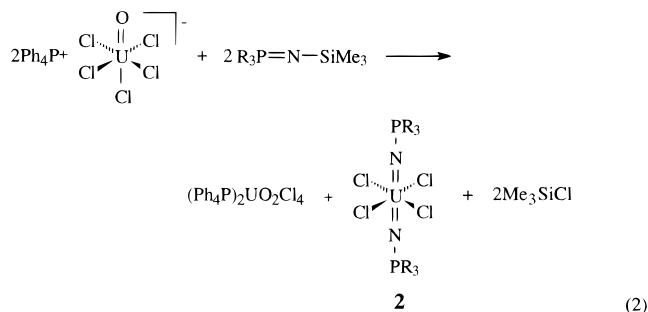
The oxopentachlorouranate(VI) is a useful starting material, because it is both reactive and convenient to handle. As such, it represents a compromise between the very robust uranyl ion in $UO_2Cl_4{}^{2−}$, and the highly unstable and oxidizing hexachloride, UCl_6. It is prepared as a red solid by the partial deoxygenation of $[Ph_4P]_2[UO_2Cl_4]$ in refluxing thionyl chloride.[11] The chloride in the $UOCl_5{}^−$ anion provides a driving force for reactions 1 and 2, through the elimination of volatile trimethylsilyl chloride. Trimethylsilylphosphoranimine precursors are prepared by the reaction of tertiary phosphines R_3P with trimethylsilyl azide.[12,13]

In a typical preparation, 1−2 g of $[Ph_4P][UOCl_5]$ was stirred for several hours with a slight molar excess of triphenylphos-

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Table 1. Vibrational Frequencies (cm^{-1}) of Uranium Iminato Complexes[a]

compound	no.	ν_{as}(U−N−P)	ν_s(U−N−P)	ν(U−O)
[Ph$_4$P][OUCl$_4$(NPPh$_3$)]	3	1090	561	862
(Ph$_3$PN)$_2$UCl$_4$	4	1042	552	
[Ph$_4$P][OUCl$_4$(NPTol$_3$)]	5	1080	556	850
		1079$_{Raman}$		849$_{Raman}$
(Tol$_3$PN)$_2$UCl$_4$	6	1046	554	
		1068$_{Raman}$		
[Me$_2$PhPNH$_2$][OUCl$_4$(NPMe$_2$Ph)][a]	7	1059		856
(Me$_2$PhPN)$_2$UCl$_4$	8	1053		

[a] Infrared data, unless otherwise indicated. [b] N−H stretching frequencies were observed at 3341 and 3260 cm^{-1}.

phoranimine, Ph$_3$PNSiMe$_3$, in dichloromethane at room temperature. During this time the sparingly soluble [Ph$_4$P][UOCl$_5$] dissolves, forming a clear red solution that contains a mixture of [Ph$_4$P][OUCl$_4$(NPPh$_3$)] (**3**), (Ph$_3$PN)$_2$UCl$_4$ (**4**), and the uranyl salt [Ph$_4$P]$_2$[UO$_2$Cl$_4$]. Compound **3** is an ionic solid, soluble in polar organic solvents such as dichloromethane, and is precipitated by addition of nonpolar solvents, *e.g.* toluene, in which it is very insoluble. **4** is neutral and is usually precipitated first when a solution is concentrated by removing some of the solvent under vacuum. Crystalline samples of **3** may be isolated by carefully adding a layer of toluene to the top of the reaction mixture, which is left undisturbed to interdiffuse over a period of weeks. **4** is formed as a microcrystalline solid when the solvent is evaporated slowly.

During the preparation [Ph$_4$P]$_2$[UO$_2$Cl$_4$] is usually deposited as yellow crystals, but these are easy to remove by hand; its presence in powdered samples can be identified by an intense infrared absorption[14] at 912 cm^{-1}. Reactions performed in acetonitrile also yield a brown reduction product. On the basis of IR, analytical, and crystallographic data,[15] we tentatively identify this as [Ph$_4$P]$_2$[UCl$_6$]·4MeCN, containing a small amount of UO$_2$Cl$_4{}^{2-}$ as a solid solution. Solids containing only the UCl$_6{}^{2-}$ ion are pale green, and the brown color may be due to uranium intervalence charge-transfer. This product forms large crystalline masses and can also be separated by hand.

Both the bis(iminato) and the oxoiminato compounds are stable indefinitely in air and in dry solutions. Even if solutions are heated above 200 °C the compounds can be recovered unchanged after removal of the solvent. However, they are immediately hydrolyzed in solution by traces of water. The oxo−iminato compounds, [Ph$_4$P][OUCl$_4$(NPR$_3$)], **1**, are dark red crystalline solids and are very soluble in polar organic solvents such as dichloromethane or acetonitrile. The bis(iminato) complexes, (R$_3$PN)$_2$UCl$_4$, **2**, are formed as red crystalline solids, and are less soluble in polar organic solvents.

