should stabilize the lower oxidation state (Re^V) to a greater extent than the higher one, thereby causing a net positive shift in E_f (or, alternatively, an increase in charge-transfer transition energy). If the solvent acceptor number is an appropriate measure of solvent acidity (or some closely related quantity), then the observed correlations (Figures 9–12) can be rationalized.

Water evidently is an exception to the general pattern of solvent effects; both E_f and E^{MLCT} show "anomalously" high values in this solvent. It may simply be that the acceptor number scale does not accurately represent the acidity or polarity of H_2O relative to other solvents.[40] Alternatively, the nature of the solute/solvent interactions may differ in a qualitative way for water versus other solvents. For example, there is independent evidence to suggest that stable molecular adducts (as opposed to weakly hydrogen-bound "complexes") are formed between *trans*-$(O)_2Re(py)_4^+$ and water.[4b,c,41] In any case, the current experiments clearly imply that an exceptionally large degree of oxidation-state tuning of ligand/solvent interactions occurs in water, in comparison to other solvents.

Finally, returning to the substituent effects, those ligands that impart the greatest Brönstead basicity to the dioxorhenium(V) complex (see Table IV) also appear (from Figure 13) to induce the greatest Lewis basicity at the oxo sites—a result that certainly makes intuitive sense (assuming that the acceptor number can be taken as an approximate measure of solvent Lewis acidity characteristics). More precisely, the most basic pyridyl ligands seem to induce the greatest *differential* in basicity between dioxorhenium(V) and -(VI). If we assume that at least the relative Lewis basicity of dioxorhenium is indicated by the corresponding Brönstead measurement and if we note further that for $(O)_2Re^V$ the basicity is ligand variant, we are lead to the additional conclusion that the basicity of $(O)_2Re^{VI}$ must be ligand independent (or at least less dependent than in the lower oxidation state). In work to be reported elsewhere[42] for tetrapyridyl oxo alkoxide species, we have been able to confirm (indirectly, through appropriate thermochemical cycles) the very weak dependence of dioxorhenium(VI) basicity on ancillary ligand composition (as well, of course, as the exceedingly weak absolute basicity ($pK_a \approx -13$) in this oxidation state).

Supplementary Material Available: Figure S1, showing experimental and digitally simulated cyclic voltammograms for reduction of *trans*-$(O)_2Re(py)_4^+$ (1 page). Ordering information is given on any current masthead page.

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(40) It should be mentioned that in the "restricted" solvatochromic correlation proposed by Beard and Murmann (so called "protic" solvents only) water is not anomalous.[39]

(41) From previous studies,[1b] one manifestation of specific oxo/water interactions is a large solvent isotope effect upon $(O)_2Re(py)_4^+$ excited-state lifetimes. We searched for solvent isotope effects in the E_f studies but did not observe any (despite their known importance in transition-metal *aqua* redox thermodynamics; see: Nettles, S. M.; Weaver, M. J. *Inorg. Chem.* **1980**, *19*, 1641).

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Synthesis and Voltammetry of Two Series of Isonitrile/Halide Complexes of Ruthenium: $RuX_{6-n}(CNBu^t)_n$ (X = Cl, Br)

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Two new Ru^{III} isonitrile/halide complexes, $(Bu_4N)[RuX_4(CNBu^t)_2]$ (X = Cl, Br), have been prepared by reaction of *tert*-butyl isocyanide ($CNBu^t$) with $(Bu_4N)_2[RuCl_6]$ and $K_3Ru_2Br_9$, respectively. The Ru^{II} bromide complex $RuBr_2(CNBu^t)_4$ has been prepared by reduction of $[RuBr_4(CNBu^t)_2]^-$ in the presence of the isonitrile. The haldie-to-metal charge-transfer spectra and the mid- and far-infrared spectra are reported as are the voltammetric data for the two series $RuCl_{6-n}(CNBu^t)_n$ and $RuBr_{6-n}(CNBu^t)_n$ (n = 0, 2, 4, 6) measured in CH_2Cl_2, CH_3CN, and liquid SO_2. Electrode potentials and redox-linked ligand substitution are discussed relative to ligand additivity.

