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Groups 5 and 6 Terminal Hydrazido(2−) Complexes: N_β Substituent Effects on Ligand-to-Metal Charge-Transfer Energies and Oxidation States

Ian A. Tonks, Alec C. Durrell, Harry B. Gray,* and John E. Bercaw*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125, United States

Supporting Information

ABSTRACT: Brightly colored terminal hydrazido(2−) (dme)$MCl_3(NNR_2)$ (dme = 1,2-dimethoxyethane; M = Nb, Ta; R = alkyl, aryl) or (MeCN)$WCl_4(NNR_2)$ complexes have been synthesized and characterized. Perturbing the electronic environment of the β (NR_2) nitrogen affects the energy of the lowest-energy charge-transfer (CT) transition in these complexes. For group 5 complexes, increasing the energy of the N_β lone pair decreases the ligand-to-metal CT (LMCT) energy, except for electron-rich niobium dialkylhydrazides, which pyramidalize N_β in order to reduce the overlap between the $Nb{=}N_\alpha$ π bond and the N_β lone pair. For W complexes, increasing the energy of N_β eventually leads to reduction from formally $[W^{VI}{\equiv}N{-}NR_2]$ with a hydrazido(2−) ligand to $[W^{IV}{=}N{=}NR_2]$ with a neutral 1,1-diazene ligand. The photophysical properties of these complexes highlight the potential redox noninnocence of hydrazido ligands, which could lead to ligand- and/or metal-based redox chemistry in early transition metal derivatives.

End-on (κ^1)-bound hydrazido(2−) complexes of early transition metals have been identified as important intermediates in an increasingly diverse range of stoichiometric and catalytic processes. Because one of the proposed complexes along a Chatt-type[1] cycle of N_2 reduction is a κ^1-bound hydrazido(2−) moiety ($M{=}NNH_2$), much research into possible models for these intermediates, most notably on central metals Mo and W, has been undertaken.[2] It also is of interest that group 4 hydrazido(2−) complexes have been utilized for the catalytic diamination and hydrohydrazination of alkynes with 1,1-disubstituted hydrazines.[3−7]

Although the chemistry of hydrazides of groups 4 and 6 has been well-studied, there is a paucity of reports on similar group 5 complexes, in particular the heavier congeners Nb[8] and Ta.[9] We recently reported on the synthesis of (dme)$MCl_3(NNPh_2)$ (dme = 1,2-dimethoxyethane; M = Nb, Ta) and its use as a synthon for a variety of $M{=}NNR_2$ complexes.[10] One notable feature of (dme)$TaCl_3(NNPh_2)$ is its blue color (λ_{max} = 585 nm), which we postulated to arise from a π^* interaction between the $M{=}N_\alpha$ π bond and the N_β lone pair that destabilizes the highest occupied molecular orbital (HOMO) and lowers the ligand-to-metal charge-transfer (LMCT) energy relative to the parent imido (Figure 1). Here we report the photophysical properties of (dme)$MCl_3(NNR_2)$ (M = Ta, Nb) complexes as well as those for a similar (MeCN)$WCl_4(NNR_2)$ series.