In an attempt to produce (Ph$_3$PN)$_2$UCl$_4$ more directly, we have examined the reaction of Ph$_3$PNSiMe$_3$ with uranium hexachloride. Stoichiometric amounts of UCl$_6$ and 2Ph$_3$PNSiMe$_3$ were loaded into a glass vessel and cooled to −78 °C. Slow addition of dichloromethane resulted in the precipitation of a heavy olive-green solid, identical in appearance to uranium tetrachloride, that contains no strong features in the infrared above 400 cm^{-1}; we infer that the hexachloride has been reduced. No red coloration was observed in the final mixture and no iminato complexes could be isolated.

Coordination Geometry. The full determination of a crystal structure of a uranium bis(iminato) compound has proved elusive because it has not been possible to grow crystals of sufficient size and quality for X-ray work. The compounds *do* crystallize, but usually as very thin platelets clumped together around a central axis. Varying the organic groups on the phosphorus

Table 2. Infrared Vibrational Frequencies (cm^{-1}) of Transition Metal Bis(iminato) Complexes

compound	ν_{as}(M−N−P)	ref
WCl$_4$(NPPh$_3$)$_2$	1110, 1220	6
WF$_4$(NPMe$_3$)$_2$	1065−1110(br)	45
VCl$_3$(NPPh$_3$)$_2$	1080, 1110	46
VOCl(NPPh$_3$)$_2$	1095, 1120	46
TiCl$_2$(NPPh$_3$)$_2$	1090, 1110	46

atom, for example to the asymmetrical PhMe$_2$P, failed to produce an improvement in crystal quality. In an attempt to obtain some crystallographic data, a very small single crystal of (Ph$_3$PN)$_2$UCl$_4$, **4**, was mounted on a diffractometer. Decomposition occurred in the X-ray beam over a period of hours, and only a few hundred weak reflections were recorded. It proved impossible to obtain an acceptable refined structure from this data set. However, the heavy atoms U, Cl, and P, could be located, and their positions indicate that the molecule contains a square planar UCl$_4$ unit (U−Cl $\sim$ 2.6 Å) with phosphorus atoms in *trans* axial positions at a distance of $\sim$3.5 Å from uranium. These distances match those that have been accurately determined in the oxo−iminato compound [Ph$_4$P][OUCl$_4$-(NPTol$_3$)].[2]

Table 1 shows the bis(iminato) and oxo−iminato complexes that have been isolated as pure crystalline samples, together with selected infrared and Raman data. The assignment of the vibrational frequencies is made by analogy with the phosphorane-iminato complexes of the transition metals.[16−19] These display characteristic strong absorptions in the range 1050 to 1150 cm^{-1} that are attributed[6] to the antisymmetric stretching vibrations of the M−N−P group. The corresponding symmetric M−N−P stretches occur[6] at about 550 cm^{-1}, although they are generally weak.

Bis(iminato) compounds of d-block transition metals are generally found with a *cis* geometry,[6] and both symmetric and antisymmetric combinations of the ν_{as}(M−N−P) modes are infrared active. Table 2 gives the available infrared data for compounds of this class. The uranium bis(iminato) compounds have only a single infrared-active band at $\sim$1050 cm^{-1} (Table 1), while the Raman spectrum of compound **6** contains just a single feature, 22 cm^{-1} above the IR frequency. The absence of any bands common to the IR and Raman spectra supports a centrosymmetric configuration, with the nitrogen atoms located in *trans* positions. Taken together with the heavy atom positions implied by the X-ray data on **4**, we conclude that the gross geometry of the bis(iminato) compounds is *trans*.

The uranium oxo−iminato complexes have IR absorptions at $\sim$850 cm^{-1}, in addition to those of the U−N−P and organic groups, and these are assigned to the uranium-oxygen stretch. Their frequencies are close to that of U=O stretching mode in

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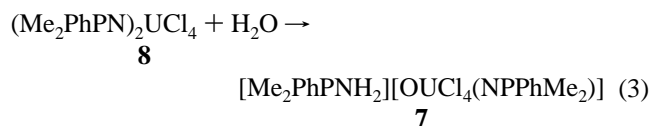
[Ph$_4$P][UOCl$_5$] (837 cm^{-1}, Raman)[11] and clearly the binding of the oxo group is similar to that in the uranyl ion.

The infrared-active antisymmetric U$-$N$-$P stretching frequencies, listed in Table 1, fall in two regions; those in the oxo$-$iminato compounds occur near 1080 cm^{-1}, and those in the bis(iminato) complexes occur at $\sim$1050 cm^{-1}. Because of its large mass, the uranium atom is effectively motionless in these vibrations, and the frequencies are indicative of the force constants within the U$-$N$-$P unit. Apparently the presence of an oxo group *trans* to the iminato group in **3**, **5**, and **7** leads to an increase in the U$-$N$-$P stretching frequencies relative to those in **4**, **6** and **8**, where a second iminato group occupies this position.