We have been studying the electrochemistry and optical spectroscopy of several series of simple binary complexes of ruthenium as part of a broader interest in ligand effects and the additive effect of these on physical characteristics.[1] The initial investigation into mixed nitrile/halide systems has expanded to include ligands that exhibit more varied bonding behavior. In particular, we are interested in systems employing ligands that are good π-acceptors and contrast these to simple σ-donors.

Isonitrile ligands are intriguing because they are among the few ligands that can exhibit both strong σ-donating and π-accepting character. In addition, it has been noted that metal complexes with isonitrile ligands do not always follow a simple electrochemical ligand additivity relationship.[2] We feel it is the deviations from typical linear ligand additivity theory such as these that will ultimately yield the most information about bonding in coordination complexes and have chosen to investigate simple isonitrile/halide complexes.

The majority of reports on isonitrile complexes found in the literature concentrate on metals in low oxidation states; many of these are in combination with other π-accepting ligands such as carbonyl and alkylphosphines. In particular, there are few Ru^{III} (d^5) isonitrile complexes known, these being the oxidized forms of $RuCl_2(isonitrile)_4$. This paper reports the synthesis of two new Ru^{III} complexes, $[RuCl_4(CNBu^t)_2]^-$ and $[RuBr_4(CNBu^t)_2]^-$, where $CNBu^t$ is *tert*-butyl isocyanide, and the voltammetry of two series $RuX_{6-n}(CNBu^t)_n$ (X = Br, Cl; n = 0, 2, 4, 6). The electrode potentials of the present series are related to ligand additivity and Lever's electrochemical ligand parameter (E_L).[2]

Experimental Section

All solvents were distilled under N_2 from appropriate drying agents; $RuCl_3 \cdot xH_2O$ and $CNBu^t$ were purchased from Aldrich. Microanalyses were performed by the Research School of Chemistry Microanalytical Laboratory, Australian National University. The complexes $(Bu_4N)_2[RuCl_6]$,[3] $(Bu_4N)_2[RuBr_6]$,[4] $K_3[Ru_2Br_9]$,[5] $[(CNBu^t)_6Ru](PF_6)_2$,[6] and *trans*-$RuCl_2(CNBu^t)_4$[7] were prepared as reported.

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Infrared and Charge-Transfer Spectra. Both mid- and far-infrared spectra were collected on a Perkin-Elmer 1600 Fourier transform spectrometer. Samples were run both as solid KCl disks and as CH_2Cl_2 solutions in a NaCl cell (3300–600 cm^{-1}) and both as solid polyethylene disks and as CH_2Cl_2 solutions in a polyethylene cell (500–150 cm^{-1}). Charge-transfer spectra were collected for CH_2Cl_2 solutions of the compounds at room temperature with a Varian Cary 5 spectrophotometer (225–3000 nm) interfaced to an IBM PS50/2 computer.

Voltammetry. Voltammetric measurements were performed with a BAS 100A electroanalyzing unit. The electrolyte, Bu_4NBF_4, was prepared by neutralizing Bu_4NOH (40% in water) with HBF_4 to pH 5. The precipitate was filtered off and recrystallized twice from methanol/water and then twice from ethyl acetate/ether and dried in vacuo at 100 °C for 8 h. The final recrystallization was repeated until a clean electrochemical background was achieved. Electrochemical solutions, 0.5 M Bu_4NBF_4 in CH_2Cl_2 and approximately 10^{-3} M in sample, were purged with Ar. Low-temperature measurements were done in a 5-mL jacketted glass cell with a Pt working microelectrode (0.5 mm), a Pt wire counter electrode, and a nonaqueous Ag/AgCl reference electrode. Preparation of the reference electrode has been reported elsewhere.[1] The ferrocenium/ferrocene (Fc^+/Fc) couple appeared at +0.564 V under ambient conditions and was used as an internal standard (0 V) in every case. Low temperatures were achieved with a Lauda Model RL6 (−30 to −70 °C) or a Colora Model WK5 (room temperature to −30 °C) circulating cryostat bath.

Experiments done in CH_3CN used solutions 0.1 M in Bu_4NBF_4 but otherwise were identical with those performed in CH_2Cl_2. The Fc^+/Fc couple appears at +0.482 V in CH_3CN under these conditions.