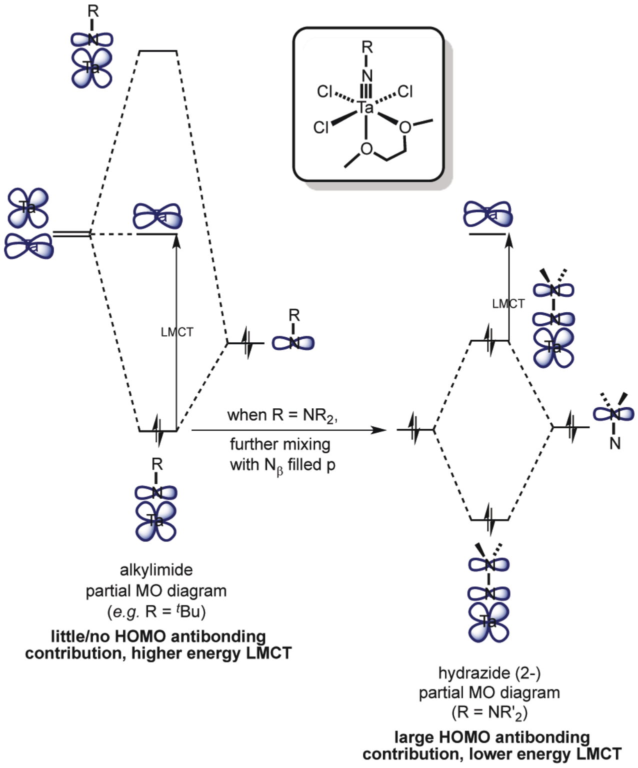

Figure 1. MO energy level diagrams for (dme)$TaCl_3(NR)$ and (dme)$TaCl_3(NNR_2)$ π interactions. N_β filled p mixing raises the hydrazido(2−) HOMO energy (right) relative to the imido HOMO (left).

The resonance Raman spectrum (585 nm excitation) of (dme)$TaCl_3(NNPh_2)$ (**1d**) (Figure 2) shows enhancement of the Ta−N, N−N, and aryl stretches. These enhancements confirm our assignment of this low-energy band to CT between Ta and the hydrazido ligand. Importantly, the Raman spectrum also indicates that there is aryl character in the HOMO, which led us to investigate further the effect of substituted arylhydrazides on the CT behavior. We hypothesized that tuning the electronic properties of N_β would make possible a

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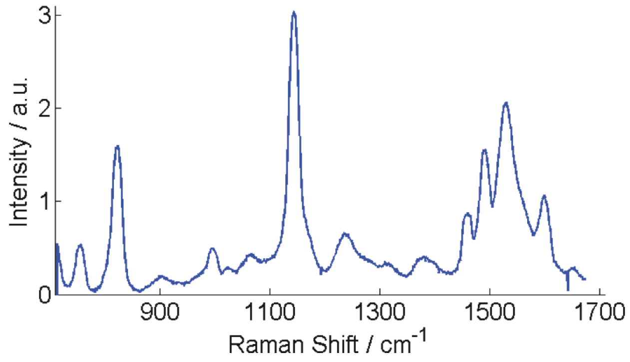
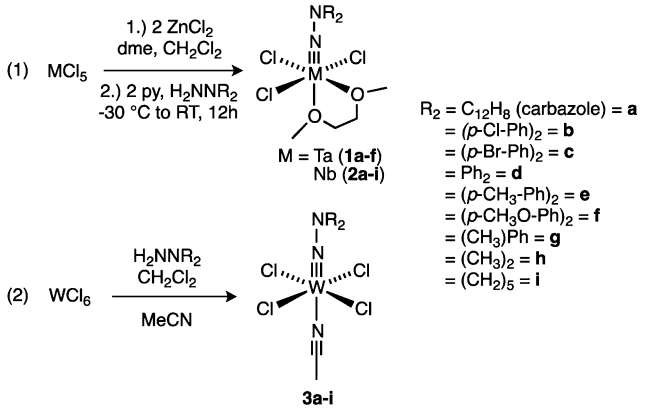


Figure 2. Resonance Raman spectrum of (dme)$TaCl_3(NNPh_2)$ (**1d**) showing features attributable to N−N (865 cm^{-1}), Ta−N (1175 cm^{-1}), and aryl (1500−1650 cm^{-1}) stretching vibrations.

change in the formal donor ability of the [NNR_2] ligand from a dianionic hydrazido(2−) to a neutral 1,1-diazene, thereby accessing a new two-electron "redox-noninnocent" manifold.



