Table IV. Comparison of Relative Self-Exchange Electron-Transfer Rate Constants and Bond Length Differentials for $[N_4Mn^{III}O_2Mn^{IV}N_4]^{3+}$ Dimers[a]

redox couple	*R*	Δ(Mn–O), Å	Δ(Mn–N$_{ax}$), Å	Δ(Mn–N$_{eq}$), Å
$[Mn_2(tmpa)_2O_2]^{3+/2+}$	1.0	0.061	0.220	0.026
$[Mn_2(bispicen)_2O_2]^{3+/2+}$	2.6×10^2	0.040	0.077	0.000
$[Mn_2(bpy)_4O_2]^{3+/2+}$	7.4×10^{-1}	0.071	0.194	0.057
$[Mn_2(phen)_4O_2]^{3+/2+}$	2.5×10^{-1}			

[a] Relative $[Mn_2N_8O_2]^{3+/2+}$ self-exchange electron-transfer rate constants (eq 1), defined as $R = k_{11}([Mn_2N_8O_2]^{3+/2+})/k_{11}([Mn_2(tmpa)_2O_2]^{3+/2+})$, were calculated from eq 5 as described in the text. Δ(Mn–O), Δ(Mn–N$_{ax}$), and Δ(Mn–N$_{eq}$) correspond to the average differences between Mn–O, Mn–N$_{axial}$, and Mn–N$_{equatorial}$ bond lengths on the Mn(III) and Mn(IV) centers of mixed-valence $[Mn_2N_8O_2]^{3+}$ dimers. Bond length data are from refs 4, 6, and 9.

vation are poorly understood for these systems. Consequently, a quantitative extrapolation from $E_{1/2}(CH_3CN)$ to $E_{1/2}(H_2O)$ is not possible, ruling out the calculation of absolute k_{11} values from eq 4. For the purpose of determining *relative* k_{11} values, however, we assume that differentials among $E_{1/2}$(III,IV/III,III) values remain essentially constant from acetonitrile to the aqueous phase. On this basis, $R = k_{11}([Mn_2N_8O_2]^{3+/2+})/k_{11}([Mn_2(tmpa)_2O_2]^{3+/2+})$ is calculated from eq 5, where $\Delta E' = E_{1/2}([Mn_2(tmpa)_2O_2]^{3+/2+}) - E_{1/2}([Mn_2N_8O_2]^{3+/2+})$. *R* ratios based on reductions of manganese(III,IV) dimers by $Co(bpy)_3{}^{2+}$ are displayed in Table IV with comparisons among Mn–N$_{axial}$, Mn–N$_{equatorial}$, and Mn–O bond lengths for the Mn(III) and Mn(IV) centers.

$$R = [k_{12}{}^2([Mn_2N_8O_2]^{3+/2+})/k_{12}{}^2([Mn_2(tmpa)_2O_2]^{3+/2+})] \times \exp(38.94(\Delta E')) \quad (5)$$

This approximate Marcus calculation shows the self-exchange electron-transfer rates of the bpy and phen dimers to be slightly smaller than that of $[Mn_2(tmpa)_2O_2]^{3+/2+}$, while the bispicen analogue evidently is more reactive by 2 orders of magnitude. The agreement between *R* values for the $[Mn_2(bispicen)_2O_2]^{3+/2+}$ couple calculated from cross reactions with $Co(bpy)_3{}^{2+}$ (2.6×10^2) and HQ$^-$ (2.4×10^2) reinforces the hypothesis of distinctively high electron-transfer reactivity. From comparisons of both bond lengths and angles, Hodgson and co-workers conclude[3,4,23] that $[Mn_2(tmpa)_2O_2]^{3+}$, $[Mn_2(bpy)_4O_2]^{3+}$, and $[Mn_2(phen)_4O_2]^{3+}$ are fully localized, Robin and Day[24] class I mixed-valence dimers, while $[Mn_2(bispicen)_2O_2]^{3+}$ exhibits partially delocalized, Robin and Day class II bonding characteristics. Thus, the former dimers exhibit large Mn–N$_{axial}$ bond length differences of about 0.2 Å between localized d^3 Mn(IV) and Jahn–Teller-distorted d^4 Mn(III) centers; smaller, but distinct Mn–O and Mn–N$_{equatorial}$ bond length inequalities also distinguish the Mn(III) and Mn(IV) atoms (Table IV).[4]

