Structural and Mechanistic Studies of Oxo-Transfer Reactions of Bis(arylimido)oxorhenium(VII)

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Kinetic, spectroscopic, and crystallographic studies have been carried out on products derived from the compound $MeRe(NAr)_2(O)$ (**1**, Ar = 2,6-diisopropylphenyl) in reactions with $PR_n(OR)_{3-n}$, abbreviated PY_3. This reaction yields $Y_3P{=}O$ and a mononuclear Re(V) compound, $MeRe(NAr)_2(PY_3)_2$. The molecular structures of $MeRe(NAr)_2(PMe_2Ph)_2$ (**3a**) and $MeRe(NAr)_2(dmpe)_2$ (**3j**, dmpe = 1,2-bis(dimethylphosphino)ethane) were determined by X-ray crystallography. In benzene solution at room temperature **3a** exchanges with free PMe_2Ph, based on variable-temperature ^1H and ^{31}P NMR data. A kinetic study of the reactions between **1** and $PR_n(OR)_{3-n}$ revealed that **3** forms at a rate proportional to the concentrations of PY_3 and **1**. Alkoxy-containing compounds are highly reactive compared with others; for example, for $P(OMe)_2Ph$ and PMe_2Ph, the respective values of k/L mol^{-1} s^{-1} at 298 K in benzene solution are 7.2×10^1 and 2.1×10^{-4}. The rate-enhancing effect of alkoxy groups can be found in all comparable reagents used in this work. The kinetic data were analyzed by considering σ-bonding effects (as represented by pK_a values), steric effects (in terms of cone angles), and composite quantities (such as the stereoelectronic parameter χ). The π-acidity of PY_3 appears to play a dominant role, suggesting an intermediate, [Re]−O−PY_3, the stability of which depends strongly upon the π-acidity of PY_3 and thus governs the reaction rate. This strong acceleration of reactivity by an OR group bound to phosphorus appears unprecedented. The role of competitive Lewis π-acids appears to be predominant in these reactions. This mechanism is supported by the activation parameters: $\Delta S^{\ddagger}$ is nearly invariant, whereas the variation of $\Delta H^{\ddagger}$ determines the trend in reactivity. When the reaction between **1** and an insufficient quantity of $P(OMe)_nPh_{3-n}$ (n = 1−3) was carried out, the product was a $Re^{VII}-Re^{V}$ adduct, $MeRe(NAr)_2O{\cdot}MeRe(NAr)_2$ (**2′**), suggesting a step in which the nonligated Re(V) intermediate $MeRe(NAr)_2$ reacts with **1**, when the concentration of $P(OMe)_nPh_{3-n}$ does not allow its reaction with $MeRe(NAr)_2$. Compound **2′** slowly rearranged to an isolable compound, $\{MeRe(NAr)_2\}_2(\mu\text{-}O)$ (**2**), which has been structurally characterized.

Introduction

Oxo-transfer reactions are key steps in many catalytic and enzymatic transformations. Attention has been paid to those high-valent transition metal−oxo complexes that catalyze the oxidation of various substrates and their relevance to enzyme function.[1−5] Particular emphasis has been directed toward oxo-transfer reactions involving oxo complexes of Mo^{VI}/Mo^{IV} and W^{VI}/W^{IV} because they mimic molybdenum and tungsten oxo-transferase enzymes.[6,7] Kinetic studies show that $[MoO_2(mnt)_2]^{2-}$ with mnt^{2-} = 1,2-dicyanoethylenedithiolate reacts more rapidly with any given phosphine than $[WO_2(mnt)_2]^{2-}$ does.[8] The stereoelectronic effects of the oxygen acceptors have been studied in great detail with alkyl and aryl phosphines, PEt_nPh_{3-n}.[9,10] The steric influence of phosphines, as measured by cone angles in the range 132−145°, is not important in the oxo-transfer reactions; reactivity differences are governed by differences in their basicity. We have shown that high-valent methylrhenium complexes catalyze oxygen and sulfur transfer reactions, in which Re(VII) and Re(V) species play an important role.[11,12] The Re(VII)−Re(V) conversion was studied both in aqueous solution with hypophosphorous acid as the stoichiometric sink for oxygen and in organic media with trisubstituted phosphines in that role. The reverse transformation has been studied with a variety of oxygen donors and with episulfides.[12]