The complexes (dme)$MCl_3(NNR_2)$ (**1a−f** for M = Ta, **2a−i** for M = Nb; R = alkyl, aryl) were synthesized from MCl_5 and the corresponding 1,1-disubstituted hydrazine via the previously reported Lewis acid-assisted dehydrohalogenation (eq 1).[10,11] While the niobium dialkylhydrazide reactions (**2g−i**) proceed cleanly in good yield, we were not able to synthesize any tantalum dialkylhydrazides via this route. The complexes (MeCN)$WCl_4(NNR_2)$ (**3a−i**) were synthesized by treating WCl_6 with the corresponding 1,1-disubstituted hydrazine and MeCN in CH_2Cl_2 (eq 2).[12] All of the metalations proceeded in good to excellent yields. However, obtaining spectroscopically pure material proved to be difficult (lower yields), as the impurities of the reactions tend to be highly colored with extinction coefficients orders of magnitude larger than those of the desired metal hydrazido(2−) complexes. For **2e**,**f**, and **3b**,**c**,**f**,**g**, spectroscopically pure materials were not obtained in reproducible quantities.

The absorption spectra of **1a−f**, **2a−d**,**g-i**, and **3a**,**d**,**e**,**h**,**i** in $C_2H_4Cl_2$ were measured. In addition to low-energy M=NNR_2 CT, higher-energy bands associated with M−Cl LMCT transitions were observed. In most cases, the lowest-energy band, which was well-resolved from other absorptions, exhibited a nearly Gaussian shape. The absorption spectra of **1a−e** are presented in Figure 3, and λ_{max} and ε values for all compounds are reported in Table 1. Absorbances for the Ta derivatives had λ_{max} between 15300 and 18900 cm^{-1} and ε between 100 and 250 M^{-1} cm^{-1}, while the Nb congeners gave lower-energy λ_{max} values between 13800 and 16500 cm^{-1} with ε values of 17−66 M^{-1} cm^{-1}. Unlike the related imido complexes, **1** and **2** did not exhibit fluorescence.[13] Absorbances for the W complexes ranged from 15800 to 23200 cm^{-1} with ε values of 330−570 M^{-1} cm^{-1}. Bands for the tungsten dialkylhydrazides were not well resolved from higher-energy absorptions and appeared as shoulders on the much more intense W−Cl LMCT systems. The extinction coefficients for these transitions are quite small because the transition occurs between two essentially orthogonal orbitals (Figure 1).

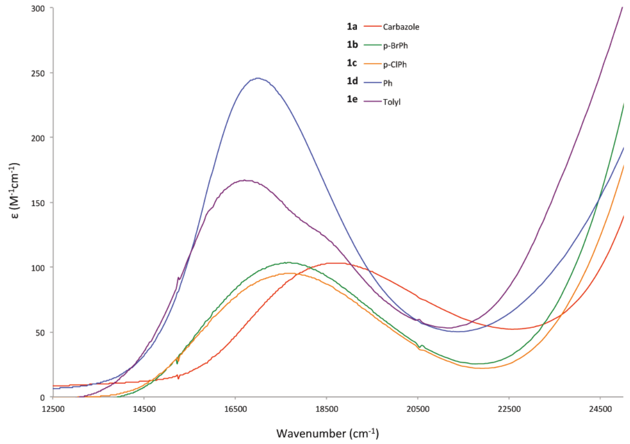


Figure 3. Absorption spectra of **1a−e** in $C_2H_4Cl_2$ solution.

Table 1. Lowest-Energy CT Peaks in the Spectra of (dme)$MCl_3(NNR_2)$ and (MeCN)$WCl_4(NNR_2)$ Complexes[a]