Although the Mn atoms of $[Mn_2(bispicen)_2O_2]^{3+}$ are not equivalent, as would be the case in a Robin and Day class III dimer, Δ(Mn–O), Δ(Mn–N$_{axial}$), and Δ(Mn–N$_{equatorial}$) values are uniformly smaller than those pertaining to the tmpa, bpy, and phen complexes, signalling electron delocalization between formally Mn(III) and Mn(IV) metal centers.[3,4] Indeed, bond length and angle variations throughout a series of manganese(IV,IV), manganese(III,IV), and manganese(III,III) dimers containing bispicen and its derivatives are remarkably small considering the overall two-electron change and steric crowding which lengthens Mn–N$_{axial}$ bonds in the latter species (bispicen ligand substituted with methyl groups in the 6-pyridyl positions).[2-5] Therefore, crystallographic evidence supports the proposal that Mn–N$_{axial}$ bond lengthening induced by reduction of Mn(IV) to Mn(III) within $[N_4Mn^{III}O_2Mn^{IV}N_4]^{3+}$ should be smallest when N$_4$ = bispicen, specifically promoting k_{11} through a decrease in the inner-sphere rearrangement contribution to the activation free energy. The crystal structure of $[Mn_2(bispicen)_2O_2]^{2+}$ has not been reported, however, so the relative extents to which Mn–O, Mn–N$_{axial}$, and Mn–N$_{equatorial}$ bond length changes govern the self-exchange rate constant of the $[Mn_2(bispicen)_2O_2]^{3+/2+}$ couple cannot be stated with certainty.

Finally, the reductant-independent k_0 pathways found in the reactions of $Co(bpy)_3{}^{2+}$ with all four $[Mn_2N_8O_2]^{3+}$ dimers should be addressed. The oxidants may be ranked according to decreasing k_1/k_0 ratio: bispicen (1.8×10^3) > tmpa (9.5×10^2) > phen (3.3×10^2) > bpy (2.0×10^2). Thus, the k_0 pathways are most important for the bpy and phen complexes, which exhibit the highest susceptibility toward decomposition in aqueous solution.[10] The possibility that the k_0 pathways derive from activation by Mn–O bond cleavage is presently under investigation.

Acknowledgment is made to the Robert A. Welch Foundation (Grant D-735) for generous support of this research. We thank Professor D. J. Hodgson for helpful discussions.

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Synthesis and Characterization of Bis(2,2'-bipyridyl)nitrocarbonylruthenium(II) Hexafluorophosphate

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Received September 12, 1991

Reductions of not only carbon dioxide[1] but also nitrite[2] have been of much interest in connection with environmental problems. Carbon dioxide and nitrite ligated on ruthenium(II) complexes

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0020-1669/92/1331-1971$03.00/0

Table I. Data for Crystal Structure Analysis of $[Ru(bpy)_2(CO)(NO_2)]PF_6$

formula	$C_{21}H_{16}N_5F_6O_3PRu$
fw	632.46
a, Å	11.112 (4)
b, Å	12.318 (4)
c, Å	17.501 (4)
Z; V, Å^3	4; 2395.5
space group	$P2_12_12_1$
D_{calcd}, g/cm^3	1.75
θ range, deg	<30
no. of data used ($F_o > 3\sigma(F_o)$)	1792
no. of variables	417
final R/R_w,[a] %	6.44/6.82

[a] $R = (\sum||F_o| - |F_c||)/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$.

can be smoothly converted into carbon monoxide and nitrosyl ligands by acid–base equilibria. For example, *cis*-$[Ru(bpy)_2(CO)_2]^{2+}$ (bpy = 2,2′-bipyridyl) reversibly reacts with OH^- in a neutral aqueous solution to afford *cis*-$[Ru(bpy)_2(CO)C(O)OH]^+$, which dissociates the hydroxycarbonyl proton to form $[Ru(bpy)_2(CO)COO]$ in alkaline solution. Carbonyl, hydroxycarbonyl, and carbon dioxide complexes exist as an equilibrium mixture in weak alkaline conditions (eqs 1 and 2).[3] Similarly,

$$[Ru(bpy)_2(CO)_2]^{2+} + OH^- \rightleftharpoons [Ru(bpy)_2(CO)C(O)OH]^+ \quad (1)$$

$$[Ru(bpy)_2(CO)C(O)OH]^+ + OH^- \rightleftharpoons [Ru(bpy)_2(CO)COO]^+ + H_2O \quad (2)$$