In d-block chemistry an oxo group creates a strong *trans* influence, polarizing the metal in such a way as to *weaken* the bond to the group opposite, and to reduce its vibrational frequency.[20] Phosphorane iminato groups might be expected to possess a weaker *trans* influence than the oxo group, because the M$-$N bond is considerably longer than the M$-$O bond. However, the available structural data is sparse,[21–23] and all that can be said is that the magnitudes of the *trans* influences of iminato and oxo groups are similar and substantial.[6]

Recently it has been argued that an **inverse** *trans* influence operates in actinide compounds.[1] For example, in the UOCl$_5^-$ anion[11,24] the U$-$Cl bond *trans* to the oxygen is shorter than the *cis* U$-$Cl bond, and their stretching frequencies are 345 and 302 cm^{-1} respectively; similar observations are reported for the PaOCl$_5^{2-}$ anion.[25] The effect has been attributed[1,26] to the superposition of the 5f shell and the pseudo-core 6p shell of the actinide ion, and is analogous to the d$-$s hybridization that underlies the preponderance of linearly bonded compounds of d^{10} ions. One result of this is the linearity and strength of the uranyl ion, which contrasts with transition-metal dioxo species that are found predominantly in the *cis* configuration.[40] If the same effect operates in uranium iminato complexes, the large inverse *trans*-influence of the oxo ligand should strengthen the U$-$N bond to the *trans* iminato group in compounds **3**, **5**, and **7** relative to that in compounds **4**, **6**, and **8**, where the more weakly bound *trans* phosphiniminato group would exert a smaller influence. The vibrational data provide clear support for this argument.
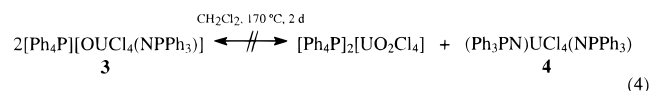
Reactivity and Mechanisms of Formation. Hydrolysis converts the bis(iminato) species first into oxo$-$iminato compounds and subsequently into uranyl compounds if sufficient water is present. The first step in this conversion was observed accidentally during an attempted recrystallization of (Me$_2$PhPN)$_2$UCl$_4$, **8** (eq 3) from inadequately dried dichlo-

$$(\text{Me}_2\text{PhPN})_2\text{UCl}_4 + \text{H}_2\text{O} \rightarrow$$
$$\textbf{8}$$

$$[\text{Me}_2\text{PhPNH}_2][\text{OUCl}_4(\text{NPPhMe}_2)] \quad (3)$$
$$\textbf{7}$$

romethane. The solubility of **8** in dichloromethane is low, *ca.* 0.05 g in 30 cm^3, and when a layer of toluene was added to

such a solution, crystallization of a red solid occurred over a period of several weeks. The product was obviously different from the starting material, but had similar elemental ratios. Further investigation identified it as [Me$_2$PhPNH$_2$][OUCl$_4$-(NPPhMe$_2$)], **7**. The infrared spectrum displayed a medium intensity U$=$O band at 856 cm^{-1}, and symmetric and antisymmetric N$-$H stretches of the cation were observed at 3341 and 3260 cm^{-1}. The crystal structure[15] is consistent with this formulation.

A variety of pathways can be postulated for the formation of the bis(iminato) complexes. To investigate one of them, a solution of pure [Ph$_4$P][OUCl$_4$(NPPh$_3$)] **3** in dichloromethane was heated (*CAUTION*! high pressure) to 170 °C for 2 days, in an attempt to force its disproportionation into a uranyl complex and the corresponding bis(iminato) species (eq 4). After

$$2[\text{Ph}_4\text{P}][\text{OUCl}_4(\text{NPPh}_3)] \xLeftrightarrow[\text{CH}_2\text{Cl}_2,\ 170\,°\text{C},\ 2\ \text{d}]{\ \ \not/\!/\ \ } [\text{Ph}_4\text{P}]_2[\text{UO}_2\text{Cl}_4] + (\text{Ph}_3\text{PN})\text{UCl}_4(\text{NPPh}_3)$$
$$\textbf{3} \hspace{6cm} \textbf{4}$$
$$(4)$$

cooling and rapid removal of the solvent, the solid was found to be identical to the starting material; no other products could be detected.

Similarly, when equimolar quantities of [Ph$_4$P]$_2$[UO$_2$Cl$_4$] and **4** were heated together in dichloromethane (195 °C, 5 h), the solid obtained after removal of the solvent exhibited an IR spectrum identical to the starting mixture. No trace of **3** could be detected, so the interconversion in eq 4 does not occur in either direction.

Formation of the oxo$-$iminato complexes **1**, from [Ph$_4$P]-[UOCl$_5$] and phosphoranimines, can be postulated to occur by one of two mechanisms. Because the equatorial coordination number of the uranyl ion can be as large as six, an associative mechanism, in which the imine nitrogen initially coordinates to the uranium to give an equatorial coordination number of 5, seems plausible (eq 5a). A coordination sphere with this form is known in UOCl$_2$·H$_2$O, which contains a linear uranyl ion with planar equatorial coordination by four chloride ions and a water molecule.[27] Furthermore, compounds with the formula MCl$_2$(Me$_3$SiNPMe$_3$)$_2$ (M = Co, Zn) have been isolated[28] in which the phosphoraniminato ligands are bound in the same manner as in the postulated intermediate. Such an intermediate could eliminate Me$_3$SiCl in a second step.