Voltammetry in liquid SO_2 was performed between −20 and −65 °C. Solutions were 0.2 M in Bu_4NBF_4. A Pt working electrode, Pt auxiliary electrode, and a Pt quasireference electrode (PQRE) were employed. High-purity SO_2 was condensed into a 5-mL cell fitted with a dry ice condenser. The entire apparatus was oven-dried prior to use, dried 4 Å molecular sieves were placed in the cell solution, and a slow stream of dry Ar was maintained over the cell to ensure the absence of moisture. The ferrocene $Fe^{III/II}$ couple was observed at 0.043 V, and the anodic wave of the nonreversible $Fe^{IV/III}$ couple appeared at 2.83 V.

***trans*-$(Bu_4N)[RuCl_4(CNBu^t)_2]$.** The isocyanide (0.3 mL, 2.7 mmol) was added to a stirred solution of $(Bu_4N)_2[RuCl_6]$ (50 mg, 0.06 mmol) in CH_2Cl_2, and then the solution was heated to reflux until it turned from red-brown to yellow. The reaction mixture was reduced to dryness under vacuum to remove excess $CNBu^t$. The residue was recrytallized twice from CH_2Cl_2/diethyl ether and dried in vacuo to give a yellow powder (30 mg, 74%). Anal. Calcd for $C_{26}H_{54}N_3Cl_4Ru$: C, 47.92; H, 8.86; N, 6.45; Cl, 21.76. Found: C, 48.68; H 8.86; N, 6.29; Cl, 22.00.

***trans*-$(Bu_4N)[RuBr_4(CNBu^t)_2]$.** To a suspension of $K_3[Ru_2Br_9]$ (0.2 g, 0.19 mmol) in CH_2Cl_2 were added Bu_4NBr (0.125 g, 0.39 mmol) and $CNBu^t$ (0.07 g, 0.8 mmol). The flask was stoppered, and the mixture was stirred for 7 days. The resultant mixture was reduced to dryness under vacuum to remove excess ligand. The residue was redissolved in CH_2Cl_2, and the mixture was filtered through Celite to remove the fine KBr precipitate. The volume of the purple solution was reduced under vacuum and diethyl ether added to initiate precipitation. Recrystallizations from CH_2Cl_2/diethyl ether and then from CH_2Cl_2/*n*-hexane were necessary to obtain a pure purple crystalline product (0.13 g, 81%). Anal. Calcd for $C_{26}H_{54}N_2Br_4Ru$: C, 37.65; H, 6.65; N, 5.07; Br, 38.53. Found: C, 37.28; H, 6.57; N, 4.69; Br, 38.60.

***trans*-$RuBr_2(CNBu^t)_4$.** The isocyanide (0.3 mL, 2.7 mmol) was added to a solution of $(Bu_4N)[RuBr_4(CNBu^t)_2]$ (30 mg, 0.036 mmol) in 5 mL of dry methanol. After 30 h, the solution had changed from purple to yellow. The solution was reduced to dryness under vacuum to remove excess ligand and the yellow residue recrystallized from CH_2Cl_2/diethyl ether. A final recrystallization from thf/diethyl ether yielded a yellow powder (17 mg, 80%). Anal. Calcd for $C_{20}H_{36}N_4Br_2Ru$: C, 40.47; H, 6.12; N, 9.44; Br, 26.93. Found: C, 40.53; H, 6.30; N, 9.16; Br, 26.54.

Results and Discussion

Syntheses of the dichloro tetrakis(isonitrile) complexes are well-known, and the oxidation of these and the osmium analogues to $[M^{III}Cl_2(RNC)_4]^+$ has been described in the literature. Yamamoto et al. have reported the oxidation of $RuCl_2$(mesityl isocyanide)$_4$ to the Ru^{III} cation by electrolysis and by Ce^{IV},[8] and the oxidation of $[OsCl_2(Me_2CNC)_4]$ to Os^{III} by $NOBF_4$ has been reported by Tetrick and Walton.[9] We have found that the oxidation of $[RuCl_2(CNBu^t)_4]$ can be achieved electrochemically or chemically by use of $NOBF_4$. In addition to this oxidized species, two new Ru^{III} halide/isonitrile stoichiometries have been isolated, $(Bu_4N)[RuX_4(CNBu^t)_2]$ (X = Cl, Br).

