= Ce, Zr, Hf, U)[19] and Ti$_2$Cl$_2$(OR)$_2$(HOR)$_2$ (R = CH$_2$CH$_2$Cl).[12] We also note that the longer U(1)–U(1) distance of 3.807 (1) Å and the U(1)–O(4)–U(1') angle of 112.4° are indicative of a net repulsive interaction of the two f^2 uranium atoms.

The iodine oxidation of uranium in 2-propanol has resulted in the synthesis and structural characterization of a new uranium–iodo–alkoxide dimer. We are currently investigating the extension of this chemistry to other actinide metals, to other alcohols, and to other oxidants.

Supplementary Material Available: Tables of crystal data, atomic positional parameters, anisotropic thermal parameters, and selected bond lengths and angles for **1** (6 pages). Ordering information is given on any current masthead page.

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Electronic Absorption and Resonance Raman Spectra of [Re(CO)₃(pTol-DAB)X] (DAB = 1,4-Diaza-1,3-butadiene; X = Halide). Evidence for a Lowest Ligand to Ligand Charge-Transfer (LLCT) Transition

Although low-lying ligand to ligand charge-transfer (LLCT) transitions have been reported for many compounds containing both an oxidizing and reducing ligand, such transitions have only been observed for a few halide complexes[1] and not, e.g., for [Re(CO)$_3$(bpy)Br], which is an efficient photosensitizer for energy- and electron-transfer processes. On the contrary, the lowest excited state of this complex has MLCT character.[2] This is rather surprising in view of the fact that MO calculations performed on complexes such as [Mn(CO)$_5$I][3] and [Re(CO)$_3$(H$_2$DTO)Br] (DTO = dithiooxamide)[4] have shown that their HOMO's have predominant halide character. Moreover, the preliminary results of our LCAO–Xα calculations on [Mn(CO)$_3$(bpy)X] (X = Cl, Br, I) show that also in this case the HOMO is mainly halide in character (85% X, 10% Mn for X = I; 60% X, 25% Mn for X = Cl).[5] The LUMO of these complexes is the lowest π* orbital of bpy. In the latter case the lowest excited state is therefore most likely a LLCT state.

This tentative conclusion is supported by our recent findings that these complexes produce the dimer [Mn$_2$(CO)$_6$(bpy)$_2$] via the radicals Mn(CO)$_3$(bpy), upon irradiation into their visible absorption band.[6] LLCT excitation of [Mn(CO)$_3$(bpy)X] is then
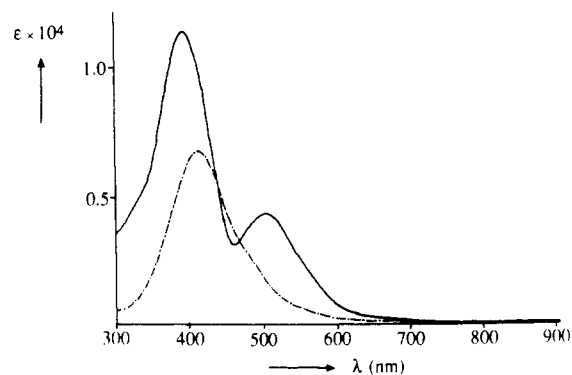
Figure 1. UV–vis spectra in CH$_2$Cl$_2$ of [Re(CO)$_3$(pTol-DAB)Br] (—) and [Re(CO)$_3$(pTol-DAB)]OTf (- - - -).
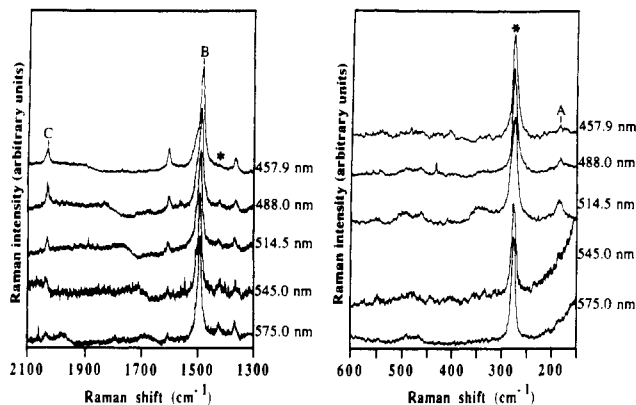
Figure 2. Resonance Raman spectra (λ$_{exc}$ = 457.9–575.0 nm) of [Re(CO)$_3$(pTol-DAB)Br] in CH$_2$Cl$_2$ in the wavenumber regions 150–600 cm^{-1} (right) and 1300–2100 cm^{-1} (left). A = ν(Re–Br), B = ν$_s$(CN), C = ν$_s$(CO), and an asterisk = solvent band.

responsible for the formation of Mn(CO)$_3$(bpy) and X radicals. The fate of the X radicals is not yet clear. The corresponding complex [Mn(CO)$_3$(bpy)]OTf (OTf⁻ = trifluoromethanesulfonate) gave only rise to photodecomposition.

