The rhenium(V) complex \([\text{HCpz} \, 3 \text{ReOCl}_2]\)\(^{+}\) (11\(^{+}\)), the tris(pyrazolyl)methane analogue of the known tris-(pyrazolyl)borate complex \((\text{HBpz} \, 3 \text{ReOCl}_2)\) (2), has been prepared. The two complexes are strikingly similar, as are the phosphine oxide adducts \((\text{HCpz} \, 3 \text{ReCl}_2(\text{OPPh}_3))\)Cl (13Cl) and \((\text{HBpz} \, 3 \text{ReCl}_2(\text{OPPh}_3))\) (4), which have been characterized by X-ray crystallography. Comparison of the bimolecular reduction of \([1\text{BF}_4]\) and \(2\) by triarylphosphines reveals a pronounced charge effect, with the cationic species being reduced by \(\text{PPh}_3\) about 1000 times faster than its neutral analogue in \(\text{CH}_2\text{Cl}_2\) at room temperature. Ligand substitution of the adducts \([3]^{+}\) and \(4\) is dissociative, with the cationic complex dissociating phosphate oxide about 56 times more slowly than the neutral compound. The relative impact of charge on ground and transition states in atom transfer reactions is discussed.

Introduction

There is considerable interest in the chemistry of inorganic compounds containing an oxygen atom that is multiply bonded to a transition metal in a high oxidation state. The salient feature of these compounds is their redox properties: such compounds can transfer an oxygen atom to reductants such as phosphines, sulfides, and alkenes.\(^8\) Oxygen atom transfer chemistry has been implicated in various reactions of industrial and biological importance, including olefin epoxidation\(^3\) and catalysis by cytochrome P-450.\(^4\)

There is a clear need to establish the factors which control the reactivity of the metal–oxo moiety. The effects of ancillary ligands and metal oxidation state have received the most attention.\(^5\) The effect of overall charge on metal-mediated oxygen atom transfer, in contrast, has not been explored systematically. We chose to try to isolate the effects of charge in a simple model system involving the reduction of rhenium(V) by triarylphosphines. Rhenium(V) forms a large number of stable octahedral complexes with multiple bonds to oxygen.\(^6\) Triphenylphosphine is widely used to study oxygen atom transfer because the reactions proceed cleanly and rapidly.\(^5,7\) Phosphine oxidation has been used to study the redox behavior of molybdenum-containing enzymes,\(^8\) models of tungsten enzymes,\(^9\) and oxometal porphyrin models of cytochrome P-450.\(^10\)

Here we describe the preparation of the cationic tris-(pyrazolyl)methane complex \([\text{HCpz} \, 3 \text{ReOCl}_2]\)\(^{+}\), which differs from the known\(^11\)–\(^13\) tris(pyrazolyl)borate complex \((\text{HBpz} \, 3 \text{ReOCl}_2)\) only in the substitution of carbon for boron and in the corresponding overall charge. It was anticipated that this change remote from the coordination sphere would only minimally perturb other steric and electronic features of the complexes. The results of a detailed kinetic study of the reduction of the two complexes by \(\text{PPh}_3\), as well as the subsequent dissociation of \(\text{OPPh}_3\) from the reduced species, thus speak directly to the differences in reactivity engendered by the change in overall charge.

Experimental Section

General Methods. Unless otherwise noted, all procedures were carried out on the benchtop. When necessary, acetonitrile, chloroform, and methylene chloride were dried over 4 Å molecular sieves, followed by CaH\(_2\). Pyridine was dried over CaH\(_2\). Anhydrous 1,2-dichlorobenzene (99%) was obtained from Aldrich and used without further purification. Dry ether was vacuum transferred from sodium benzophenone ketyl, \(\text{HCPz}_3\)^14, \((\text{HBpz} \, 3 \text{ReOCl})\) (2),\(^13\) and \(\text{ReOCl}_3(\text{OPPh}_3)(\text{SMes})\)\(^15\) were prepared using literature procedures. All other reagents were commercially available and used without further purification.