cis-[4a] and *trans*-$[Ru(bpy)_2Cl(NO)]^{2+}$[4b] are converted into *cis*- and *trans*-$[Ru(bpy)_2Cl(NO_2)]$ via $[Ru(bpy)_2Cl(NO_2H)]^+$ by a reversible nucleophilic attack of OH^- to nitrosyl ligand, followed by a dissociation of a terminal proton of hydroxylnitrosyl moiety (eqs 3 and 4).[4] We have prepared $[Ru(bpy)_2(CO)(NO_2)]^+$ in

$$[Ru(bpy)_2Cl(NO)]^{2+} + OH^- \rightleftharpoons [Ru(bpy)_2Cl(NO_2H)]^+ \quad (3)$$

$$[Ru(bpy)_2Cl(NO_2H)]^+ + OH^- \rightleftharpoons [Ru(bpy)_2Cl(NO_2)] + H_2O \quad (4)$$

order to compare electrophilicity of CO and nucleophilicity of NO_2^- among $[Ru(bpy)_2(CO)(NO_2)]^+$, $[Ru(bpy)_2(CO)_2]^{2+}$, and $[Ru(bpy)_2Cl(NO_2)]$. This paper describes the crystal structure of *cis*-$[Ru(bpy)_2(CO)(NO_2)]PF_6$ and the reactivity of the complex toward OH^- and H^+.

Experimental Section

Preparation of $[Ru(bpy)_2(CO)(NO_2)]PF_6$. A CH_3OH/H_2O solution (30:1 (v/v), 30 cm^3) containing $[Ru(bpy)_2(CO)Cl]PF_6$[3] (165 mg, 0.27 mmol) and $NaNO_2$ (49 mg, 0.71 mmol) was refluxed under N_2 atmosphere for 24 h. On cooling the solution to −20 °C, orange $[Ru(bpy)_2(CO)(NO_2)]PF_6$ was crystallized in a 70% yield. Anal. Calcd for $C_{21}H_{16}N_5F_6O_3PRu$: C, 39.88; H, 2.55; N, 11.07. Found: C, 39.94; H, 2.69; N, 11.09. IR spectrum (KBr): $\nu(C{\equiv}O)$ 1983 cm^{-1}, $\nu_{as}(NO_2)$ 1372 cm^{-1}, $\nu_s(NO_2)$ 1316 cm^{-1}. Quite similarly, $[Ru(bpy)_2(CO)(^{15}NO_2)]PF_6$ was prepared by using $[Ru(bpy)_2(CO)Cl]PF_6$ and $Na^{15}NO_2$ (90% enriched, Isotech) in CH_3OH/H_2O. IR spectrum of $[Ru(bpy)_2(CO)(^{15}NO_2)]PF_6$: $\nu(C{\equiv}O)$ 1983 cm^{-1}, $\nu_{as}(^{15}NO_2)$ 1345 cm^{-1}, and $\nu_s(^{15}NO_2)$ 1293 cm^{-1}.

X-ray Crystallographic Studies. The reflections of X-ray analysis were collected by θ–2θ techniques ($0 < 2\theta < 60°$) on an Enraf-Nonius CAD4-GX21 automated four-circle diffractometer with Mo Kα radiation (0.7107 Å). The 1792 independent reflections with $F_o > 3\sigma(F_o)$ were used for the structure refinement. All the calculations were carried out on a HITAC-M680H computer, using a UNICS III program. Nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and included in the structure factor calculations. The data for the crystal structure analysis are shown in Table I. The final coordinates and average temperature factors of the atoms without hydrogen atoms of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ are shown in Table II.