Further information about the character of the lowest-energy transitions of these complexes might in principle be obtained from their resonance Raman (rR) spectra. Unfortunately, the Mn complexes are too photolabile and rapidly decompose in the laser beam. We therefore focused on the photostable Re complexes since the characters of their lowest-energy electronic transitions are not expected to differ much from those of the Mn complexes. Attempts to record high-quality rR spectra of [Re(CO)$_3$(bpy)Br] failed due to the disturbing luminescence of this complex. We therefore replaced the bpy ligand by pTol-DAB (=p-tolyl-1,4-diaza-1,3-butadiene; MeC$_6$H$_4$N=CH—CH=NC$_6$H$_4$Me) since the [Re(CO)$_3$(pTol-DAB)Br] complex is not emissive at room temperature.

Its absorption spectrum in CH$_2$Cl$_2$ is shown in Figure 1. For comparison the figure also depicts the spectrum of the [Re-(CO)$_3$(pTol-DAB)]OTf complex. There is a clear difference between both spectra. The halide complex has two bands, at 505 and 400 nm, respectively; the spectrum of the OTf⁻ compound only shows the second band. On the basis of these observations,

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(6) [Mn(CO)$_3$(bpy)X] (X = Cl, Br, I), dissolved in toluene or THF, was irradiated with 514.5-nm light into its visible absorption band (λ$_{max}$ = 425 nm (ε = 2470 mol^{-1} L cm^{-1}) for X = Br in THF). The formation of Mn$_2$(CO)$_6$(bpy)$_2$ was evident from the appearance of its characteristic absorption band (λ$_{max}$ = 840 nm in THF) and IR CO bands (1980, 1963, 1936, 1886 and 1866 cm^{-1} in THF).[7] The Mn(CO)$_3$(bpy) radicals were trapped by tBu–NO giving rise to the characteristic ESR spectrum of the adduct.[8] A detailed report of these experiments will be published elsewhere.
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the low-energy band of the Br complex is assigned to the Br → pTol-DAB (LLCT) transition. This assignment is further supported by the observation of a similar weak band at 500 nm in the spectrum of the Cl-complex.

In order to prove the origin of the two absorption bands we have recorded the rR spectra of [Re(CO)₃(pTol-DAB)Br] with exciting laser lines varying from 575 to 457.9 nm. Two important regions of these spectra, 150–600 and 1300–2100 cm⁻¹, are shown in Figure 2. The low-frequency region shows an intensity increase for a band at 190 cm⁻¹ upon going from 575- to 514.5-nm excitation. This band is assigned to ν(Re–Br) since it shifts to 290 cm⁻¹ when the Br⁻ ion is replaced by Cl⁻.[9] Its intensity decreases upon going to still shorter-wavelength excitation. The high-frequency region shows an increasing rR effect for a band at 1495 cm⁻¹ belonging to ν_s(CN) of the pTol-DAB ligand when the exciting wavelength is varied from 575 to 457.9 nm.

Finally, the spectra excited with wavelengths shorter than 545 nm show an increasing rR effect for a symmetrical CO-stretching vibration at 2035 cm⁻¹ upon going to shorter-wavelength excitation.

These results clearly show that excitation into the lowest-energy band influences both the pTol-DAB and Re–Br bonds which confirms the assignment of this band to a Br → pTol-DAB(LLCT) transition. The increasing rR effect for ν_s(CO) and the disappearance of the band belonging to ν(Re–Br) upon shorter-wavelength excitation is in accordance with the assignment of the second band to one or more MLCT transitions since the electron transfer from a metal-d_π orbital to the ligand will weaken the metal to CO π-back-bonding.[10] Both the MLCT and LLCT transitions will of course strongly influence the CN bonds of the pTol-DAB ligand (the π^*-orbital is antibonding between C and N), which explains the strong rR effect for ν_s(CN) in all Raman spectra.