NMR spectra were measured on a General Electric GN-300 or a Varian-300 FT-NMR spectrometer. Chemical shifts for \(\text{H}\) and \(\text{C}\) spectra are reported in parts per million referenced to TMS; those for \(\text{P}\) spectra are reported in parts per million referenced to external \(\text{H}_3\text{PO}_4\). The peaks due to the pyrazole protons are listed only as their chemical shifts and multiplicities; their coupling constants are always 2 H. Pyrazole H-4 protons appear as triplets, and pyrazole H-3 and H-5 protons appear as doublets. Infrared spectra were recorded

as evaporated films on KBr plates on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. UV–vis data were collected on a Beckman DU-7500 diode-array spectrophotometer equipped with a multiecell transport block. Mass spectra were obtained on a JEOL JMS-AX 50HSA mass spectrometer using the FAB ionization mode and 3-nitrobenzyl alcohol as a matrix. In all cases, observed intensities were in satisfactory agreement with calculated isotopic distributions. Elemental analyses were performed by M-H-W Laboratories (Phoenix, AZ).

[HCp2]ReOCl3(Cl) (1). To a 50 mL round-bottom flask were added a magnetic stirbar, ReOCl3(OPPh3)(SM2) (1.28 g, 1.97 mmol), and HClp (0.44 g, 2.04 mmol). A Teflon needle valve was attached to the flask, which was then affixed to a vacuum line. Dry CH2Cl2 (20 mL) was added by vacuum transfer, and the solution was stirred for 4.5 h. After the volume was reduced by 50%, ether (10 mL) was condensed on top of the blue solution. The next day, the flask was removed from the vacuum line and the blue solid collected on a glass frit, washed with ether, and air-dried to yield 0.94 g of 1 (59 mg, 0.11 mmol). 1H NMR (CD2Cl2): δ 6.24 (t, 1H, pz trans to oxo); δ 6.92 (t, 2H, pz cis to oxo); 7.56 (d, 1H, pz trans to oxo); 8.42 (d, 2H, pz cis to oxo); 8.66 (d, 1H, pz trans to oxo); 9.32 (d, 2H, pz cis to oxo); 12.54 (s, 1H, pz,CH). 13C(NMR) (CDCl3): δ 150.8, 148.8, 141.0, 135.2, 111.3, 108.8, 75.3, 3.6. IR (cm−1): 1504 (m), 1444 (m), 1410 (w), 1399 (m), 1271 (s), 1244 (s), 1094 (m), 1062 (s), 1007 (s), 986 (s, Re=O), 908 (m), 854 (m), 830 (w), 765 (s), 1448 (w), 1409 (w), 1393 (m), 1264 (m), 1248 (m), 1224 (w), 1065 (vs, br, BF3). FABMS: m/z 487 (M+). Anal. Calcd for C28H25N6Cl3OPRe: C, 42.83; H, 3.10; N, 11.00. Found: C, 42.82; H, 3.22; N, 10.70. Found: C, 43.00; H, 3.10; N, 11.00.

[HCp2]ReOCl3(OPPh3)(Cl) (1). To a 25 mL Erlenmeyer flask were added [HCp2]Cl (59 mg, 0.11 mmol), PPh3 (102 mg, 0.39 mmol), and CH2CN (10 mL). After the mixture was stirred for 1 h, the crude brown product was collected by filtration and washed with two 10 mL aliquots of ether. More product was precipitated by adding ether to the mother liquor. The combined brown solids were recrystallized from chloroform/ether. The yellow crystals were collected on a glass frit, washed with ether, and air-dried. The yellow crystals were recrystallized from chloroform/ether with methanol. The yellow crystals were recrystallized from chloroform/ether, washed with ether, and air-dried. The yellow crystals were recrystallized from chloroform/ether, washed with ether, and air-dried. The yellow crystals were recrystallized from chloroform/ether, washed with ether, and air-dried.

X-ray Structure Determinations of [HCp2]ReOCl3(OPPh3)(Cl) (2.5, 3.05, 0.5, 0.95, and 2.05). Orange plates of the salt [3Cl] were deposited after slow diffusion of ether into a solution of the complex in CDCl3. A crystal was glued to the tip of a glass fiber in the air and examined on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation with a graphite monochromator (λ = 0.71073 Å). The crystal was triclinic (space group P1). The unit cell was determined on the basis of 24 reflections with 15.0° < θ < 15.9°. Crystal quality was monitored by recording three standard reflections approximately every 180 reflections measured; decay was negligible. An empirical absorption correction was applied (μ = 4.336 mm−1, transmission factors 0.8166–0.9999).