Table II. Positional Parameters and B(eq) Values for $[Ru(bpy)_2(CO)(NO_2)]^+$

atom	x	y	z	B, Å^2
Ru1	0.0324 (1)	0.2438 (1)	0.3637 (0)	3.5
N1	−0.0812 (8)	0.0975 (7)	0.3627 (5)	3.7
N2	0.1385 (7)	0.3847 (7)	0.3752 (6)	4.0
N3	0.0417 (8)	0.2598 (7)	0.4817 (5)	4.1
N4	0.0088 (8)	0.2524 (7)	0.2464 (5)	4.1
N5	0.1198 (9)	0.3445 (6)	0.3564 (5)	3.9
O1	0.2472 (11)	0.1024 (10)	0.3668 (8)	10.8
O2	−0.0536 (16)	0.0289 (11)	0.3963 (11)	16.1
O3	−0.1481 (14)	0.1010 (12)	0.3322 (11)	15.4
C1	0.1887 (11)	0.4409 (11)	0.3151 (8)	4.9
C2	0.2613 (13)	0.5264 (9)	0.3305 (8)	5.6
C3	0.2838 (13)	0.5645 (9)	0.4058 (8)	5.4
C4	0.2325 (12)	0.5056 (11)	0.4643 (9)	5.2
C5	0.1590 (10)	0.4157 (8)	0.4465 (6)	2.9
C6	0.1012 (10)	0.3515 (8)	0.5067 (6)	3.5
C7	0.1010 (13)	0.3778 (10)	0.5843 (6)	4.8
C8	0.0410 (13)	0.3142 (10)	0.6333 (7)	5.7
C9	−0.0174 (11)	0.2211 (9)	0.6077 (7)	4.7
C10	−0.0152 (12)	0.1975 (9)	0.5321 (7)	4.7
C11	0.0784 (13)	0.2053 (11)	0.1916 (7)	5.4
C12	0.0490 (15)	0.2067 (12)	0.1173 (7)	6.4
C13	−0.0470 (14)	0.2640 (11)	0.0919 (7)	6.5
C14	−0.1194 (13)	0.3127 (10)	0.1459 (8)	6.0
C15	−0.0885 (11)	0.3072 (9)	0.2246 (6)	4.1
C16	−0.1618 (11)	0.3620 (8)	0.2839 (6)	3.9
C17	−0.2614 (12)	0.4262 (10)	0.2679 (8)	5.1
C18	−0.3214 (13)	0.4750 (10)	0.3289 (9)	5.6
C19	−0.2779 (12)	0.4612 (10)	0.4019 (9)	5.8
C20	−0.1753 (13)	0.3956 (10)	0.4121 (8)	5.0
C21	0.1730 (10)	0.1476 (8)	0.3720 (7)	3.9

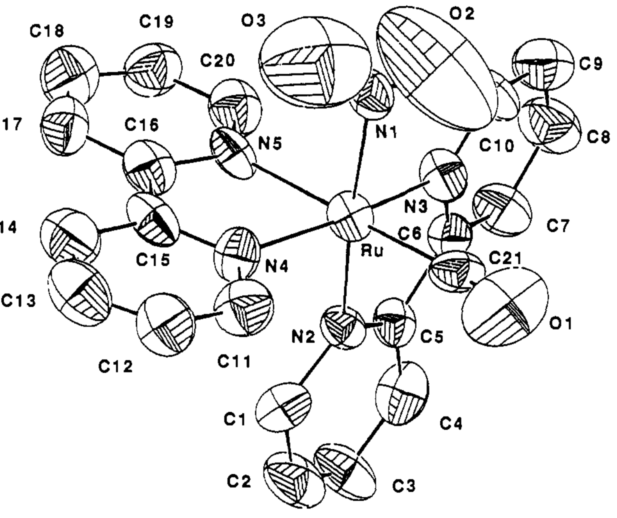

Figure 1. Molecular structure of $[Ru(bpy)_2(CO)(NO_2)]^+$.

Results and Discussion

The structure of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ is presented in Figure 1. Carbon monoxide and nitro on Ru(II) coordinate in cis position. The structural parameters of two bipyridyl ligands are not so different from those of the cis type of bis(2,2′-bipyridyl)ruthenium complexes reported so far.[5] The two oxygen atoms of the nitro group were disordered presumably due to a rotation around the Ru–N1 bond (2.20 (1) Å), and the O2–N1–O3 angle of the nitro ligand (126 (2)°) is also approximately the same as that of nitro complexes reported elsewhere.[6] The Ru–C and C–O bond lengths are 1.97 (1) and 1.02 (2) Å, respectively. Ru–C–O angle, 170 (1)°, shows slight distortion. The Ru–N3 distance (trans to bpy), 2.08 (1) Å, is very close to that for Ru–N4 (trans to bpy), 2.07 (1) Å. In addition, the Ru–N5