Apparently, the character of the lowest excited state of these [Re(CO)₃(α-diimine)X] complexes strongly depends on the α-diimine ligand used. For complexes containing an innocent ligand such as bpy, the lowest excited state has MLCT character.[2] If bpy is, however, replaced by an α-diimine ligand such as pTol-DAB having a strong π-back-bonding interaction with the metal, the Re(d_π) orbitals decrease in energy with respect to the X(p_π) ones. As a result the LLCT transition, absorbing at higher energy than the MLCT transitions in the case of [Re(CO)₃(bpy)X], appears as a separate band at the low-energy side of the MLCT band for [Re(CO)₃(pTol-DAB)X].

Contrary to [Mn(CO)₃(bpy)X], the [Re(CO)₃(pTol-DAB)X] complexes are very photostable, which means that the metal–halide bond strength in the LLCT state strongly depends on the metal. This difference in behavior between the Mn and Re complexes as well as the other excited-state properties of these α-diimine compounds and of related ones such as [Ru(CO)₂(CH₃)(α-diimine)X] are the subject of a detailed investigation.

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Tris(phenylimido) Complexes of Niobium and Tantalum: Preparation and Properties of the d⁰ [M(=NR)₃]⁻ (M = Nb, Ta) Functional Group

Organoimido ligands[1] (M=NR or M≡NR) are implicated in various catalytic processes,[2] may function as [NR] transfer intermediates,[3] and constitute invaluable ancillary groups in olefin and acetylene metathesis.[4] Achieving reactive early transition metal imido moieties may require destabilizing the strong metal–ligand d{π} ← p{π} interactions,[5] for example by "π-loading"[6] single metal sites with multiple imido ligands. Established imido functional groups of d⁰ niobium and tantalum include M=NR[7] and M(=NR)₂.[8] We now report the preparation of the d⁰ [M(=NR)₃]⁻ (M = Nb, Ta) functional group and present evidence for its formation via an intermolecular pathway.

Upon reaction of [Nb(NEt₂)₂Cl₃]₂[9] with 2 equiv of LiNHmes per niobium in THF (mes = 2,4,6-C₆H₂Me₃), orange Nb(=Nmes)₂Cl(py)₂ (1) can be obtained in 75% yield after addition of pyridine.[10] NMR data for 1 suggest a TBP structure analogous to Ta(=NAr)₂Cl(py)₂ (Ar = 2,6-C₆H₃ⁱPr₂), i.e. with equatorial imido and chloride ligands and axial pyridines.[7a] Upon reaction of [Nb(NEt₂)₂Cl₃]₂ with 4 equiv of LiNHmes per niobium (in THF) a mixture of products is obtained; however, using an excess (≥6 equiv) of LiNHmes affords yellow, crystalline compound 2 in high yield. Spectroscopic and analytical data support the formulation of 2 as the tris(imido) complex [Li(THF)₂]₂[Nb(=Nmes)₃(NHmes)]. The analogous complex of tantalum, pale yellow [Li(THF)₂]₂[Ta(=Nmes)₃(NHmes)] (3), is prepared from [Ta(NEt₂)₂Cl₃]₂[8a] by a parallel procedure. Solid samples of 2 appear to slowly lose THF, but the reaction of 2 with pyridine affords less labile [Li(py)₂]₂[Nb(=Nmes)₃(NHmes)] (4).

The formation of the bis(imide) Nb(=Nmes)₂Cl(py)₂ most likely involves a two-step, *intra*molecular α-H abstraction sequence as proposed in the formation of Ta(=NAr)₂Cl(py)₂ from Ta(NEt₂)₂Cl₃(OEt₂)[8a] and consistent with the *coordinated*, "sacrificial" amido ligands in the starting material. However, the tris(imido) functional group [Nb(=NR)₃]⁻ could arise through either (i) an *inter*molecular deprotonation of incipient "Nb(=Nmes)₂(NHmes)Lₙ" or "[Nb(=Nmes)₂(NHmes)₂]⁻" or (ii) an *intra*molecular α-H abstraction in the latter complex with loss of H₂Nmes (Scheme I). The following experiments were performed: (i) When the reaction of [Nb(NEt₂)₂Cl₃]₂ with excess

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