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$_\pi$ 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$_\pi$) orbitals decrease in energy with respect to the X(p$_\pi$) 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)$_2$(CH$_3$)(α-diimine)X] are the subject of a detailed investigation.

Acknowledgment. The Netherlands Foundation for Chemical Research (SON) and the Netherlands Organization for Pure Research (NWO) are thanked for financial support.

Registry No. [Mn(CO)$_3$(bpy)Cl], 108267-31-8; [Mn(CO)$_3$(bpy)Br], 38173-71-6; [Mn(CO)$_3$(bpy)I], 54348-82-2; [Mn$_2$(CO)$_6$(bpy)$_2$], 128927-36-6; [Re(CO)$_3$(pTol-DAB)Br], 139495-10-6; [Re(CO)$_3$(pTol-DAB)OTf], 139495-11-7.

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Received November 21, 1991

Tris(phenylimido) Complexes of Niobium and Tantalum: Preparation and Properties of the d^0 [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 d^0 niobium and tantalum include M=NR[7] and M(=NR)$_2$.[8] We now report the preparation of the d^0 [M(=NR)$_3$]$^-$ (M = Nb, Ta) functional group and present evidence for its formation via an intermolecular pathway.

Upon reaction of [Nb(NEt$_2$)$_2$Cl$_3$]$_2$[9] with 2 equiv of LiNHmes per niobium in THF (mes = 2,4,6-C$_6$H$_2$Me$_3$), orange Nb(=Nmes)$_2$Cl(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)$_2$Cl(py)$_2$ (Ar = 2,6-C$_6$H$_3{}^i$Pr$_2$), i.e. with equatorial imido and chloride ligands and axial pyridines.[7a] Upon reaction of [Nb(NEt$_2$)$_2$Cl$_3$]$_2$ 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(NEt$_2$)$_2$Cl$_3$]$_2$[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)$_2$Cl(py)$_2$ most likely involves a two-step, *intra*molecular α-H abstraction sequence as proposed in the formation of Ta(=NAr)$_2$Cl(py)$_2$ from Ta(NEt$_2$)$_2$Cl$_3$(OEt$_2$)[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)L$_n$" or "[Nb(=Nmes)$_2$(NHmes)$_2$]$^-$" or (ii) an *intra*molecular α-H abstraction in the latter complex with loss of H$_2$Nmes (Scheme I). The following experiments were performed: (i) When the reaction of [Nb(NEt$_2$)$_2$Cl$_3$]$_2$ with excess

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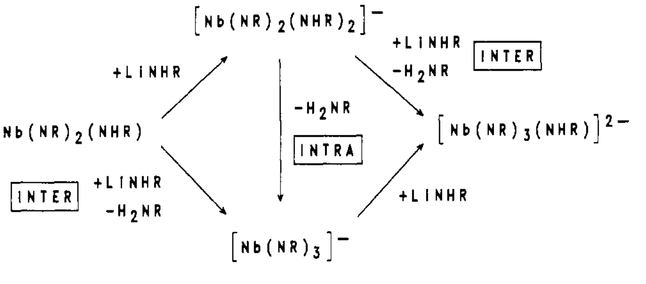
(10) Analytical and spectroscopic data for compounds **1**–**7** are available as supplementary material.

0020-1669/92/1331-1319$03.00/0

Scheme I



LiNHmes in THF-d_8 is monitored (over 29 h), 2 equiv of $HNEt_2$ and ca. 1 equiv of H_2Nmes are produced/equiv of niobium consumed (^1H NMR). (ii) Yellow crystals of $[Li(THF)_4][Nb({=}NAr)_2(NHAr)_2]$ (**5**) are formed when the more crowded imido complex $Nb({=}NAr)_2Cl(py)_2$[7a] is reacted with 2 equiv of LiNHAr (in toluene/THF). Heating a toluene-d_8 solution of **5** in the presence of PMe_2Ph (90 °C) or heating a pyridine-d_5 solution of **5** (90 °C) for hours does not induce the elimination of H_2NAr (^1H NMR).[11] (iii) Compound **5** however can be deprotonated with ^tBuLi (in THF) to afford the tris(imido) complex $[Li(THF)_2]_2[Nb({=}NAr)_3(NHAr)]$ (**6**). These experiments are *most* consistent with the $[Nb({=}NR)_3]^-$ functional group having arisen via an *inter*molecular deprotonation of $[Nb({=}NR)_2(NHR)_2]^-$ (Scheme I).