Table I. Selected Infrared Vibrations for Isonitrile Complexes of Ru^{II} and Ru^{III} [a]

	ν_{NC}	ν_{RuX}		ν_{NC}	ν_{RuX}
$(Bu_4N)[RuCl_4(CNBu^t)_2]$	2174	311	$RuCl_2(CNBu^t)_4$	2145	305
$(Bu_4N)[RuBr_4(CNBu^t)_2]$	2167	236	$RuBr_2(CNBu^t)_4$	2144	240

[a] Recorded as CH_2Cl_2 solutions in a NaCl cell.

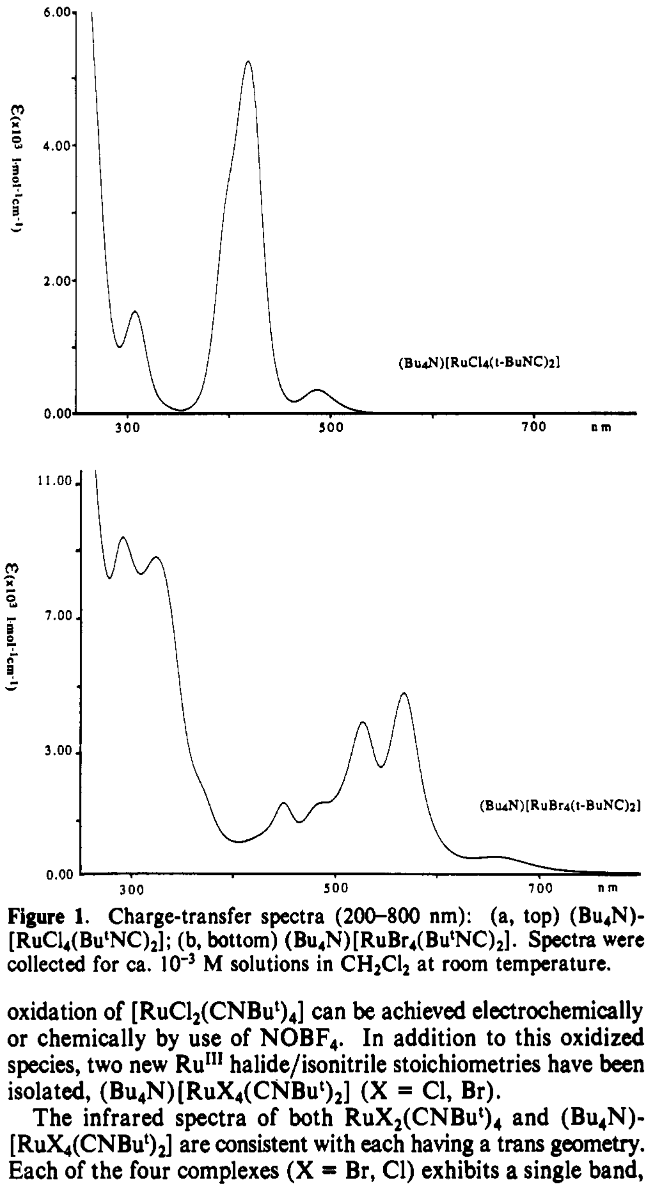

Figure 1. Charge-transfer spectra (200–800 nm): (a, top) $(Bu_4N)[RuCl_4(Bu^tNC)_2]$; (b, bottom) $(Bu_4N)[RuBr_4(Bu^tNC)_2]$. Spectra were collected for ca. 10^{-3} M solutions in CH_2Cl_2 at room temperature.

The infrared spectra of both $RuX_2(CNBu^t)_4$ and $(Bu_4N)[RuX_4(CNBu^t)_2]$ are consistent with each having a trans geometry. Each of the four complexes (X = Br, Cl) exhibits a single band, both in solution and in the solid state, for the NC stretching mode (ν_{NC}) and a similar situation for ν_{RuX} (Table I). Identification of the ν_{RuX} mode is verified by the shift of this band between the bromide and chloride analogues (Br/Cl: 0.76 and 0.79).[10]