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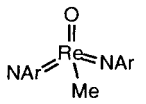
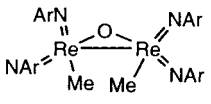
Chart 1. Structural Formulas of Rhenium Compounds



1



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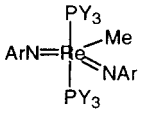

3

3a PMe_2Ph **3f** $P(OEt)_2Ph$

3b $P(OMe)Ph_2$ **3g** $P(OEt)Ph_2$

3c $P(OMe)_2Ph$ **3h** PMe_3

3d $P(OMe)_3$ **3i** PEt_3

3e $P(OEt)_3$ **3j** dmpe

Here we address the kinetics and mechanism of oxo-transfer reactions from Re(VII) in the compound $MeRe(NAr)_2O$ with Ar = 2,6-diisopropyl, **1**, to phosphines PR_nPh_{3-n}, phosphinites ($P(OR)Ph_2$), phosphonites ($P(OR)_2Ph$), and phosphites ($P(OR)_3$). The marked accelerating effect of the alkoxy group on the oxophilicity of the phosphorus compounds may be without precedent. Depending on conditions, one can isolate a μ-oxo compound, **2**, or a bis(phosphine) complex of rhenium(V), **3**. We have studied these reactions with spectroscopy, crystallography, and kinetics.

Experimental Section

Reagents. *tert*-Butylisocyanide and the phosphorus compounds were purchased from Aldrich or Strem and used as received. The solvents benzene, toluene-d_8, and benzene-d_6 were dried with sodium/benzophenone and stored in a nitrogen-filled glovebox. Samples of $MeRe(NAr)_2O$ with Ar = 2,6-diisopropyl, **1**, were prepared according to the literature procedure.[13] NMR spectra were determined with a Bruker DRX-400 spectrometer. Chemical shifts for ^1H and ^{13}C were measured relative the residual resonances in deuterated solvents, C_6D_5H (δ_H 7.16 ppm, δ_C 128.39 ppm) and $C_6D_5CD_2H$ (δ_H 2.09 ppm). ^{31}P chemical shifts were referenced to 85% H_3PO_4. Elemental analyses were performed by Desert Analytics.

Kinetics. A stock solution of **1** in benzene was prepared and stored in a nitrogen-filled glovebox. Kinetic studies were carried out under nitrogen at 298 K with spectrophotometric measurements using Shimadzu UV 3101PC or Applied Photophysics DX 17MV stopped-flow instruments as appropriate for the rate of a given reaction. The phosphorus reagent was used in at least 10-fold excess over the rhenium species, allowing data analysis by first-order kinetics. Kinetic traces were recorded to >4 half-times for the more rapid reactions of $P(OR)Ph_2$, $P(OR)_2Ph$, and $P(OR)_3$. This equation was used to fit the absorbance−time data:

$$\mathrm{Abs}_t = \mathrm{Abs}_\infty + (\mathrm{Abs}_0 - \mathrm{Abs}_\infty)e^{-k_\psi t} \qquad (1)$$