Alternatively an initial nucleophilic displacement of the phosphoraniminate anion at the silicon atom, by a coordinated chloride ion, can be postulated. This would create a reactive five-coordinate UOCl$_4$ intermediate,[29] to which the iminate anion can subsequently add, eq 5b.

$$(5a)$$

$$(5b)$$
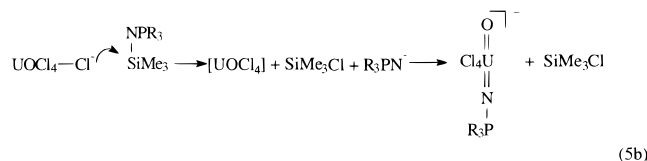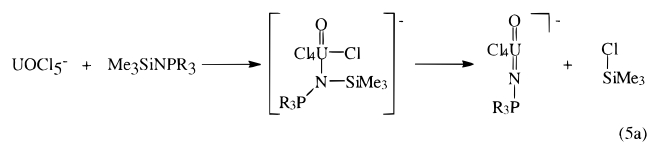
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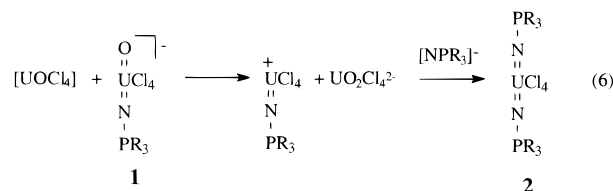(24) De Wet, J. F.; du Preez, J. G. H. *J. Chem. Soc., Dalton Trans.* **1978**, 592–597.
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The key question, however, is how the tightly bound oxo group is lost in the formation of the bis(iminato) compounds. Because **3** and **4** are not interconvertible even under forcing conditions, we assume that **4** must be formed with the aid of the other components in the initial reaction mixture, *i.e.* $[UOCl_5]^-$ as well as free phosphoranimine. If eq 5b is a good model for the initial substitution, the reactive intermediate $UOCl_4$ could also remove an oxide ion from **3** to yield $UO_2Cl_4{}^{2-}$. This is an attractive hypothesis because the latter species is the other major product isolated from the reaction, and it is not formed by the disproportionation of **3**. This mechanism is summarized in eq 6.

$$[UOCl_4]^- + \underset{\mathbf{1}}{\overset{\overset{\displaystyle O}{\overset{\|}{U}Cl_4}}{\underset{\underset{\displaystyle PR_3}{\overset{\|}{N}}}{}}} \longrightarrow \underset{\mathbf{}}{\overset{+}{\underset{\underset{\displaystyle PR_3}{\overset{\|}{N}}}{UCl_4}}} + UO_2Cl_4{}^{2-} \overset{[NPR_3]^-}{\longrightarrow} \underset{\mathbf{2}}{\overset{\overset{\displaystyle PR_3}{\overset{\|}{N}}}{\underset{\underset{\displaystyle PR_3}{\overset{\|}{N}}}{UCl_4}}} \quad (6)$$

The critical step in the formation of **2** is the abstraction of the oxo atom from **1** and we believe that this succeeds because of the intrinsic stability of the uranyl ion in the form of $UO_2Cl_4{}^{2-}$. Addition of the second phosphoraniminato group follows the deoxygenation. If this model is correct eq 5b appears to be a better representation of the initial substitution than eq 5a.

Electronic Structure and Bonding. The stability of these new compounds should be seen in the context of the properties of the uranyl ion. The $U{=}O$ bond strength in this species is significantly larger than that of most comparable transition metal$-$oxo bonds.[30] For example, the mean bond enthalpies (kJ mol^{-1}) for dissociation to neutral oxygen atoms, in some gaseous dioxo species are as follows: UO_2, 712 ± 15;[30] MoO_2, 578; WO_2, 635; RuO_2, 509; OsO_2, 770.[31] The equivalent quantity for $UO_2{}^+(g)$ has been estimated[32] to be 785 kJ mol^{-1}, while a calculation of the lattice enthalpy of UO_2F_2,[33] together with a theoretical value for the second ionization energy of uranium,[34] gives a $UO_2{}^{2+}(g)$ value of 701 ± 50 kJ mol^{-1}.[30] Clearly the mean U$-$O bond strength approaches that of C$-$O in carbon dioxide[31] (802 kJ mol^{-1}), and indeed gaseous UN^+ reacts exothermically with CO_2 to give the UON^+ ion.[9] The uranyl ion is also so inert that the rate of exchange between the oxo atoms and water occurs with a half-life approaching 40 000 h at room temperature.[35]