The rhenium atom was located on a Patterson map, the remaining non-hydrogen atoms were found on difference Fourier syntheses, and hydrogens were placed in calculated positions. Two additional peaks were found on difference Fourier syntheses that were assigned to the Cl and a CI of a disordered chloroform molecule located on the inversion center. There were additional small peaks near these on the difference map, but the other two Cl atoms could not be refined successfully and were omitted from the final model. Final full-matrix least-squares refinement on F2 converged at R = 0.0301 for 5166 reflections with Fobs > 4σ(Fobs) and R = 0.0330 for all data (wR2 = 0.0830 and 0.0866, respectively).
and isostructural analogue to the known tris(pyrazolyl)borate complex \( \text{[HPbz3]ReOCl}_2 \) (2).11–13 We set out to isolate salts of the hitherto unknown tris(pyrazolyl)methane complex \( \text{[HCpz3]ReOCl}_2 \) \( \text{[III]} \). While the rhenium(VII) complex \( \text{[HCpz3]ReO}_2 \) has been isolated,14 no other high-valent rhenium tris(pyrazolyl)methane complexes have been reported. This contrasts with the rich chemistry of rhenium(V) and rhenium(III) involving tris14 and tetrakis20 pyrazolylborate ligands.

Stirring ReOCl(1)(OPPh3)(SMc2)15,21 in dichloromethane with HCPz212 for 4.5 h yields a blue solution; addition of ether precipitates the air stable salt [I][Cl] (eq 1). [I][Cl] is sparingly soluble in polar organic solvents such as CH2Cl2, CHCl3, and CH3CN, and insoluble in ether, benzene, alcohols, and water. Its 1H NMR spectrum indicates that the complex has mirror symmetry, consistent with tridentate coordination of the HCPz3 ligand. FAB mass spectrometry confirms the composition of the cation, and a strong stretch in the IR at 985 cm\(^{-1}\) indicates the presence of the terminal oxo group.

Attempts to grow a crystal of [I][Cl] suitable for X-ray diffraction structure determination were unsuccessful. A crystal of the perrenated salt [I][ReO4] was studied by X-ray diffraction, which confirmed tridentate binding of the HCPz3 ligand.23 Refinement of the structure was complicated by the presence of two independent molecules in the unit cell, and the determination of accurate metrical data was frustrated by positional disorder involving the oxo and chloride ligands.24 A similar disorder problem is observed with crystals of (HBPz3)ReOCl2 (2).25 The latter is isostructural with (HBPz3)MoOCl3, whose disorder has been described in detail in the literature.26

The tetrafluoroborate salt of [I][Cl] was prepared by metathesis of [I][Cl] with AgBF4 in acetonitrile. Surprisingly, the 1H NMR spectra of [I][Cl] in acetonitrile-D3 and CDCl3 revealed an unusual \( \text{[HCpz3]ReOCl}_2 \) decoupled to a singlet at 8.50 ppm, while the 1H NMR spectrum of the hexafluoroborate salt in CDCl3 was dominated by a signal at 8.36 ppm, possibly due to a change in the coordination of the oxy anion.

Results

Synthesis and Characterization of Tris(pyrazolyl)methane Rhenium Complexes. In our efforts to prepare an isostructural analogue of 1 with a similar chemical and spectroscopic behavior, we decided to prepare an isoelectronic compound. This compound was found to be \( \text{[HCpz3]ReOCl}_2 \), which has a similar structure to 1 but lacks the 

\[ \text{[HCpz3]ReOCl}_2 \] 

(1)


(23) Crystal data for [I][ReO2(CDC13)2]·CH2Cl2·C6H6·NaO2Re, green, M = 198.14 T = 293 K, triclinic, space group P1, a = 12.028(3) Å, b = 15.492(3) Å, c = 16.024(4) Å, α = 78.52(2)°, β = 74.90(2)°, γ = 67.94(2)°, V = 2654.71(11) Å³, Z = 4, ρ = 2.297 g cm⁻³, μ(Mo Kα) = 0.979 mm⁻¹, F(000) = 1692, crystal size 0.20 x 0.18 mm. A total of 9345 unique reflections with θ = 2.00-2.49° were collected. For 7179 reflections with θ = 2.00-2.49°, R = 0.1292 and GOF= 

\[ F_o^2 = 1.078. \]

spectrum of [1]BF₄ differs from that of the chloride salt in the location of the methine proton (δ 9.19 in [1]BF₄ vs δ 12.19 in [1]Cl in CD₃CN). Other spectroscopic characteristics (UV–vis, IR) are essentially unaffected by the counterion.