The data for the more slowly reacting compounds were fit by the method of initial rates. The early stages of the absorbance−time curve were fit to the equation of a straight line; the slope of that line, Abs′, was converted into the initial rate (in concentration units, mol L^{-1} s^{-1}) by division by $\Delta\epsilon_\lambda$, the difference in molar absorptivity between reactants and products at wavelength λ: v_i = Abs′/$\Delta\epsilon_\lambda$. Activation parameters were calculated from the least-squares fit of values of $\ln(k/T)$ to $1/T$, which were linear over the range studied, according to the equation

$$\ln(k/T) = 23.76 + \Delta S^\ddagger/R - (\Delta H^\ddagger/RT) \qquad (2)$$

Table 1. Spectroscopic Data for $MeRe(NAr)_2L_2$ Complexes at 298 K

L	NMR, δ/ppm ^1H NMR	^{13}C NMR	^{31}P NMR	λ_{max} (ϵ/ L mol^{-1} cm^{-1})
$P(OMe)_3$	3.00	−29.3	104.7[a]	581 (13 400)
$P(OMe)_2Ph$	2.86	−28.5	120.2[b]	595 (13 000)
$P(OMe)Ph_2$	2.78	−27.5	90.9[c]	598
$P(OEt)_3$	2.99	−30.0	101.3[a]	582 (13 600)
$P(OEt)_2Ph$	2.74	−27.2	*d*	598 (12 700)
$P(OEt)Ph_2$	2.56	−25.0	89.0[e]	622
PMe_3	2.73	−31.8	−33.0	630 (12 000)
PMe_2Ph	2.38	−27.5	−23.6	629 (12 000)
PEt_3	2.90	−31.8	−11.2[b]	638 (3200)
dmpe	2.84	−31.3	−24.7, −47.5	632 (11 200)

[a] 243 K. [b] 253 K. [c] 203 K. [e] 223 K. [d] The resonance due to the coordinated ligand is too broad to be seen at 298 K.

Characterization of Rhenium Products. **{MeRe(NAr)$_2$}$_2$-(μ-O) (2).** A 10 mL benzene solution of 100 mg (0.18 mmol) of **1** and 11 μL of $P(OMe)_3$ (0.093 mmol) was stirred for 16 h at room temperature under N_2. The solvent was then removed under vacuum, and the residue was recrystallized with CH_2Cl_2/Et_2O. The orange-red crystals were collected by filtration. Yield: 65 mg (66%). ^1H NMR (C_6D_6, 298 K): 1.03 (d, J = 6.8 Hz, 24H), 1.11 (d, J = 6.8 Hz, 24H), 3.16 (s, 6H), 3.76 (septet, J = 6.8 Hz, 8H), 6.9−7.0 (m, 12H). ^{13}C NMR (C_6D_6, 298 K): 14.3 (**C**H_3Re). CI MS, m/z = 1119. Anal. Found: C, 53.50; H, 6.79; N, 4.97. Calcd for $C_{50}H_{74}N_4ORe_2$ (fw = 1119.56): C, 53.64; H, 6.66; N, 5.00.

MeRe(NAr)$_2$(PMe$_2$Ph)$_2$ (3a). It was formed quantitatively; although no effort was made to isolate a large quantity of it, crystals were grown from a toluene/hexane mixture in an NMR tube at −30 °C. The green solution, which is air-sensitive, gives the following NMR data. ^1H NMR (C_6D_6, 283 K): 1.22 (d, J = 6.8 Hz, 12 H), 1.30 (d, J = 6.8 Hz, 12 H), 1.39 (m, 12 H), 2.40 (t, J = 4.6 Hz, 3 H), 3.25 (septet, J = 6.8 Hz, 2 H), 3.77 (septet, J = 6.8 Hz, 2 H), 6.9−7.1 (m, 8 H), 7.1−7.2 (m, 8 H). ^{13}C NMR (C_6D_6, 298 K): −27.5 (*C*H_3Re), 14.9 (Re−P(*C*H_3)$_2$Ph), 23.7 (CH(*C*H_3)$_2$), 25.0 (CH(*C*H_3)$_2$), 27.4 (*C*H(CH$_3$)$_2$), 27.6 (*C*H(CH$_3$)$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K): −23.0.