The electronic structure and bonding of actinyl ions has been reviewed recently,[1] and it is evident that the presence on uranium of both f and d valence orbitals leads to unusually favourable interactions with oxygen p orbitals, and an effective bond order of three for the U$-$O bond in the uranyl ion. An oxo group is isoelectronic with imido (R$-$N$=$) or iminato (R$_3$P$-$N$=$) groups with respect to their donor ability, and so

the dioxo cation is a good reference point. In comparing $UO_2{}^{2+}$ with the $[UONPR_3]^{3+}$ unit in the oxo$-$iminato compounds, it is helpful to consider the results of some quasi-relativistic density functional theory calculations on $UO_2{}^{2+}$ and the isoelectronic ion UON^+ due to Heinemann and Schwarz.[9] The replacement of an oxide ion in the former by a nitride ion in the latter has the effect of narrowing the HOMO$-$LUMO gap from 2.4 to 1.1 eV. In UON^+ the LUMO is a nonbonding uranium f orbital, and the HOMO has s symmetry with the composition 35% N, $2p_z$; 1% O, $2p_z$; and 41% U, $5f_{z^3}$. The reduction of the gap and the strong bias of the HOMO toward the nitrogen atom can be understood in terms of a notional removal of a positive charge from one of the oxygen nuclei in $UO_2{}^{2+}$ to create a nitrogen atom. The reduced nuclear charge lowers the binding energy of the valence electrons on the nitrogen atom relative to those on oxygen, so that the bond to the nitrogen atom is weakened and the system becomes more susceptible to an internal charge transfer in which the uranium is reduced at the expense of the nitrogen ligand. Such a reduction occurs, for example, when phosphines are added to transition metal nitrides to give phosphorane iminato complexes.[6]

In agreement with their calculations, Heinemann and Schwarz report experimental bond dissociation enthalpies of 429 ± 122 and 739 ± 164 kJ mol^{-1} for the U$-$N and U$-$O bonds of UON^+ respectively.[9] In $[UONPR_3]^{3+}$ the energy of the HOMO should be lower in energy than that in UON^+ because a nitrogen-centered σ-lone pair now forms part of the valence shell of the phosphorus atom; nevertheless the basis of the weakness of the U$-$N bond relative to the U$-$O bond is clear. The reduction in the HOMO$-$LUMO gap associated with the iminato group, compared to the dioxo cation is consistent with the red color of the phosphoraniminato compounds. The nature of the first electronic excited states of the uranyl ion are well-understood and correspond to parity forbidden charge-transfer transitions from an oxygen-centered HOMO to a uranium-centered LUMO.[1] Thus the reduced gap in the UON^+ unit should lead to a red shift in these transitions. The electronic absorption of the iminato complexes is broad and unstructured. The low energy threshold occurs near 750 nm for **6** and 560 nm for **5**, compared to less than 500 nm in yellow uranyl compounds,[1] as would be predicted by this model.

Although the U$-$O bond distance[2] in **5** [175.9(13) pm] is typical of uranyl compounds, the U$-$N distance [190.1(14) pm] is significantly shorter than those of most other uranium iminato and imido compounds,[2] implying that there is significant mutual cooperation in bonding between the *trans* components. Moreover the chemical stability of both series of compounds **1** and **2** in solution in polar solvents at 200 °C resembles that of uranyl compounds more closely than do the strongly-oxidizing and reactive properties associated with other uranium(VI) compounds, such as UF_6, UCl_6, and, to a lesser extent, $[Ph_4P]$-$[UOCl_5]$.

Redox Stability. We have been able to prepare compounds of general formula **1** or **2** that include the following residues: Ph_3P, 3-Tol_3P, Me_2PhP, $MePh_2P$, i-$PrPh_2P$. It seems that stable products are only obtained if there is at least one aromatic substituent on the phosphorus atom. Although our study cannot claim to be comprehensive, reactions of tri*alkyl*phosphoranimines with $[Ph_4P][UOCl_5]$ led only to reduction products. For example, addition of n-$Bu_3PNSiMe_3$ to a stirred suspension of $[Ph_4P][UOCl_5]$ in MeCN or CH_2Cl_2 resulted in the immediate precipitation of the pale green uranium(IV) compound $[Ph_4P]_2$-$[UCl_6]$, which was identified by its elemental analysis and infrared spectrum. The analogous reaction with $Cy_3PNSiMe_3$ (Cy = cyclohexyl) was very slow at room temperature, but on

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heating brown solutions were formed from which no iminato compounds could be isolated.

Thus, although the steric bulk associated with cyclopentadienyl and trimethylsilylamido ligands found in previous examples of uranium imides is not a prerequisite for stability, the resistance of the ligands to oxidation seems to be vital. This can be emphasized by comparison with transition metal analogues. The greater redox stability of W(VI) compared to U(VI), can be seen from the fact that WCl_6 boils without decomposition at 346 °C,[36] while UCl_6 partially decomposes to lower halides during sublimation near 100 °C.[37] Indeed at 300 K the free energy of the reaction $UCl_4(s) + Cl_2(g) \rightarrow UCl_6$-(s) is reported to be only -2.3 kJ mol^{-1}.[38] The phosphoraniminato group can be written as $R_3P^+-N^{2-}$, and so can be notionally derived from the isoelectronic imido group R_3C-N^{2-} by introducing an extra nuclear charge at the α-carbon atom. It is this increase in positive charge that provides the superior stability of the iminato ligands to oxidation in relation to imido ligands.

Even so it appears from our results that electron-withdrawal by at least one aromatic group in the phosphorane is required to prevent the reduction of the uranium by the ligand. Therefore, despite the stability of nitrido and imido ligands in tungsten (VI) species such as $[Cl_5WN-i-Pr]^-$,[39] attempts to prepare their counterparts using the more oxidizing uranium (VI) are likely to lead to the reduction of the uranium. Clearly other strongly covalent ligands, such as the cyclopentadienyl groups in $(CpMe_5)_2U(NPh)_2$,[4] should be bound to the uranium atom if its charge is to be reduced sufficiently to overcome this source of instability.