Solutions of [1]Cl are stable for weeks at room temperature in noncoordinating solvents. However, [1]Cl undergoes ligand substitution in acetonitrile over several days to form an equilibrium mixture of products. [1]H NMR and FAB mass spectrometric analyses show unreacted starting material, free HCpz₃, and a new species which we assign as {[(n²-HCpz₃)ReOCl₂]₂(μ-HCl)}⁺. The mass spectrum shows a prominent peak at m/z = 1009 which possesses an isotope pattern consistent with the presence of two rhenum and five chlorine atoms. The [1]H NMR shows new pyrazole triplets in a 2:1 ratio, four new singlets (2:2:1:1 ratio), and a methine singlet; these all identify a species possessing mirror symmetry. The methine doublets (2:2:1:1 ratio), and a methine C–H resonances of the dimer and of free HCpz₃ always appear in a 2:1 ratio, which suggests that 3 equiv of [1]Cl is required to form 1 equiv of the dimer, consistent with the stoichiometry of eq 2. The tetrafluoroborate salt [1]BF₄ is stable indefinitely in CD₃CN.

\[\text{3} \text{[(HCpz}_3\text{)ReOCl}_2\text{]Cl} \rightarrow \text{CD}_3\text{CN} \]

Synthesis and Structure of Rhenium(III) Compounds. When [1]Cl is stirred in the presence of PPh₃, oxygen atom transfer takes place within 1 h to produce the isolable phosphine oxide adduct ([HCpz₃]ReCl₂(OPPh₃))Cl ([3]Cl, eq 3). The tetrafluoroborate salt reacts analogously to give [3]BF₄.

\[\text{[1]Cl} + \text{PPh}_3^+ \rightarrow \text{[3]BF}_4^- \]

Mass spectra show the parent ion [3]⁺ at m/z = 749, and the presence of bound phosphine oxide is confirmed by the P–O stretch in the IR (νPO = 1122 cm⁻¹ for [3]Cl). The [1]H NMR spectra are paramagnetically shifted but extremely sharp, which is characteristic of octahedral Re(III) complexes. The sharp spectrum allows one to observe normal H–H coupling constants, which in cationic [3]⁺ are slightly shorter than in neutral 4. The observed phosphorus–oxygen distances (1.499(4) Å av) and Re–Cl bond lengths, which in cationic [3]⁺ are typical of d⁴ phosphine oxide adducts.

The neutral tris(pyrazolyl)methane complex [3]Cl (Figure 1) and the tris(pyrazolyl)borate complex 4 (Figure 2) were determined by single-crystal X-ray diffraction. Crystallographic details are listed in Table 1, and bond distances and angles in Table 2. The structures are remarkably similar. The only statistically significant differences in metal–ligand distances are the Re–Cl bond lengths, which in cationic [3]⁺ are slightly shorter than in neutral 4. The observed phosphorus–oxygen distances (1.499(4) Å av) and Re–O–P bond angles (151° av) are typical of d⁴ phosphine oxide adducts.

Reduction Kinetics. The kinetics of the reduction of the rhenium(V) oxo complexes [1]Cl, [1]BF₄, and 2 by triphenylphosphine were studied spectrophotometrically under pseudo-first-order conditions (excess PPh₃) at 25.3 °C in dichloromethane. The reactions obey first-order kinetics to t ≥ 0 halves (Figure S1, Supporting Information), and are also observed to be first-order in triphenylphosphine. Second-order rate constants were extracted from the linear plots of kobs versus [PPh₃] (Figure S2); these give kred = 0.047(8) M⁻¹ s⁻¹ for the o xo complex 2, PPh₃, and excess ligand. However, the phosphine oxide adduct 4 has never been isolated or observed directly because oxygen atom transfer is usually slower than subsequent displacement of the phosphine oxide ligand. We have successfully prepared 4 by using high concentrations of PPh₃ and relatively low temperatures. Under these conditions, bimolecular atom transfer is much faster than unimolecular ligand exchange (vide infra), and 4 can be isolated uncontaminated by the phosphine adduct (HPbz₃)ReCl₂(PPh₃).