MeRe(NAr)$_2$(dmpe)$_2$ (3j). A 50 mL hexane solution that contained 50 mg (0.088 mmol) of **1** and 50 μL of dmpe (0.30 mmol) was stirred for 8 h. About 40 mL of the solvent was then removed under vacuum, and dark blue crystals were collected by filtration. Yield: 60 mg (45%). ^1H NMR (C_6D_6, 283 K): 0.66 (d, J = 2.8 Hz, 12H), 1.00 (m, 4H), 1.09 (m, 12H), 1.33 (d, J = 6.8 Hz, 12H), 1.38 (d, J = 6.8 Hz, 12H), 1.72 (m, 4H), 2.84 (t, J = 4.6 Hz, 3H), 3.49 (septet, J = 6.8 Hz, 2H), 3.80 (septet, J = 6.8 Hz, 2H), 6.9−7.1 (m, 6 H). ^{13}C NMR (C_6D_6, 298 K): −31.3 (*C*H_3Re). $^{31}P\{^1H\}$ NMR (C_6D_6, 283 K): −24.7 (t, J = 10 Hz), −47.5 (t, J = 10 Hz). Anal. Found: C, 52.15; H, 8.36; N, 3.26; P, 14.19. Calcd for $C_{37}H_{69}N_2P_4Re$ (fw = 852.02): C, 52.16; H, 8.16; N, 3.29; P, 14.54. Other rhenium complexes of the same type were identified by NMR techniques, as summarized in Table 1.

Crystallography. The crystals of **2**, **3a**, and **3j** were selected under oil. Data collection was performed using a Bruker CCD-1000 diffractometer with Mo Kα (λ 0.71073 Å) radiation. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[14] The systematic absences in the diffraction data were consistent for space groups *Pnma* and *Pna*2$_1$ for **2** and *Cc* and *C*/2*c* for **3a** and **3j**, but only the

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Table 2. Crystallographic Data for 2, 3a, and 3j

	2	3a	3j
chemical formula	$C_{50}H_{74}N_4ORe_2$	$C_{41}H_{59}N_2P_2Re$	$C_{37}H_{69}N_2P_4Re$
fw	1119.53	828.04	852.02
temp	173(2) K	173(2) K	173(2) K
λ	0.71073 Å	0.71073 Å	0.71073 Å
cryst syst	orthorthombic	monoclinic	monoclinic
space group	$Pna2_1$	$C2/c$	$C2/c$
unit cell dimens	$a = 18.0488(8)$ Å	$a = 22.0978(12)$ Å	$a = 25.585(2)$ Å
	$b = 14.1615(6)$ Å	$b = 9.7329(5)$ Å	$b = 9.5889(8)$ Å
	$c = 19.2969(9)$ Å	$c = 18.5748(10)$ Å	$c = 18.1936(16)$ Å
	$\alpha = \beta = \gamma = 90°$	$\beta = 94.437(1)°$	$\beta = 109.361(1)°$
volume	4932.3(4) Å^3	3983.0(4) Å^3	4211.1(6) Å^3
Z	4	4	4
density (calcd)	1.508 g/cm^3	1.381 g/cm^3	1.344 g/cm^3
μ	49.42 cm^{-1}	31.60 cm^{-1}	30.63 cm^{-1}
F_{000}	2240	1696	1760
R^a	0.0268	0.0188	0.0353
$R_w{}^a$	0.0454	0.0437	0.0705

[a] $R(wF^2) = \sum[w(F_o^2 - F_c^2)]/\sum[w(F_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$.