Experimental Section

General Data. All reactions were performed under an inert atmosphere. Involatile solids were generally handled in a nitrogen-purged glovebox, while all other operations were performed using Schlenk techniques. IR spectra were recorded between 400 and 4000 cm^{-1} on a Mattson Galaxy 6020 Fourier transform infrared spectrometer. Samples were dispersed in a dry potassium bromide matrix prepared under nitrogen and mounted in a cell equipped with cesium iodide windows. Raman spectra were measured on a Perkin-Elmer 2000 Fourier transform Raman/infrared instrument, equipped with an InGeAs detector. The source was a 100 mW, 1064 nm Nd:YAG laser and the spectral resolution was 4 cm^{-1}. **5** did not fluoresce when excited at 1064 nm, but **6** was found to fluoresce weakly. Fluorescence prevented any measurements under 647 nm laser excitation.

X-ray Crystallography. Crystals of **4** (with dimensions ~0.1 × 0.1 × 0.005 mm) were mounted on an Enraf Nonius CAD4 diffractometer. Data were collected with the following parameters: $\lambda = 0.701\,69$ Å, μ(Mo Kα) = 29.41 cm^{-1}, room temperature, and θ range $1-16°$ yielding a total of 350 unique reflections, although intensity checks decreased by 75% over 12 h. The data were of insufficient quality to present a completed structure. No improvements were obtained on cooling the samples or by the use of plate-detection systems. Crystal data: $C_{36}H_{30}Cl_4N_2P_2U$, $M = 931.8$, space group $P2_1/a$ (nonstandard setting), $a = 12.187$ Å, $b = 15.143$ Å, $c = 10.176$ Å, $\beta = 97.32°$, $V = 1862.7$ Å^3, $Z = 2$, $D_c = 1.64$ g cm^{-3}. The heavy atoms (U, Cl, P) were located with Patterson methods; their arrangement showed clearly a square-planar array of four chlorine atoms at a distance of *ca.* 2.6 Å, and two phosphorus atoms at *ca.* 3.5 Å in a *trans*

configuration and about 2° away from the axial direction. Location of lighter atoms and further refinement were unsuccessful. Direct methods yielded no additional structural information.

Reagents. Dichloromethane was refluxed over phosphorus pentoxide for several hours, distilled, and stored over molecular sieves (type 4A). Acetonitrile was refluxed over phosphorus pentoxide for several hours and distilled onto fresh P_2O_5, the last quarter fraction being discarded, and the process was repeated three times prior to storage over molecular sieves. Toluene was refluxed over sodium metal, and distilled onto molecular sieves. Phosphines were obtained from Aldrich Chemical Co.; the solids were melted under vacuum prior to use. Trimethylsilyl azide was obtained from Lancaster Synthesis and used as supplied.

[Ph$_4$P][UOCl$_5$] was prepared by the method of Bagnall *et al.*,[11] but the solid produced in this way contained occluded thionyl chloride. This interfered with subsequent reactions, but could be removed by heating the solid to 120 °C at 10^{-3} torr until evolution of the gas had ceased. The solid may be recrystallized from dichloromethane, in which it is very soluble at elevated temperatures (~120 °C). *Caution*! High pressure. Uranium hexachloride was prepared according to the published procedure.[37]

Phosphorane imines were generally prepared by the method of Staudinger.[41] Triaryl-, trialkyl-, or mixed aryl/alkylphosphines were heated for several hours with a small mole ratio excess of trimethylsilyl azide in a sealed vessel, after which all volatiles were removed and the product purified by distillation or sublimation. In each case we list the reaction temperature (°C), its duration (hours), the physical state at room temperature, and the temperature (°C) and pressure (Torr) of sublimation or distillation: Ph$_3$PNSiMe$_3$, 150, 5, s, 170, 0.04;[42,43] 3-Tol$_3$-PNSiMe$_3$, 150, 5, s, 120, 0.02; Me$_2$PhPNSiMe$_3$, 110, 3, l, 52−54, 0.01;[44] MePh$_2$PNSiMe$_3$, 140, 5, l, 105−106, 0.02; *n*-Bu$_3$PNSiMe$_3$, 110, 3, l, 85−86, 0.01;[12] *i*-PrPh$_2$PNSiMe$_3$, 160, 8, s, 125, 0.01; Cy$_3$PNSiMe$_3$, 150, 8, s, 120, 0.01. 2-Tol$_3$P did not react with trimethylsilyl azide below 200 °C. All the imines were characterized by elemental analysis and infrared spectroscopy. Analyses for new imines: Calcd for *i*-PrPh$_2$-PNSiMe$_3$, C$_{18}$H$_{28}$NPSi: C, 68.14; H, 8.33; N, 4.42. Found: C, 68.36; H, 8.35; N, 4.42. Calcd for Cy$_3$PNSiMe$_3$, C$_{21}$H$_{42}$NPSi: C, 68.66; H, 11.44; N, 3.81. Found: C, 68.67; H, 12.31; N, 4.70. Calcd for 3-Tol$_3$-PNSiMe$_3$, C$_{24}$H$_{30}$NPSi: C, 73.66; H, 7.67; N, 3.58. Found: C, 74.03; H, 7.52; N, 4.71. Calcd for MePh$_2$PNSiMe$_3$, C$_{16}$H$_{22}$NPSi: C, 66.90; H, 7.67; N, 4.88. Found: C, 66.48; H, 6.74; N, 4.57.