The charge-transfer spectra of the complexes $[RuX_4(CNBu^t)_2]^-$ (X = Cl, Br) are shown in Figure 1. Although shifted, the spectra closely resemble those of *trans*-$[RuX_4(PhCN)_2]^-$, for which the crystal structure has been solved (X = Cl),[11] suggesting a similar trans geometry for the $CNBu^t$ complex. Spectral features that are characteristics of *trans*-$[RuX_4(L)_2]^-$ complexes include a weak leading band (parity forbidden $A_{2g} \rightarrow B_{2g}$) followed by a strong band that is split to a variable degree by spin–orbit coupling ($E_u \rightarrow B_{2g}$).[3] Additional features of the spectra will not be dealt with here but can be analyzed as for spectra of other *trans*-$[RuX_4L_2]^-$ species.[3]

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Table II. Voltammetric Data for The $\mathrm{Ru^{III/II}}$ Couple of $\mathrm{RuX_{6-n}(CNBu^t)_n}$, Measured As Described in the Text at the Temperatures Indicated[a,b]

	E_a	E_c	I_a/I_c	$E_{1/2}$	T, °C
$\mathrm{(Bu_4N)_2[RuCl_6]}$	*c*	−2.3			−30
$\mathrm{(Bu_4N)_2[RuBr_6]}$	*c*	−2.0			−35
$\mathrm{(Bu_4N)[RuCl_4(CNBu^t)_2]}$	−0.814	−0.910	0.94	−0.862	−25
$\mathrm{(Bu_4N)[RuBr_4(CNBu^t)_2]}$	−0.724	−0.810	0.82	−0.767	−25
$\mathrm{RuCl_2(CNBu^t)_4}$	0.624	0.534	0.97	0.579	−25
$\mathrm{RuBr_2(CNBu^t)_4}$	0.540	0.639	1.1	0.590	−25
ferrocene ($\mathit{Fe^{III/II}}$)[d]	*0.602*	*0.526*	*1.1*	*0.564*	*−25*

[a] E_a and E_c are the anodic and cathodic peak positions in volts. [b] $\mathrm{Ru^{IV/III}}$ couples not included in the table are as follows. $E_{1/2}$($\mathrm{Ru^{IV/III}}$): $\mathrm{(Bu_4N)_2[RuCl_6]}$, −0.378 V (−30 °C); $\mathrm{(Bu_4N)_2[RuBr_6]}$, −0.354 V (−30 °C). E_a($\mathrm{Ru^{IV/III}}$): $\mathrm{(Bu_4N)[RuCl_4(CNBu^t)_2]}$, 0.972 V; $\mathrm{(Bu_4N)[RuBr_4(CNBut)_2]}$, 0.852 V. [c] This couple was not reversible under these conditions; E_a is absent. [d] All Ru electrode potentials are given relative to the $\mathrm{Fc^+/Fc}$ couple (0 V). The ferrocene data are given as measured from the voltammogram.

No cis isomers were encountered, and attempts to convert trans isomers at elevated temperatures or to prepare the cis isomers independently were unsuccessful. The cis isomer of $\mathrm{RuCl_2(CNBu^t)_4}$ has been reported;[7] however, repetition of the synthesis yielded a crystalline product that proved to be a purely organic polymer of $\mathrm{CNBu^t}$.

The stoichiometries $\mathrm{RuX_5(CNBu^t)}$ and $\mathrm{RuX_3(CNBu^t)_3}$ could not be prepared by chemical or electrochemical methods. Electrochemical reduction induced halide substitution has been used in this laboratory to generate unstable stoichiometries through control of temperature and ligand concentration;[3] however, such voltammetric and bulk electrolysis experiments involving $\mathrm{CNBu^t}$ yielded only disubstituted products: $\mathrm{[RuX_4(CNBu^t)_2]}$ from $\mathrm{[RuX_6]}$, and $\mathrm{[RuX_2(CNBu^t)_4]}$ from $\mathrm{[RuX_4(CNBu^t)_2]}$. The apparent inability to generate $\mathrm{RuX_5(CNBu^t)}$ and $\mathrm{RuX_3(CNBu^t)_3}$ suggests that $\mathrm{CNBu^t}$ imposes a strong kinetic trans effect, labilizing the halide in the trans position.