latter yielded chemically reasonable and computationally stable refinements.[15] A successful solution by direct methods located most of the non-hydrogen atoms from the E-map; the remaining ones were located in an alternating series of least-squares cycles and difference Fourier maps. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients, except H(19) for **3a**. Atom H(19) was located from the difference map, and its isotropic displacement coefficient was refined independently while the C(19)−H(19) distance was constrained. The carbon atoms C(4), C(5), C(6), C(7), C(8), C(9), C(20), and C(21) in **3a** are equally disordered over two positions. Some "soft" restraints were used to refine these disordered atoms. The final least-squares refinement of 262 parameters against 4066 data resulted in residuals R and R_w of 0.0188 and 0.0437, respectively. In the case of **3j**, the final least-squares refinement of 209 parameters against 4114 data resulted in residuals R and R_w of 0.0353 and 0.0705, respectively. The final difference Fourier map contained one high peak (ca. 2.17 e/Å^3) 1.2 Å from the atom P(2). This peak corresponds to the phosphorus lone pair of electrons. The final least-squares refinement of 532 parameters against 10 065 data for **2** resulted in residuals R and R_w of 0.0268 and 0.0454, respectively. The final difference Fourier map was featureless. Crystallographic data for compounds **2**, **3a**, and **3j** are given in Table 2.

Results

Formation of 3a. When excess PMe_2Ph was added to a C_6D_6 solution of **1**, the color of the solution slowly changed to intense green. The NMR data for the resulting solution showed that the reaction had occurred quantitatively according to the following equation:

$$MeRe(NAr)_2O\ (\mathbf{1}) + 3\ PMe_2Ph \rightarrow MeRe(NAr)_2(PMe_2Ph)_2\ (\mathbf{3a}) + Me_2PhP{=}O \quad (3)$$

A broad singlet from *Me*Re in the ^{1}H spectrum was seen at 2.38 ppm, and its corresponding ^{13}C resonance was found at −27.5 ppm. The ^{1}H−^{1}H 2-D COSY NMR spectrum showed that a multiplet at 3.23 ppm was coupled with a doublet at 1.18 ppm, whereas the other multiplet at 3.74 ppm was coupled with a doublet at 1.26 ppm; the isopropyl groups of the arylimido ligands are responsible. The other broad singlet at 1.38 ppm in the ^{1}H spectrum was assigned to the coordinated *Me*$_2$PPh protons. The intensities of the signals are consistent with the formula written for **3a**. The ^{31}P{^{1}H} NMR signal from the free phosphine has δ −45.45 ppm; the spectrum of the products showed two singlets at 28.26 and −23.35 ppm in a 1:2 ratio, consistent with $Me_2PhP{=}O$ and **3a**, respectively. The broadening of certain resonances results from ligand exchange of **3a**. When that compound, which has been structurally characterized, was studied by NMR, the same broadening phenomenon was seen. The agreement of NMR with crystallography confirms that phosphine and not phosphine oxide is coordinated to rhenium.

The other $P(OR)_nPh_{3-n}$ and PR_3 (R = Me, Et) phosphines also reacted with **1** to yield **3b**−**i**. It should point out that the reaction of dmpe with **1** yielded a trans bis-dmpe product, **3j**, instead of a cis chelating-dmpe compound. This has been confirmed by both ^{1}H and ^{31}P NMR studies, as well as X-ray structural analysis. Table 1 presents the NMR and UV/vis data for **3**. The ^{1}H and ^{13}C NMR chemical shifts of the compounds are similar for all the complexes. Compared with other rhenium(VII) compounds, $MeRe(NR)_nO_{3-n}$, R = 1-adamantyl[16] or 2,6-diisopropylphenyl,[13] the ^{1}H resonance for *Me*Re in **3** is shifted downfield; its ^{13}C resonance is shifted significantly upfield to around −30 ppm. The ^{31}P resonances of the coordinated phosphine ligands of **3** are closer to the resonances of the free ligands than to those of the phosphine oxides. The electronic spectra of compounds in series **3** are also similar to one another except for $MeRe(NAr)_2(P(OR)Ph_2)_2$ (R = Me, Et) and $MeRe(NAr)_2(PEt_3)_2$. Two intense bands are found at ~440 ($\epsilon \approx 12\,000$ L mol^{-1} cm^{-1}) and 600 nm ($\epsilon \approx 12\,000$ L mol^{-1} cm^{-1}), Figure 1. The intensities are similar to those of the complexes formed from $P(OR)_3$ and $P(OR)_2Ph$, but for the phosphines the 440 nm peak is more intense than the one at 600 nm. From PR_3 to $P(OR)_2R$, the bands are blue shifted; a further blue shift was noted for the $P(OR)_3$ compounds. For example, $MeRe(NAr)_2(PY_3)_2$ has λ_{max} 630 nm for $PY_3 = PMe_3$, but 580 nm for $PY_3 = P(OMe)_3$.