Syntheses. (Ph$_3$PN)$_2$UCl$_4$, 4. [Ph$_4$P][UOCl$_5$] (1.5 g, 1.95 mmol) and Ph$_3$PNSiMe$_3$ (0.68 g, 1.95 mmol) were loaded into a flamed-out Schlenk tube inside a nitrogen-purged glovebox. A 30 cm^3 aliquot of dry acetonitrile was transferred onto the mixture, which was heated gradually to 90 °C while stirring. The red solid dissolved giving a dark red solution which was cooled to room temperature and allowed to stand for 1 day, when a fine deposit of red microcrystalline product was formed. This was washed with acetonitrile and dried under vacuum. Yields were about 20%. Anal. Calcd for C$_{36}$H$_{30}$N$_2$P$_2$Cl$_4$U: C, 46.35; H, 3.22; N, 3.00; P, 6.65; Cl, 15.21; U, 25.21. Found: C, 47.04; H, 3.34; N, 3.27; P, 6.50; Cl, 15.18; U, 25.36. At room temperature the red starting material reacts over several hours, during which time the product begins to deposit. The precipitation is complete in ~12 h. Dichloromethane can also be used as the solvent.

Crystals of **4** were grown by scaling up the above preparation 4-fold. Samples of the resulting solution were then removed periodically (every 24 h), filtered, and transferred into Schlenk tubes that had been previously silylated with Me$_2$SiCl$_2$. The solution remains supersaturated for several days and crystallization is very slow; early samples deposit large amounts of powdered solid. Those that are removed later deposit smaller amounts more slowly, and so on, until the crystal quality of the product is good. At this stage there is very little product left in solution, and the crystals formed are very small. A similar method

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can be used with $(Tol_3PN)_2UCl_4$. Crystals produced in this way had dimensions of about $0.1 \times 0.1 \times 0.005$ mm.

Preparation of $[Ph_4P][OUCl_4(NPPh_3)]$, 3. $[Ph_4P][UOCl_5]$ (0.5 g, 0.65 mmol), $Ph_3PNSiMe_3$ (0.23 g, 0.66 mmol) and CH_2Cl_2 (30 cm^3) were loaded into a glass vessel guarded by a Young's greaseless valve, and heated to 100 °C. The solids dissolved, forming a clear dark red solution. After cooling, the solution was filtered, and an equal volume of dry toluene added carefully so as to form a layer above the CH_2Cl_2. After several weeks small red crystals had formed and were washed with a dry dichloromethane/toluene mixture. $[Ph_4P]_2[UO_2Cl_4]$ is also produced during the reaction; if crystallization occurs it may normally be removed by hand. Yield: ~20%. Anal. Calcd for $C_{42}H_{35}NOP_2Cl_4U$: C, 49.55; H, 3.46; N, 1.38, P, 6.13; U, 23.54. Found: C, 49.75; H, 3.38; N, 1.21; P, 6.06; U, 23.58.

Preparation of $[Ph_4P][OUCl_4NPTol_3]$, 5. $[Ph_4P][UOCl_5]$ (1.39 g, 1.8 mmol) and 3-$Tol_3PNSiMe_3$ (0.78 g, 2.00 mmol) were allowed to react in dry CH_2Cl_2 (30 cm^3) at room temperature for 5 h, forming a clear red solution. Onto this was added an equal volume of dry toluene. After interdiffusion for several weeks, well-formed needles of **5** were isolated in *ca.* 30% yield. Large clusters of $[Ph_4P]_2[UO_2Cl_4]$ crystals were codeposited, but were easily removed by hand. Anal. Calcd for $C_{42}H_{35}NOP_2Cl_4U$: C, 51.28; H, 3.89; N, 1.33. Found: C, 50.49; H, 4.39; N, 1.45.

Preparation of $(Me_2PhPN)_2UCl_4$, 8. $[Ph_4P][UOCl_5]$ (1.5 g, 2 mmol) and $Me_2PhPNSiMe_3$ (0.6 g, 2.7 mmol) were stirred together in CH_2Cl_2 (30 cm^3) at room temperature for 1 h, after which all of the solid had dissolved leaving an orange solution. After filtering, the solution was left undisturbed, and was observed to darken considerably in color. Over a period of 1 day, the red microcrystalline product was deposited and was washed carefully with a small volume of dry CH_2Cl_2. Yield: ~15%. Typically, yellow $[Ph_4P]_2[UO_2Cl_4]$ also crystallized, and was removed by hand. Anal. Calcd for $C_{16}H_{22}N_2P_2Cl_4U$: C, 28.09; H, 3.24; N, 4.09, P, 9.05; Cl, 20.73; U, 34.79. Found: C, 29.01; H, 3.24; N, 3.81; P, 8.31; Cl, 20.12; U, 33.80.