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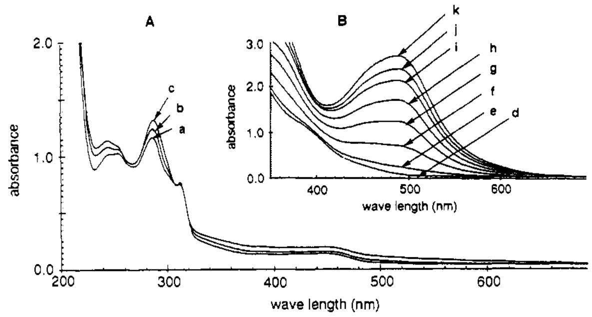

Figure 2. Electronic absorption spectra of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ (5.50×10^{-5} mol/dm^3 (A) and 4.08×10^{-4} mol/dm^3 (B)) in CH_3CN in the presence of various concentrations of Bu_4NOH: 0 (a and d); 1.73 (b); 3.46 (c); 2.04 (e); 3.06 (f); 4.04 (g); 5.10 (h); 6.08 (i); 7.10 (j); 8.16 $\times 10^{-4}$ mol/dm^3 (k).

(trans to CO) distance, 2.10 (1) Å, is also close to the Ru–N2 (trans to NO_2) distance, 2.11 (1) Å. A distinct difference in electron-donor and/or -acceptor character of the carbonyl and nitro ligands of $[Ru(bpy)_2(CO)(NO_2)]^+$ was not observed from the comparison of bond lengths between Ru and bpy ligands.

Although two oxygen atoms of the nitro group of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ are disordered in the solid state, dissociation of NO_2^- from $[Ru(bpy)_2(CO)(NO_2)]^+$ may be neglected in a solution, since no ligand exchange between NO_2^- and $^{15}NO_2^-$ took place at all in the reaction of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ with 2 equiv of $Na^{15}NO_2$ in MeOH for 2 days.[7] The electronic absorption spectrum of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ showed no change between acidic (pH 1.0) and alkaline (pH 12.0) aqueous solutions. On the basis of smooth reactions of eqs 1 and 4 in H_2O, both the CO and NO_2^- of $[Ru(bpy)_2(CO)(NO_2)]^+$ are considered to be less reactive than the CO of $[Ru(bpy)_2(CO)_2]^{2+}$ and NO_2^- of $[Ru(bpy)_2Cl(NO_2)]$. It is well-known that basicity of OH^- is effectively enhanced in organic solvents compared with that in H_2O.[8] In fact, addition of a methanolic solution of Bu_4NOH (0.26 mol/dm^3) to a CH_3CN solution of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ (0.055 mmol/dm^3) results in an increase in electronic absorption bands at 290 and 490 nm with an isosbestic point at 310 nm up to a certain concentration of OH^- (0.35 mmol/dm^3) (Figure 2), and neutralization of the resulting solution by aqueous $HClO_4$ (0.20 mol/dm^3) regenerated the electronic absorption spectrum of $[Ru(bpy)_2(CO)(NO_2)]^+$. However, an addition of a large excess of Bu_4NOH into a CH_3CN solution of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ (0.102 mmol/dm^3) caused a decrease in the absorbance at the 490-nm band and an appearance of a new band at 585 nm, which remained even after neutralization by aqueous $HClO_4$. In accordance with these observations, a crude product obtained in the reaction of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ with 2 equiv of KOH in CH_3OH showed strong IR bands at 1650, 1378, and 1331 cm^{-1} assigned to $\nu(C{=}O)$ of a hydroxycarbonyl moiety,[9] $\nu_{as}(NO_2)$, and $\nu_s(NO_2)$, respectively, with a weak $\nu(C{\equiv}O)$ band at 1983 cm^{-1} due to a contamination of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ and neutralization of the product by aqueous HCl in MeOH regenerated $[Ru(bpy)_2(CO)(NO_2)]^+$. On the other hand, when $[Ru(bpy)_2(CO)(NO_2)]PF_6$ was allowed to react with 20 equiv of Bu_4NOH in MeOH, the reaction product exhibited only a strong band at 1574 cm^{-1} without any $\nu(NO_2)$ band. These observations suggest that $[Ru(bpy)_2(CO)(NO_2)]^+$ reversibly is converted into $[Ru(bpy)_2(C(O)OH)(NO_2)]$ in low OH^- concentrations in MeOH (eq 5),[10] while $[Ru(bpy)_2(CO)(NO_2)]^+$ decomposes in the presence of large excess of OH^- presumably by dissociation of NO_2^- from unstable $[Ru(bpy)_2(C(O)O)(NO_2)]^-$.