Tris(imido) complexes like $[Nb({=}Nmes)_3(NHmes)]^{2-}$ seem ideally suited as precursors to the tetrakis(imido) metalates $[Nb({=}NR)_4]^{3-}$. However, the reaction of $[Li(THF)_2]_2[Nb({=}Nmes)_3(NHmes)]$ (**2**) with 1 equiv of ^nBuLi (initiated at −40 °C, room temperature for 24 h, Et_2O/THF) afforded pale yellow crystals whose spectroscopic and analytical data support the formulation $[Li(THF)_2]_2[Nb({=}Nmes)_3(^nBu)]$ (**7**). White crystals of LiNHmes are also isolated (in ca. 50% yield); thus, ^nBuLi functions as a nucleophile rather than a base in this reaction. A rather imprecise structure of $[Li(THF)_2]_2[Nb({=}Nmes)_3(^nBu)]$ (**7**) was obtained by X-ray crystallography;[12,13] however, the general features of the tris(imido) moiety and associated $[Li(THF)_2]^+$ ions are clear. The tetrahedral coordination at niobium includes a disordered ^nBu group. Imido nitrogens N(2) and N(3) are coordinated by a lithium,[14] which results in Nb–N–C_{ipso} angles of 149.2 (9)° at N(2) and 155.1 (9)° at N(3) and implies a diminished π-donation to the metal. The remaining lithium is coordinated to N(1) in a mode that is reminiscent of the first tantalum alkylidyne complex, $[Li(dmp)][Ta({\equiv}CCMe_3)(CH_2CMe_3)_3]$ (dmp = *N,N′*-dimethylpiperazine)[15] in a structure

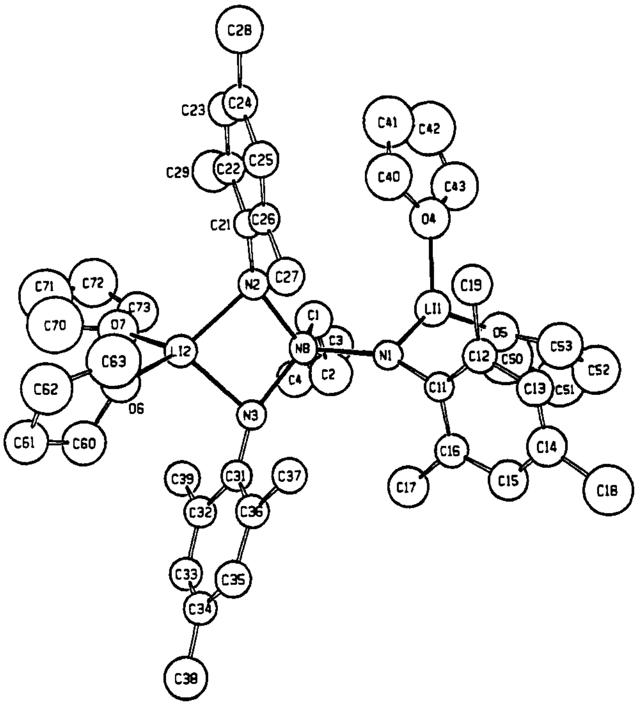


Figure 1. Molecular structure of $[Li(THF)_2]_2[Nb({=}Nmes)_3(^nBu)]$ (**7**) (mes = 2,4,6-$C_6H_2Me_3$) with atoms shown as 30% ellipsoids and atoms C(3) and C(4) further reduced artificially (see footnote 12).