M	R_2	λ_{max} (cm^{-1})	ε (M^{-1} cm^{-1})
Ta	$C_{12}H_8$ (**1a**)	18650	103
	(p-ClPh)$_2$ (**1b**)	17670	93
	(p-BrPh)$_2$ (**1c**)	17640	103
	Ph_2 (**1d**)	17100	245
	(p-CH_3Ph)$_2$ (**1e**)	16690	167
Nb	$C_{12}H_8$ (**2a**)	15700	66
	(p-ClPh)$_2$ (**2b**)	14580	28
	(p-BrPh)$_2$ (**2c**)	14560	30
	Ph_2 (**2d**)	14370	38
	(CH_3)(Ph) (**2g**)	13790	44
	(CH_3)$_2$ (**2h**)	16420	17
	C_5H_{10} (**2i**)	16260	25
W	$C_{12}H_8$ (**3a**)	17860	350
	Ph_2 (**3d**)	16501	370
	(p-CH_3Ph)$_2$ (**3e**)	15750	570
	(CH_3)$_2$ (**3h**)	23260 (*sh*)	400
	(CH_2)$_5$ (**3i**)	22990 (*sh*)	330

[a] The data are ordered according to increasing electron density of N_β within each metal series.

The LMCT ε values for these complexes also reinforce our assignment of the lowest-energy bands, since alternatives such as allowed π/π^* transitions would be expected to give rise to more intense absorptions. Also, since fully conjugated **2a** has a higher-energy λ_{max} than the other diaryls, a solely ligand π-based transition can be ruled out, as an increase in conjugation should decrease λ_{max} for a π/π^* system.

In each metal series, the energy of the CT in the diarylhydrazide complexes decreased dramatically with increasing electron density around N_β, as correlated to the Hammett parameter σ_{para}. This bathochromic shift shows that increasing the N_β lone-pair energy increases the M=N_α π bond and N_β

lone pair antibonding interactions in the HOMO, thus raising its energy and shrinking the HOMO−LUMO gap (Figure 4). It should be noted that this shift is not strictly attributable to an inductive effect of N_β, as the more inductively withdrawing alkoxyimidos (dme)MCl_3(NOMe) have higher-energy LMCTs (M = Ta, 23 750 cm^{-1}; M = Nb, 21 300 cm^{-1}) than the hydrazido complexes.

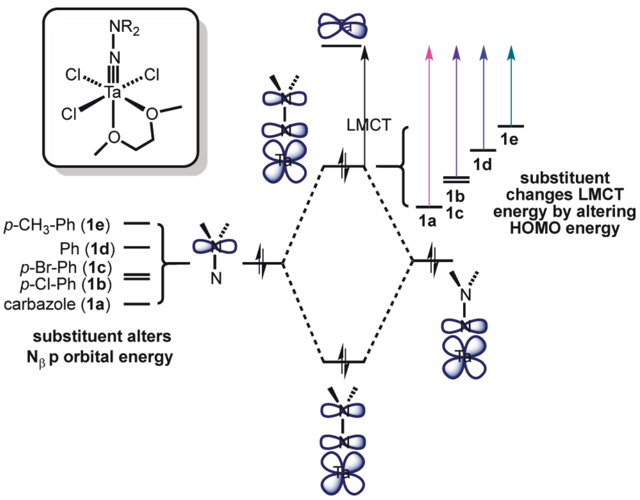


Figure 4. Increasing the energy of the N_β p orbital increases the HOMO energy and decreases the LMCT energy in diarylhydrazides.

The observed trend in the peak energies is similar to the "aryl effect" that has been observed in related (dme)MCl_3(NR) (R = alkyl, aryl) imido complexes, in which small aryl−(M=N_α) π antibonding interactions lower the LMCT energy of the arylimidos relative to the alkylimidos.[14] However, the antibonding effect on the band energies is much more dramatic in the hydrazido complexes than in the arylimidos.

On the basis of the observations for the arylhydrazides, we would expect the dialkylhydrazide complexes (**2h**, **2i**, **3h**, and **3i**), which are more electron-rich, to display much lower energy LMCT bands than the diarylhydrazides. However, both the Nb and W dialkylhydrazides exhibited much *higher* energy absorptions than the arylhydrazides.