Voltammetry. For the isonitrile complexes reported here, the $\mathrm{Ru^{IV/III}}$ couple was observed only for the $\mathrm{RuX_4(CNBu^t)_2}$ stoichiometry and was not reversible in $\mathrm{CH_2Cl_2}$, even at very low temperatures (−65 °C). The $\mathrm{Ru^{III/II}}$ couple was observed clearly for the bis- and tetrakis(isonitrile) complexes, but no electrochemical response was detected for the hexakis(isonitrile) complex $\mathrm{[Ru(CNBu^t)_6]^{2+}}$. The absence of the $\mathrm{[Ru(RNC)_6]^{3+/2+}}$ couple has been reported by Doonan and Balch, who examined the electrochemistry of $\mathrm{[Ru(MeNC)_6](PF_6)_2}$ and $\mathrm{[Fe(MeNC)_6](PF_6)_2}$ in $\mathrm{CH_3CN}$.[12] This prompted us to look for the $\mathrm{[Ru(CNBu^t)_6]^{3+/2+}}$ couple in solvents other than dichloromethane that have a wider electrochemical window. The voltammetry of the chloride series was then reexamined in these solvents in order to detect solvent-dependent shifts in potential or reactions involving solvent or electrolyte.

Voltammetry in $\mathrm{CH_2Cl_2}$. The dc voltammetric window in $\mathrm{CH_2Cl_2}$ was typically +1.4 to −2.6 V vs the $\mathrm{Fc^+/Fc}$ couple (0 V). The electrochemical data from experiments in $\mathrm{CH_2Cl_2}$ are listed in Table II. All the $\mathrm{Ru^{III/II}}$ couples were quasi-reversible, and no associated chemical reactions were observed. It should be noted, however, that when the electrochemical medium is not scrupulously dry, aquo-substituted species can interfere with the reversibility of these processes.

Voltammetry in $\mathrm{CH_3CN}$. The dc voltammetric window in $\mathrm{CH_3CN}$ was typically +2.0 V to −2.3 V vs the $\mathrm{Fc^+/Fc}$ couple (0 V). The reversibility of the $\mathrm{Ru^{III/II}}$ couple for $\mathrm{[RuCl_4(CNBu^t)_2]^-}$ was found to be temperature dependent. At low temperatures (−20 to −30 °C) the process was quasi-reversible, with the peaks centered at −0.809 V (Table III). At higher temperatures, chloride displacement by the solvent followed reduction, rendering the overall process nonreversible. The reversible voltammetric response of the substituted product was then observed, being shifted to a higher potential by 0.61 V from that of the initial material.

Table III. Voltammetric Data for the $\mathrm{Ru^{III/II}}$ Couple of $\mathrm{RuX_{6-n}(CNBu^t)_n}$ in $\mathrm{CH_3CN}$ and $\mathrm{SO_2}$, Measured As Described in the Text at the Temperatures Indicated[a]

	E_a	E_c	I_a/I_c	$E_{1/2}$	T, °C
	$\mathrm{CH_3CN}$ Solvent				
$\mathrm{(Bu_4N)[RuCl_4(CNBu^t)_2]}$	−0.843	−0.774	0.98	−0.809	−30
$\mathrm{RuCl_2(CNBu^t)_4}$	0.568	0.646	0.96	0.607	20
ferrocene ($\mathit{Fe^{III/II}}$)[b]	*0.439*	*0.525*	*0.98*	*0.482*	*20*
	0.449	*0.497*	*1.0*	*0.473*	*−30*
	$\mathrm{SO_2}$ Solvent				
$\mathrm{RuCl_2(CNBu^t)_4}$[c]	0.558	0.452	1.0	0.505	
	(0.601)	(0.495)		(0.458)	−30
ferrocene ($\mathit{Fe^{III/II}}$)[b]	*0.076*	*0.010*	*0.9*	*0.043*	*−30*

[a] Potentials are given in volts. [b] All Ru electrode potentials are given relative to the $\mathrm{Fc^+/Fc}$ couple (0 V). The ferrocene data are given as measured directly from the voltammogram. [c] Since ferrocene reacts with this compound in $\mathrm{SO_2}$ (see text), the data are given relative to ferrocene, which was measured independently; raw data is given in parentheses.