The structures of the tris(pyrazolyl)methane complex 3Cl (Figure 1) and the tris(pyrazolyl)borate complex 4 (Figure 2) were determined by single-crystal X-ray diffraction. Crystallographic details are listed in Table 1, and bond distances and angles in Table 2. The structures are remarkably similar. The only statistically significant differences in metal–ligand distances are the Re–Cl bond lengths, which in cationic [3]⁺ are slightly shorter than in neutral 4. The observed phosphorus–oxygen distances (1.499(4) Å av) and Re–O–P bond angles (151° av) are typical of d⁴ phosphine oxide adducts.

Figure 1. SHELXTL plot (30% thermal ellipsoids) of the cation of [(HCpz₃)ReCl₂(OPPh₃)]Cl·0.5CDCl₃ ([3]Cl·0.5CDCl₃). Hydrogen atoms are omitted for clarity.

an excess of P(C₆D₅)₃ in CD₂Cl₂. Monitoring by ³¹P and ¹H phosphine oxide adducts entirely to a lower enthalpy of activation.

Table 1. Crystallographic Data for [(HCpz)Re(OPPh₃)Cl₂]Cl·0.5CDCl₃ (3)Cl·0.5CDCl₃ and (HBpz)Re(OPPh₃)Cl₂·C₆H₆ (4·C₆H₆)

<table>
<thead>
<tr>
<th></th>
<th>3Cl·0.5 CDCl₃</th>
<th>4·C₆H₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>C₂₈H₂₆D₂₃Cl₃N₀Re</td>
<td>C₃₀H₂₄BCl₂N₀Re</td>
</tr>
<tr>
<td>tw</td>
<td>845.75</td>
<td>826.52</td>
</tr>
<tr>
<td>temp (K)</td>
<td>293</td>
<td>293</td>
</tr>
<tr>
<td>χ (Å)</td>
<td>0.710 73 (Mo Kα)</td>
<td>0.710 73 (Mo Kα)</td>
</tr>
<tr>
<td>space group</td>
<td>P1</td>
<td>P1</td>
</tr>
<tr>
<td>total no. of data collected</td>
<td>5511</td>
<td>5890</td>
</tr>
<tr>
<td>no. of indep reflns</td>
<td>5511</td>
<td>5890</td>
</tr>
</tbody>
</table>

[55x83]° for the two reactions (Table S1a and Figure S4a, Supporting Information). Reduction of [3]Cl and [4]Cl at 25.3 °C is 0.0574(3) M⁻¹s⁻¹, a 20% increase over the rate in CH₂Cl₂; the rate for 2 is identical to that in dichloromethane. The variation of the rate of reduction of [1]⁺ with solvent and counterion suggests that ion-pairing effects have a modest influence on the reaction.

Rate constants were measured over a >30 °C temperature range in 1,2-dichlorobenzene to obtain activation parameters for the two reactions (Table S1a and Figure S4a, Supporting Information). Reduction of [1]Cl takes place with ∆H° = 13.4 ± 0.5 kcal/mol and ∆S° = −19 ± 2 cal·mol⁻¹·K⁻¹ (289–322 K), while 2 is reduced with ∆H° = 17.11 ± 0.13 kcal/mol and ∆S° = −19.7 ± 0.4 cal·mol⁻¹·K⁻¹ (291–351 K). The observed entropies of activation are identical within experimental error and are consistent with an associative process. The enhanced rate of reaction of triphenylphosphine with cationic [1]Cl is due entirely to a lower enthalpy of activation.

To determine whether oxygen atom transfer is reversible, the phosphine oxide adducts [3]Cl and [4] were each treated with an excess of P(C₆H₅)₃ in CD₂Cl₂. Monitoring by ³¹P and ¹H NMR spectroscopy revealed no free P(C₆H₅)₃ in either case; the only products observed were the ReIII–P(C₆H₅)₃ adducts and free OP(C₆H₅)₃. Thus, the degenerate exchange reaction (eq 4) does not take place at a rate competitive with phosphine oxide dissociation; oxygen atom transfer is effectively irreversible.

![Figure 2. SHELXL plot (30% thermal ellipsoids) of (HBpz)ReCl₂(OPPh₃)·C₆H₆ (4·C₆H₆). Hydrogen atoms and the solvent of crystallization are omitted for clarity.](image-url)
cal-mol\(^{-1}\) K\(^{-1}\) (306–337 K). The neutral complex 4 dissociates phosphine oxide about 56 times more rapidly than does cationic \([3]^+\) (\(k_{3\text{BPE}} = 4.99(9) \times 10^{-5}\) s\(^{-1}\) at 62 °C, \(k_4 = 2.80(6) \times 10^{-3}\) s\(^{-1}\) at 64 °C).