The origin of the dialkylhydrazide energy discrepancies was ascertained by examining the crystal structures of the series. X-ray-quality crystals of **1a**, **1c**, **1d**, **1e**, and **2a−i** were obtained by slow diffusion of pentane into saturated solutions of the metal hydrazido(2−) complex in $C_2H_4Cl_2$. **3i** was crystallized from a saturated solution of **3i** in 2:1 pentane/toluene cooled to −30 °C. Table S1 in the Supporting Information shows the M−N and N−N bond distances and the sum of all the angles around N_β for all of the crystallized complexes. The M−N bond distances are typical for triple bonds, and the N−N distances are shorter than that of free diphenylhydrazine (1.418 Å). In general, the N−N bond distances for the W complexes are shorter than in either the Nb or Ta cases and have a larger spread, but these differences are still relatively small. The sum of the angles about N_β indicates that N_β is planarized ($\sum\angle_{N2} \approx$ 360°) in all examples except for dialkylhydrazides **2h** and **2i**, which are pyramidalized ($\sum\angle_{N2} \approx 340°$) (Figure 5). The bond length data show no trend with the electron richness of the hydrazido ligand. As a result, no conclusions about either the electronic structure or the donor ability of the hydrazido ligand can be made by examining the bond lengths. However, the geometry of N_β gives insight into the nature of the LMCT energy discrepancy in the dialkylhydrazide complexes (Figure 5).

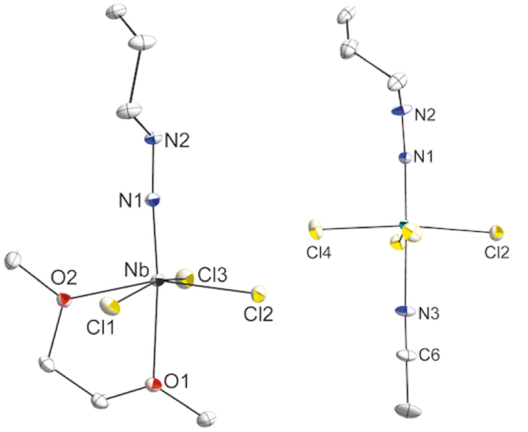
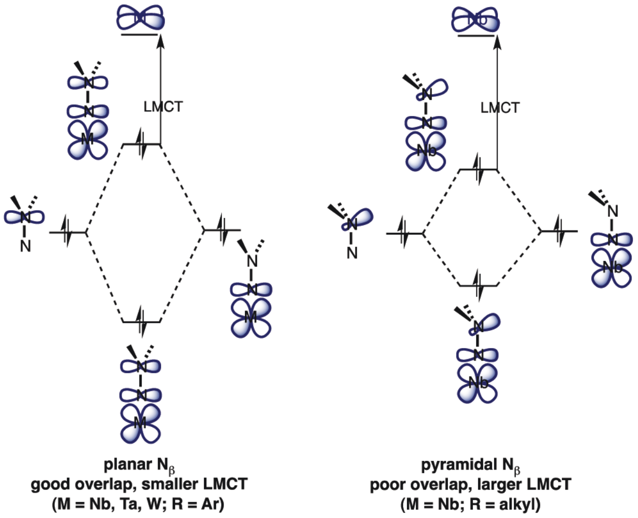


Figure 5. Thermal ellipsoid drawings of (left) (dme)$NbCl_3$[NN-$(CH_2)_5$] (**2i**) and (right) (MeCN)WCl_4[NN$(CH_2)_5$] (**3i**) viewed down the edge of the piperidyl ring. The different geometries of N2 (N_β) should be noted. Selected bond distances (Å) and angles (deg) in **2i**: Nb−N1, 1.7597(1); N1−N2, 1.3392(1); $\sum\angle_{N2}$, 341.1. In **3i**: W−N1, 1.7633(1); N1−N2, 1.2556(1); $\sum\angle_{N2}$, 359.8.