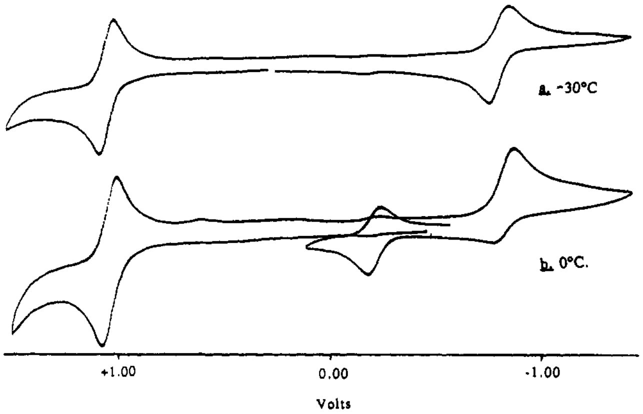

Figure 2. Cyclic voltammetry of $\mathrm{(Bu_4N)[RuCl_4(Bu^tNC)_2]}$ in $\mathrm{CH_3CN}$. The solution was ca. 10^{-4} M in sample and 0.1 M in $\mathrm{Bu_4NBF_4}$. Scan rates were 200 mV/s and potentials are given vs $\mathrm{Fc/Fc^+}$ (0 V).

The voltammetry related to the reduction-induced halide substitution is shown in Figure 2 and illustrated in the following scheme. The shift of 0.61 V in electrode potential between $\mathrm{[RuCl_4(CNBu^t)_2]^{-/2-}}$ and $\mathrm{[RuCl_3(Bu^tNC)_2(CH_3CN)]^{0/-}}$ is close to Lever's predicted value of +0.58 V for the replacement of chloride by $\mathrm{CH_3CN}$.[2]

$$\mathrm{[Ru^{III}Cl_4(CNBu^t)_2]^- + e^-} \xrightleftharpoons{-0.818\ \mathrm{V}} \{\mathrm{[Ru^{II}Cl_4(CNBu^t)_2]^{2-}}\} \xrightarrow{\mathrm{CH_3CN}} \mathrm{[Ru^{II}Cl_3(CNBu^t)_2(CH_3CN)]^-} \xrightleftharpoons{-0.213\ \mathrm{V}} \mathrm{Ru^{III}Cl_3(CNBu^t)_2(CH_3CN) + e^-}$$

A quasi-reversible response was detected for $\mathrm{RuCl_2(CNBu^t)_4}$ regardless of temperature. It has been our observation that $\mathrm{[RuClL_5]^+}$ and $\mathrm{[RuL_6]^{2+}}$ cannot usually be generated from $\mathrm{RuCl_2L_4}$ by electrochemical methods, and the absence of redox-related halide substitution here is not surprising.

The $\mathrm{Ru^{III/II}}$ couple for $\mathrm{[Ru(CNBu^t)_6]^{2+}}$ was not observed under these conditions.

Voltammetry in $\mathrm{SO_2}$. The dc voltammetric window achieved in liquid $\mathrm{SO_2}$ was +2.9 V to −0.5 V vs the $\mathrm{Fc^+/Fc}$ couple (0 V). The observable couples of $\mathrm{[RuCl_4(CNBu^t)_2]^-}$ and $\mathrm{RuCl_2(CNBu^t)_4}$ were quasi-reversible in this medium (Table III). The $\mathrm{Ru^{III/II}}$ couple for $\mathrm{[RuCl_4(CNBu^t)_2]^-}$ is predicted to be ca. −0.85 V, on the basis of voltammetry in $\mathrm{CH_2Cl_2}$ and $\mathrm{CH_3CN}$. It was not observed in $\mathrm{SO_2}$ due to the interference of solvent reduction at −0.5 V. The $\mathrm{Ru^{IV/III}}$ couple for this complex was quasi-reversible and observed at 0.984 V vs $\mathrm{Fc^+/Fc}$, which compares to 0.972 V in $\mathrm{CH_2Cl_2}$ (Table II).

The dichloride complex, $\mathrm{RuCl_2(CNBu^t)_4}$, appeared to react with ferrocene in $\mathrm{SO_2}$, changing in color from yellow to green. Sur-

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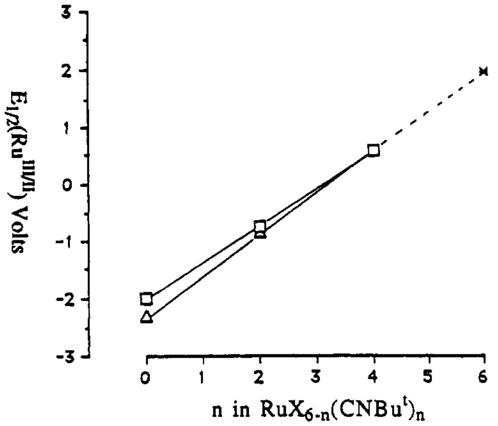