### Discussion

**Tris(pyrazolyl)borate and Tris(pyrazolyl)methane as Homologous Ligands.** To discern the effect of charge on oxygen atom transfer, we set out to prepare the tris(pyrazolyl)methane rhenium(V) oxo complex \([\text{HCPz}_3\text{ReOCl}_3]^+ (\text{[1]}^+)\) as a cationic analogue of the known\(^{11–13}\) neutral tris(pyrazolyl)borate complex \([\text{HBpz}_3\text{ReOCl}_2 (\text{OPPh}_3)]^+\) (2). It was hoped that this minimal perturbation—substitution of a carbon for a boron remote from the metal—would allow a change in charge without significant changes in other steric or electronic properties. The suitability of this comparison was in some doubt because the two ligands are known to differ in binding strength. Reger has reported in his work with lead(II) and tin(II) that neutral tris(pyrazolyl)methane ligands do not bind as tightly as the anionic tris(pyrazolyl)borate analogues.\(^{32}\) Vahrenkamp has noted similar behavior in his studies of zinc(II) coordination compounds possessing tripodal ligands: whereas tris(pyrazolyl)borate ligands are reliably tridentate, the tris(pyrazolyl)methane ligands in oxomolybdenum(V) complexes complicate their isolation.\(^{34}\) The difference in binding strength is also evident in oxorhenium complexes. Herrmann has reported that \([\text{HCPz}_3\text{ReO}]^+\) is rather sensitive to hydrolysis,\(^{18}\) in contrast to the marked stability of \([\text{HBpz}_3\text{ReO}]^+\). Likewise, \([\text{HCPz}_3\text{ReOCl}_3]\) (1) and \([\text{HBpz}_3\text{ReOCl}_2 (\text{OPPh}_3)]^+\) (2) are close analogues. The \(^1\)H NMR data for both complexes show diamagnetic species possessing tridentate poly(pyrazolyl) ligands with mirror symmetry. The rhenium-oxo stretches in the IR spectra are nearly identical (\(v_{\text{oxo}} = 987 \text{ cm}^{-1}\), \(v_2 = 975 \text{ cm}^{-1}\)), as are the \(\lambda_{\text{max}}\) and \(\epsilon\) values in the UV–vis spectra (for \([\text{HCPz}_3\text{ReOCl}_3]\) (1) \(\lambda_{\text{max}} = 678 \text{ nm}\), \(\epsilon = 120 \text{ M}^{-1} \text{ cm}^{-1}\); for 2, \(\lambda_{\text{max}} = 690 \text{ nm}\), \(\epsilon = 125 \text{ M}^{-1} \text{ cm}^{-1}\)).

Unfortunately, positional disorder involving the oxo and chloride ligands\(^{24}\) precluded obtaining reasonable metrical data for \([\text{HCPz}_3\text{ReOCl}_3]^+\) (1)\(^{23}\) and \([\text{HBpz}_3\text{ReOCl}_2 (\text{OPPh}_3)]^+\) (2).\(^{25}\) X-ray crystallographic data for the rhenium(III) phosphine oxide adducts \([\text{HCPz}_3\text{ReCl}_3(\text{OPPh}_3)]\) (3) and \([\text{HBpz}_3\text{ReCl}_3(\text{OPPh}_3)]\) (4) show that these two metal complexes have qualitatively identical structures (Figures 1 and 2). Even quantitative differences in bond lengths and angles are remarkably small (Table 2). The only statistically significant difference in bond lengths are in the Re–Cl bond distances, and even here the differences are less than 0.02 Å. These results are in line with other structural comparisons in

---

**Table 3.** Second-Order Rate Constants for the Addition of Tertiary Phosphines to \([1]\)Cl and 1,2-Dichlorobenzene, 312 K