Preparation of $(Tol_3PN)_2UCl_4$, 6. $[Ph_4P][UOCl_5]$ (0.53 g, 0.69 mmol) and 3-$Tol_3PNSiMe_3$ (0.32 g, 0.82 mmol) were reacted together in MeCN (12 cm^3) at 90 °C for 1 h, yielding a dark red solution. This was cooled, filtered, and left to stand. The product was deposited as a dark orange powder, and was washed with MeCN and dried under vacuum. Yields were typically 20%. As in the case of **4** it was necessary to separate the product by hand selection. Anal. Calcd for $C_{42}H_{42}N_2P_2Cl_4U$: C, 49.61; H, 4.13; N, 2,76; P, 6.10; U, 23.43. Found: C, 49.31; H, 3.39; N, 3.57; P, 5.03; U, 23.54.

Reaction of $[Ph_4P][UOCl_5]$ with n-$Bu_3PNSiMe_3$. MeCN (15 cm^3) was transferred to a glass vessel containing $[Ph_4P][UOCl_5]$ (1.00 g, 1.30 mmol) and n-$Bu_3PNSiMe_3$ (0.47 g, 1.63 mmol). Reduction occurred immediately, and large amounts of pale green solid were produced, shown by analysis and infrared spectroscopy to be $[Ph_4P]_2[UCl_6]$. No red coloration was observed, and no iminato compounds could be detected.

Reaction of $[Ph_4P][UOCl_5]$ with $Cy_3PNSiMe_3$. Addition of MeCN (12 cm^3) to a mixture of $[Ph_4P][UOCl_5]$ (0.75 g, 0.97 mmol) and $Cy_3PNSiMe_3$ (0.38 g, 1.04 mmol, Cy = cyclohexyl) resulted in no reaction at room temperature. When the mixture was heated, the $[Ph_4P][UOCl_5]$ dissolved but the resultant solution was brown and failed to yield any isolable products.

Reaction of $[Ph_4P][UOCl_5]$ with $Ph_2MePNSiMe_3$ or i-$PrPh_2PNSiMe_3$. $[Ph_4P][UOCl_5]$ (0.5 g, 0.65 mmol) and $Ph_2MePNSiMe_3$ (0.20 g, 0.70 mmol) were mixed in MeCN (12 cm^3) or CH_2Cl_2 (12 cm^3). In both solvents dark red solutions were produced suggesting the presence of uranium phosphoraniminato complexes; the products were, however, exceedingly soluble and could not be isolated pure. In another reaction, $[Ph_4P][UOCl_5]$ (0.5 g, 0.65 mmol) and i-$PrPh_2PNSiMe_3$ (0.21 g, 0.67 mmol) were heated in MeCN (12 cm^3) yielding a dark red solution, but for similar reasons no iminato compounds could be isolated.

Reaction of UCl_6 with $Ph_3PNSiMe_3$. Uranium hexachloride (0.20 g, 0.44 mmol) and $Ph_3PNSiMe_3$ (0.33 g, 0.95 mmol) were loaded into a glass vessel and cooled to −78 °C. CH_2Cl_2 (4 cm^3) was slowly transferred onto the stirred mixture, which was held at this temperature. When the mixture was allowed to stand, a volume of olive green solid UCl_4 was precipitated below a brown solution. No $(Ph_3PN)_2UCl_4$ could be detected.

Reaction between $[Ph_4P]_2[UO_2Cl_4]$ and $(Ph_3PN)_2UCl_4$. $[Ph_4P]_2[UO_2Cl_4]$ (0.16 g, 0.15 mmol) and $(Ph_3PN)_2UCl_4$ (0.14 g, 0.15 mmol) were loaded into a glass vessel, and 20 cm^3 of CH_2Cl_2 was added. The mixture was heated to 195 °C for 5 h, during which time the solids dissolved. When the solution was cooled to room temperature, a red solid was precipitated and its infrared spectrum was identical with that of $(Ph_3PN)_2UCl_4$.

Attempted Disproportionation of 3. A sample of $[Ph_4P][OUCl_4(NPPh_3)]$ was dissolved in CH_2Cl_2 and heated to 170 °C for 2 days, during which time no visible change was observed; after removal of the solvent the IR spectrum of the solid was found to be unchanged.

Preparation of $[Me_2PhPNH_2][OUCl_4(NPMe_2Ph)]$, 7. 50 cm^3 of toluene was carefully added to form a layer above a saturated solution of $(Me_2PhPN)_2UCl_4$ **8** (~0.05 g) in CH_2Cl_2 (50 cm^3), and allowed to stand for 2 months. The product was formed as thin flat red platelets and identified by its elemental analysis, infrared spectrum (NH_2 group, 3341 and 3260 cm^{-1}; N−P, 1058 cm^{-1}; U=O, 856 cm^{-1}) and X-ray structural data.[15] Anal. Calcd for $C_{16}H_{24}N_2OP_2Cl_4U$: C, 27.37; H, 3.45; N, 3.99. Found: C, 28.01.01; H, 3.36; N, 4.17.