$$[Ru(bpy)_2(CO)(NO_2)]^+ + OH^- \rightleftharpoons [Ru(bpy)_2(C(O)OH)(NO_2)] \quad (5)$$

Related to the $Ru–NO_2^-$ bond cleavage of $[Ru(bpy)_2(CO)(NO_2)]^+$ in the presence of a large excess of OH^- in MeOH, treatment of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ with an excess amount of gaseous HCl or aqueous HCl (10 N) in CH_3OH caused loss of NO_2^- ligand, and $[Ru(bpy)_2(CO)Cl]PF_6$ was selectively formed in a ca. 80% yield. On the basis of the fact that $[Ru(bpy)_2(CO)(NO_2)]PF_6$ undergoes no substitution reaction by either $Na^{15}NO_2$ or Et_4NCl in MeOH, the formation of $[Ru(bpy)_2(CO)Cl]^+$ in the reaction of $[Ru(bpy)_2(CO)(NO_2)]^+$ with HCl may result from fission of the $Ru–NO_2^-$ bond after protonation of NO_2^- of $[Ru(bpy)_2(CO)(NO_2)]^+$ in MeOH. The present study reveals that CO of $[Ru(bpy)_2(CO)(NO_2)]^+$ undergoes a reversible nucleophilic attack of OH^- to form $[Ru(bpy)_2(C(O)OH)(NO_2)]$. However, not only deprotonation of $[Ru(bpy)_2(C(O)OH)(NO_2)]$ but also protonation of $[Ru(bpy)_2(CO)(NO_2)]^+$ result in the cleavage of the $Ru–NO_2^-$ bond.

Acknowledgment. We thank Professor Yoshihiko Kushi and Professor Shie-Ming Peng for their advice on X-ray crystal analysis.

Supplementary Material Available: Tables of atomic parameters with averaged thermal parameters and anisotropic thermal parameters (3 pages); tables of observed and calculated structure factor data (9 pages). Ordering information is given on any current masthead page.

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(7) The IR spectrum of the reaction mixture was consistent with summation of those of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ and $Na^{15}NO_2$.

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(9) $[Ru(bpy)_2(CO)(C(O)OH)]^+$ shows a $\nu(C{=}O)$ at 1578 cm^{-1}.[3]

(10) The occurrence of eq 5 may be supported also by a reversible reaction of $[Ru(bpy)_2(CO)(NO_2)]PF_6$ with CH_3ONa in CH_3OH affording $Ru(bpy)_2(C(O)OCH_3)(NO_2)$ ($\nu(C{=}O)$ 1574 cm^{-1}).

Contribution from the Inorganic and Structural Chemistry
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Synthesis, Characterization, and X-ray Structure of $\{[K(THF)_2]_2[U(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]\}\cdot THF$

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Received May 22, 1991

In continuing our studies of uranium in the trivalent oxidation state, we have discovered $UI_3(THF)_4$ to be a convenient precursor to U(III) coordination and organometallic complexes,[2] owing to its clean metathesis reactions with potassium and sodium salts of a variety of alkoxide, amide, cyclopentadienyl, and pentadienyl ligands. In contrast to the relatively clean products obtained by metathesis with dialkylamides,[2] treatment of $UI_3(THF)_4$ with 3 equiv of the potassium salt of 2,6-diisopropylaniline (NH_2Ar) yields intractable products. The nature of the products formed in these 3:1 reactions of potassium monoalkyl amides are still under investigation. We have determined, however, that the reaction of $UI_3(THF)_4$ with excess potassium 2,6-diisopropylanilide cleanly gives the brown crystalline title complex, as shown in eq 1.

$$UI_3(THF)_4 + {\geq}5KNHAr \rightarrow \{[K(THF)_2]_2[U(NHAr)_5]\}\cdot THF + 3KI \quad (1)$$

Lithium and sodium complex salts of the actinides are well-known; their formation pervades metathesis reactions of 4f- and 5f-element compounds.[3] Formation of "ate" complexes from

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(2) (a) Clark, D. L.; Sattelberger, A. P.; Bott, S. G.; Vrtis, R. N. *Inorg. Chem.* **1989**, *28*, 1771. (b) Clark, D. L.; Watkin, J. G.; Sattelberger, A. P.; Schake, A. R.; Avens, L. R.; Burns, C. J. Manuscript in preparation.