<table>
<thead>
<tr>
<th>(\text{PAr}_3)</th>
<th>(3\sigma_P)</th>
<th>(k_{\text{HKL}}) (M(^{-1}) s(^{-1}))</th>
<th>(k_2) (M(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{PCp}_3\text{Cl}]_2)</td>
<td>0.81</td>
<td>1.18(6)</td>
<td>9.27(9) \times 10^{-4}</td>
</tr>
<tr>
<td>([\text{PCp}_3\text{H}]_2)</td>
<td>0.51</td>
<td>0.78(4)</td>
<td>9.17(7) \times 10^{-4}</td>
</tr>
<tr>
<td>([\text{PCz}_3\text{H}]_2)</td>
<td>0.00</td>
<td>0.181(3)</td>
<td>3.58(3) \times 10^{-4}</td>
</tr>
<tr>
<td>([\text{PCp}_3\text{H}]_2)</td>
<td>0.69</td>
<td>0.032(3)</td>
<td>2.08(10) \times 10^{-4}</td>
</tr>
</tbody>
</table>

---

Charge Effects on Oxygen Atom Transfer

the literature, which show that complexes of tris(pyrazolyl)-borates and tris(pyrazolyl)methanes can have essentially identical structures.32–35,36–37 We conclude that the rhenium(V) oxo compounds [1] and 2 are isometric and isoelectronic analogues, as are the phosphine oxide adducts [3] and 4. Thus, differences in reactivity may be attributed primarily to the difference in overall charge.

### Charge Effects on Atom Transfer

Most metal oxo complexes oxidize triphenylphosphine to triphenylphosphine oxide.3 Most the mechanisms have been discussed extensively, and is generally believed to involve direct attack of the phosphine at the oxo ligand.7,8–30 The reactions described here also appear to follow this mechanism. The kinetics are cleanly bimolecular, and substituent effects on the phosphine are consistent with nucleophilic attack by the phosphine at oxygen. Initial outer-sphere electron transfer appears unlikely, given the low propensity of rhenium(V) oxo complexes to act as outer-sphere oxidants.40 Prior coordination of the phosphine to the metal center41 also seems improbable given the coordinative saturation of these octahedral complexes. Note that dissociation of the HCP23 ligand is not observed in the noncoordinating solvents in which oxygen atom transfer has been studied, and even in acetonitrile takes place much more slowly than reaction with phosphine.

Compounds possessing the [Re=O]3+ core exhibit a wide range of reactivity toward PPh3. At one end of the spectrum are complexes which show no reactivity at the oxygen atom. (HBpz3)ReO(PPh3)Cl, for example, does not react with phosphine,29 and the dimeric oxorhenium(V) chelate [CH3ReO-(LS2)]2 ligates PPh3 to form 2 equiv of monomeric CH3ReO-(LS2)2PPh3 without undergoing reduction (LS2 = o-SC6H4-CH2Si).42 Many rhenium(V) oxo compounds are reduced by PPh3 to form deoxygenated products. [ReO(OSiMe3)2PPh3]+ and (PPh3)2ReOCI4 are typical examples, reacting with PPh3 in refluxing acetonitrile to form rhenium(III) phosphine adducts. At the reactive end of the spectrum is the cationic [Me3tacn]ReOCI4]+ (Me3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane), which is reduced within a day at room temperature.38

While the reduction of 2 is typical, requiring elevated temperatures or prolonged times, the reaction of [1]+ with triphenylphosphine is as fast as any reported for a rhenium(V) oxo complex. Despite having nearly identical ligand environments, the cationic complex [1]BF4 reacts about 1000 times faster than the neutral tris(pyrazolyl)borate compound 2 in dichloromethane at room temperature. This dramatic rate enhancement is the first clean and quantitative example of a change effect on oxygen atom transfer and shows that such effects can result in a rate enhancing effect by changing ligand environments.45

A key question is whether the charge effect on atom transfer is primarily kinetic or thermodynamic in origin. One could argue

---

(41) This possibility has been conclusively excluded in the reactions of [(bpy)2RuO(μ-OPMe2)]+, where atom transfer is observed to exogenous phosphine in preference to bound phosphine: Marmion, M. E.; Takeuchi, K. J. Am. Chem. Soc. 1986, 108, 510–511.