For all of the diarylhydrazidos, N_β is planarized as a result of steric and electronic factors. However, the niobium dialkylhydrazides (**2h**, **2i**) are pyramidalized at N_β, and as a result, the overlap between the Nb=N_α π and N_β orbitals is reduced (Figure 6). Consequently, the HOMO energy is not increased as much as would be predicted on the basis of the diarylhydrazide trend. Odom observed a similar trend for ligand-to-ligand CTs in titanium hydrazido complexes.[5b]



planar N_β
good overlap, smaller LMCT
(M = Nb, Ta, W; R = Ar)

pyramidal N_β
poor overlap, larger LMCT
(M = Nb; R = alkyl)

Figure 6. Pyramidalization of N_β reduces the overlap of the lone pair with the M−N π bond, resulting in greater than expected LMCT energies for the niobium dialkylhydrazides.

Conversely, the tungsten dialkylhydrazides (**3h**, **3i**) remain planarized in the solid state yet still do not display low-energy CT transitions that would be in line with the arylhydrazide trend. Since a planarized dialkylhydrazide should have a very low energy λ_{max} on the basis of the aryl trends discussed above, we speculate that the tungsten(VI) dialkylhydrazidos in fact formally consist of 1,1-diazene ligands coupled to a W^{IV} center.

In this case, the antibonding interaction between the W$=$N$_\alpha$ π and N$_\beta$ lone-pair orbitals is so strong that the MO is *higher* in energy than the metal-based orbitals, resulting in a formal reduction of W by the hydrazide; thus, the observed transition is metal-to-ligand CT (MLCT) rather than LMCT (Figure 7, right diagram). It is difficult to speculate on why the MLCT appears as a high-energy shoulder, so we focus on the qualitative *absence* of a low-energy LMCT peak as a diagnostic. Previously, extended Hückel MO and ab initio calculations on tungsten and molybdenum hydrazides have provided evidence for at least partial reduction of the metal center.[15]

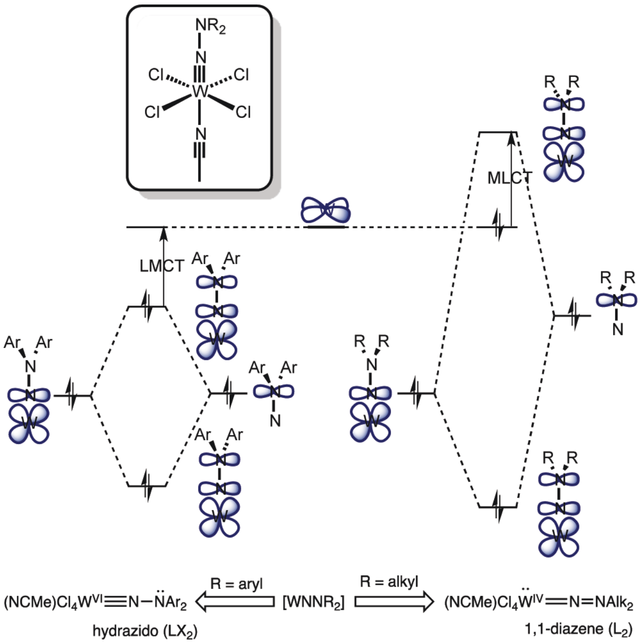


Figure 7. WNNR$_2$ units exhibit different formal donor characteristics when R is changed from (left) aryl to (right) alkyl.

In summary, examination of the spectroscopic and structural properties of group 5 and group 6 complexes highlights an important difference between their related terminal hydrazido moieties. In the case of group 6 terminal hydrazides, the formally reduced metal 1,1-diazene form can stabilize electron-rich hydrazides (such as $-$NNMe$_2$), whereas the group 5 (and group 4) metals apparently resist reduction. Since Chatt-type N$_2$ reduction cycles invoke an unusually wide range of accessible metal oxidation states, our results suggest that certain intermediates, particularly MNNH$_2$, might be stabilized by redox at noninnocent $-$NNH$_x$ ($x = 1, 2$) ligands. Analogous N$_2$ reduction cycles would thus be less favored for group 5 and group 4 transition metal systems.[1,2b]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and spectroscopic, crystallographic (CIF), and analytical data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

bercaw@caltech.edu

Notes

The authors declare no competing financial interest.

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