Figure 3. $Ru^{III/II}$ electrode potentials for the series $RuCl_{6-n}(Bu^tNC)_n$ (△) and $RuBr_{6-n}(Bu^tNC)_n$ (□) plotted against stoichiometry (n). $E_{1/2}$-($Ru^{III/II}$) values for $RuCl_6$ and $RuBr_6$ were estimated from E_c (Table II). The $Ru^{III/II}$ couple for $[Ru(Bu^tNC)_6]^{2+}$ (✱) is predicted to be +1.94 V by extrapolation.

prisingly, the $E_{1/2}$ value remained nearly constant but became irreversible. To avoid this complication, the reference Fc^+/Fc couple was approximated by measurement in an identical cell. The voltammetric data for the dichloride complex are given relative to Fc^+/Fc as well as absolutely in Table III.

There was no evidence for any reaction between ferrocene and $[Ru(CNBu^t)_6]^{2+}$; however, the $Ru^{III/II}$ couple was not detected in this medium at either a Pt or a glassy carbon electrode, at different temperatures and variant analyte concentrations.

Ligand Additivity. It is expected that complexes with π-accepting ligands will not follow a simple linear ligand additivity relationship, the deviations resulting from the additional stabilization of the metal-based HOMO upon interaction with a π-acid ligand. This topic is clearly dealt with in Bursten's general analysis of ligand additivity,[13] and the latter can be derived from AOM theory. On the basis of Lever's electrochemical ligand additivity parameter, E_L, the missing $[Ru(CNBu^t)_6]^{3+/2+}$ couple should be observed at +1.88 V vs Fc^+/Fc.[1,2] In Figure 3 the $E_{1/2}(Ru^{III/II})$ values for the series $RuX_{6-n}(CNBu^t)_n$ are plotted against stoichiometry (n), allowing extrapolation to the hexakis(isonitrile) complex and predicting a value of +1.94 V. It seems improbable that this couple occurs more positive than our electrochemical window (>+2.9 V), and it may be that the missing couple has not been detected simply because of some electrode phenomenon.

The d^5/d^6 couples of other homoleptic isonitrile complexes have been observed: $[Cr(PhNC)_6]^{0/+}$, −0.70 V;[14] $[Mn(PhNC)_6]^{+/2+}$, 0.62 V;[15] $[Re(PhNC)_6]^{+/2+}$, 0.7 V;[16] and $[Fe(MeNC)_6]^{2+/3+}$, 2.02 V[12] (corrected to correspond to our scale in CH_2Cl_2, vs Fc^+/Fc set at 0 V). Of these, the Mn and Fe complexes required a correction for the added stabilization of the metal HOMO, whereas the Cr and Re cases did not.[2,16] The degree of linearity illustrated in Figure 3 would suggest that no such correction is required for the present series. Furthermore, if a correction for the stabilization to the metal HOMO were applied, it would not account for the absence of the $Ru^{III/II}$ couple for $[Ru(CNBu^t)_6]^{2+}$, *unless the degree of added stabilization is itself nonlinear with stoichiometry.*

From Figure 3, the gradient of the line for the chloride data is +0.72 V per chloride replaced by $CNBu^t$ with a correlation coefficient (r) of 1.00. The gradient for the bromide data is +0.65 V per bromide replaced by $CNBu^t$ and $r = 0.999$. These shifts in electrode potential on substitution of halide are based on three data points each but are significantly larger than those predicted by Lever: $E_L(CNBu^t) - E_L(X^-) = +0.60$ V for Cl^- and +0.58 V for Br^-.[2] The steeper gradient observed here for the series $RuX_{6-n}(CNBu^t)_n$ suggests that the ligand $CNBu^t$ behaves as a stronger π-acceptor in the present series than in the complexes used to derive $E_L(CNBu^t)$.

The data set used to derive the individual E_L values is impressively large;[2] however, caution should be exercised when electrode potentials of complexes that contain π-acid ligands are predicted. The ability of many ligands to act as σ-donors or π-acceptors may be greatly altered by factors such as identity of the metal center or auxiliary ligands.

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