best described as a "carbyne" rather than "lithiocarbene". Similarly, the Nb–N(1) distance (1.89 (1) Å) is more consistent with an *imide* rather than a "lithio*amide*" ligand. Although somewhat imprecise, the Li(1)–C(1) distance of 2.98 (3) Å precludes any significant interaction between these atoms and the angles about the Li(1) are consistent with trigonal Li^+ coordination as in $[Li(dmp)][Ta({\equiv}CCMe_3)(CH_2CMe_3)_3]$.[15]

These studies provide evidence for an *inter*molecular deprotonation of $[M({=}NR)_2(NHR)_2]^-$ (M = Nb, Ta) in the syntheses of the d^0 $[M({=}NR)_3]^-$ functional group although the bis(imide) itself, the logical precursor to $[M({=}NR)_3]^-$, most likely arises through an *intra*molecular α-H abstraction sequence. Similar conclusions were drawn in the preparation of $[W({=}NAr)_3Cl]^-$.[6a] The synthesis and reactivity of these and related "π-loaded" metal centers are areas of our continued efforts.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8919367) for support of this work. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Biomedical Research Support Grant Program, Division of Research Resources, National Institutes of Health (Grant BRSG S07RR07002), and the Materials Characterization Program (State of Arizona) for partial support.

Supplementary Material Available: Text giving analytical and spectroscopic data for compounds **1**–**7** and full details of the structure solution and refinement for $[Li(THF)_2]_2[Nb({=}Nmes)_3(^nBu)]$ (**7**), including tables of atomic positional and thermal parameters and bond distances and angles and ORTEP figures (21 pages); a table of observed and calculated structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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(11) The reaction of $Nb({=}Nmes)_2Cl(py)_2$ with 2 equiv of LiNHmes in Et_2O/py affords the analogous complex $[Li(py)_2][Nb({=}Nmes)_2(NHmes)_2]$, but this synthesis is not always reproducible. Similar thermolysis reactions of $[Nb({=}Nmes)_2(NHmes)_2]^-$ in the presence of various ligands do not afford $[Nb({=}Nmes)_3]^-$ complexes.

(12) Compound 7 crystallized with one lattice THF. Crystal data for **7**·THF ($C_{51}H_{82}Li_2NbN_3O_5$): yellow orange, monoclinic, $P2_1/C$ (No. 14), a = 12.568 (3) Å, b = 12.494 (2) Å, c = 34.402 (7) Å, β = 92.84 (1)°, V = 5395.3 Å^3, Z = 4, D(calc) = 1.14 g cm^{-3}, μ(Mo Kα) = 2.5 cm^{-1} (T = 23 ± 1 °C); 5749 total reflections (5093 unique) with a maximum 2θ of 40° of which 2349 with $F_o^2 > 1.0\sigma(F_o^2)$ were included in the refinement. Final R = 0.112 and R_w = 0.120. Large thermal parameters of the butyl group and one lattice THF limit the precision of the structure. Thus, in Figure 1, atoms C(3) and C(4) are shown with B_{iso} artificially set at 10.0. Complete details of the structure solution and refinement are provided in the supplementary material.

(13) Selected bond lengths (Å) and angles (deg) for $[Li(THF)_2]_2[Nb({=}Nmes)_3(^nBu)]$ (**7**) are as follows. Distances: Nb–N(1) = 1.89 (1), Nb–N(2) = 1.87 (1), Nb–N(3) = 1.82 (1), Nb–C(1) = 2.26 (2), N(1)–Li(1) = 1.90 (3), N(2)–Li(2) = 2.08 (3), N(3)–Li(2) = 2.08 (3). Nonbonded distances: Li(1)–C(1) = 2.98 (3), Nb–Li(1) = 3.01 (3). Angles: N(1)–Nb–N(2) = 117.9 (4), N(1)–Nb–N(3) = 120.5 (4), N(1)–Nb–C(1) = 102.6 (5), N(2)–Nb–N(3) = 101.9 (5), N(2)–Nb–C(1) = 104.0 (5), Nb–N(1)–C(11) = 152.7 (9), Nb–N(1)–Li(1) = 105 (1), Nb–N(2)–C(21) = 149.2 (9), Nb–N(3)–C(31) = 155.1 (9).

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Received December 20, 1991