---

Figure 4. Orbital interactions in oxygen atom transfer.

that the cation reacts faster because there is a greater driving force for atom transfer, either because the cation has an intrinsically weaker Re=O bond or because the cationic fragment binds the phosphine oxide more tightly. While we cannot rule out the former effect, it seems unlikely to be large, given the body of evidence in the organic literature suggesting that polar effects on bond strength are minimal.46 The effects of charge on ligand binding can be addressed using the results of the study of ligand substitution reactions of the phosphine oxide adducts [3] and 4. Since these reactions are dissociative, the energies of activation for ligand loss are approximately equal to the equilibrium binding energies of the ligands. Cationic [3]+ does indeed bind phosphate oxide more tightly than neutral 4, as indicated by its slower rate of ligand dissociation. However, the quantitative difference in binding (ΔΔH⁰ ΔG = 1.2 kcal/mol) is much smaller than the kinetic difference in oxygen atom transfer (ΔΔH⁰ ΔE = 3.7 kcal/mol). Thus, while tighter binding of phosphate oxide may contribute to the rate difference, it cannot be its major determinant.

The observed substituent effects on atom transfer also indicate that thermodynamic effects exert a relatively minor influence on the reaction rate. The reductions of both [(HCP23)ReOCl2]+ (11)+ and (HBpz3)ReOCl2 (2) go faster as the triarylphosphines become more electron-rich (Table 3). Qualitatively, both reactions involve nucleophilic attack of the phosphine at the oxo group. Quantitatively, though, there is again a significant difference: cationic [1]+ is much more sensitive to changes in phosphine substituent than 2 (Figure 3; ρ1=−1.08; ρ2=−0.47). One would expect the opposite if reduction of [1]+ were favored by substantial driving force effects, for by the Hammond postulate the more exothermic reaction should be the less selective. The greater selectivity of [1]+ points to a kinetic effect, with the positive charge influencing the stability of the transition state. This result is in line with other studies of atom transfer that find poor correlations of reaction kinetics with thermodynamic driving force.47

The charge effect can be rationalized by considering the molecular orbitals involved in the reaction. Increasing the overall charge on the metal complex should lower the energy of all the molecular orbitals, in particular the M=O π* orbital which interacts with the phosphorus lone pair in the transition state for reduction (Figure 4). The metal LUMO–phosphine HOMO interaction will therefore be stronger for the cationic complex, and the reduction will go faster. In other words, the cationic species is more electrophilic than the neutral, a result which

has been suggested in other studies of metal oxo complexes.\textsuperscript{48} What is remarkable is the magnitude of the effect revealed by the present study: an increase of one unit of positive charge accelerates atom transfer by 2–3 orders of magnitude.

Conclusions

Spectroscopic comparison of the new rhenium(V) oxo complex \([\text{HCpz}_3]\text{ReOCl}_2]^+ (1^+)\) and the known complex \((\text{HBpz}_3)\text{ReOCl}_2 (2)\) and structural comparison of the corresponding phosphine oxide adducts \([\text{HCpz}_3]\text{Re(OPPh}_3\text{Cl}_2]^+ ([3]^+)\) and \((\text{HBpz}_3)\text{Re(OPPh}_3\text{Cl}_2 (4)\) demonstrate that \(\text{HBpz}_3\) and \(\text{HCpz}_3\) are isoelectronic and isostructural analogues. The difference in charge creates substantial differences in reaction rates. Oxygen atom transfer is accelerated by a factor of \(~1000\) in the cationic complex \([1]^+\) as compared to neutral \(2\). This effect is much larger than the difference in ligand substitution rates (cationic \([3]^+\) dissociates OPPh\(_3\) about 50 times more slowly than neutral \(4\)) and appears to be primarily a transition-state effect. This large effect suggests that charge may be as important as the nature of ancillary ligands in tuning the reactivity of oxometal species.

Acknowledgment. We thank Dr. Maoyu Shang for his assistance with the X-ray structures. Support from the National Science Foundation (Grant CHE-97-33321-CAREER), the Camille and Henry Dreyfus Foundation (New Professor Award to S.N.B.), DuPont (Young Professor Award to S.N.B.), and the University of Notre Dame are gratefully acknowledged.

Supporting Information Available: Figures and tables of kinetic data for the phosphine reductions of \([1]\)Cl and \(2\) and ligand substitution of pyridine for OPPh\(_3\) in \([3]\)BF\(_4\) and \(4\) and tables of crystallographic parameters, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen coordinates for \([3]\)Cl\(\cdot 0.5\text{CDCl}_3\) and \(4\cdot \text{C}_6\text{H}_6\). This material is available free of charge via the Internet at http://pubs.acs.org.