Other reactions analogous to those written in eq 1 were attempted. Certain other phosphines in place of

(15) All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Shdldrick, Bruker Analytical X-ray Systems, Madison, WI).

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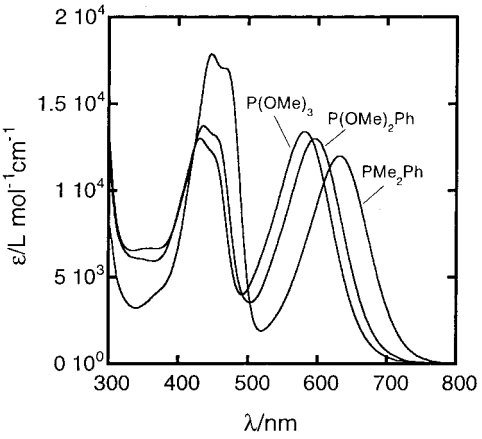

Figure 1. UV−visible spectra of $MeRe(NAr)_2L_2$, Ar = 2,6-diisopropylphenyl; L = $P(OMe)_3$, $P(OMe)_2Ph$, and PMe_2Ph, in benzene at 298 K.

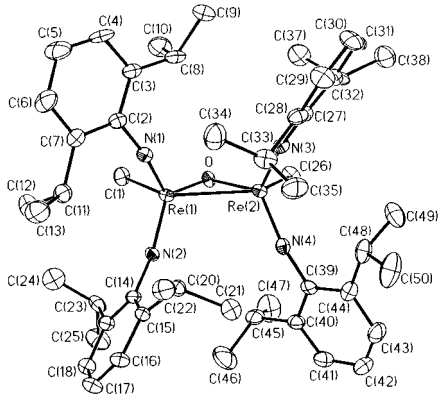

Figure 2. ORTEP view of the molecular structure of $\{MeRe(NAr)_2\}_2(\mu\text{-O})$ (**2**) with thermal ellipsoids at 30% probability level.

those specified gave no reaction; the unsuccessful ones were PPh_3 and P(c-hexyl)$_3$. Likewise, no reaction occurred with *tert*-BuNC.

Formation of 2. When only 0.5 equiv of $P(OMe)_3$ was added to **1** in benzene, the solution immediately turned to brownish green and then slowly changed to orange-red. The ^{1}H NMR of the isolated product showed a singlet at 3.16 ppm and a septet at 3.76 ppm, which are assigned to C*H*$_3$Re and −C*H*Me$_2$, respectively. The intensities of these resonances and others lead to the formulation of $\{MeRe(NAr)_2\}_2(\mu\text{-O})$ (**2**) for the isolated product, eq 4. The presence of the oxygen atom was supported by the mass and elemental analysis data and was ascertained by X-ray structure determination. The molecular structure of **2**, illustrated in Figure 2, clearly shows that the two Re centers are linked by a bridging oxygen atom. The bridge is nearly symmetrical (195.8 (3)/194.6 (3) pm), and the 268.42(4) pm Re−Re distance indicates a strong interaction between the two rheniums. Selected bond distances and angles for **2** are summarized in Table 3.

$$2MeRe(NAr)_2O\ (\mathbf{1}) + P(OMe)_3 \rightarrow \{MeRe(NAr)_2\}_2(\mu\text{-O})\ (\mathbf{2}) + (MeO)_3P{=}O \quad (4)$$

Observation of 2′. ^{1}H NMR studies showed that a mixture of **3c** and a new compound, **2′**, was initially formed when insufficient amount of $P(OMe)_2Ph$ was added to a C_6D_6 solution of **1**. This new species has a more complicated NMR spectrum. Two singlets of equal intensity were recorded at 3.07 and 3.36 ppm, and the corresponding ^{13}C resonances occur at 14.3 and 3.3 ppm; they appear to arise from *Me*Re. That product also showed two equal intensity septets at 3.75 and 3.82 ppm and four equal intensity doublets at 1.09, 1.12, 1.22, and 1.27 ppm from the arylimido ligands. On the basis of the intensities of these signals and the following observations, the initial product of the reaction with a limited amount of $P(OMe)_2Ph$ is claimed to be a Re^{VII}−Re^{V} adduct, $MeRe(NAr)_2O{\cdot}MeRe(NAr)_2$ (**2′**), an isomer of **2**.

A single product, **2′**, was also obtained from the reactions of **1** with other $P(OR)_nPh_{3-n}$ compounds, $n \geq 1$; however, **2′** was not detected for the reactions with better phosphine ligands, such as PMe_3 and dmpe. The ^{1}H and ^{13}C NMR spectra of **2′** from the cited reactions were all the same, independent of the phosphorus compound used. This adduct slowly converted to the isolable and well-characterized product **2** in solution. Addition of PMe_3 to a C_7D_8 solution of **2′** (and, necessarily, some **2**) yielded **1** and without any detectable amount of O=PMe_3, eq 5. The original amount of **2** remained unchanged during the reaction time. The slowness of the reaction between **1** and PMe_3 (see below) and the lack of O=PMe_3 demonstrate that **3h** does not arise from reactions of PMe_3 with **1** or **2**. A similar Re^{VII}−Re^{V} adduct, $MeReO_3{\cdot}MeReO_2(PPh_3)_2$, has been isolated and structurally characterized by Herrmann and co-workers.[17]

$$MeRe(NAr)_2O{\cdot}MeRe(NAr)_2\ (\mathbf{2'}) + PMe_3 \rightarrow MeRe(NAr)_2(PMe_3)_2\ (\mathbf{3h}) + MeRe(NAr)_2O\ (\mathbf{1}) \quad (5)$$

Structure of 3. The molecular structures of **3a** and **3j** are shown in Figure 3 and Figure 4, respectively. Selected bond distances and angles for **3a** and **3j** are summarized in Table 4 and Table 5, respectively. In both cases, the rhenium center adopts a distorted trigonal bipyramidal structure with nearly trans phosphines, such that the angle P1−Re−P1′ is 175.62(3)° for **3a** and 177.78(6)° for **3j**. Of the three equatorial groups, CH_3 and two NAr, the N1−Re−N1′ angle is enlarged to 153.54(12)° for **3a** and 153.4(2)° for **3j** over the ideal 120° to ease the steric demand of the two imido

Table 3. Selected Bond Lengths (pm) and Bond Angles (deg) for $\{MeRe(NAr)_2\}_2(\mu\text{-O})$ (2, Ar = 2,6-diisopropylphenyl)

Re(1)−Re(2)	268.42 (4)	Re(1)−O−Re(2)	86.85 (13)
Re(1)−O	195.8 (3)	N(1)−Re(1)−N(2)	117.7 (2)
Re(2)−O	194.6 (3)	N(1)−Re(1)−O	123.70 (19)
Re(1)−C(1)	213.4 (5)	N(1)−Re(1)−C(1)	95.3 (2)
Re(2)−C(26)	213.6 (5)	N(1)−Re(1)−Re(2)	111.13 (15)
Re(1)−N(1)	173.7 (5)	N(2)−Re(1)−Re(2)	106.53 (14)
Re(1)−N(2)	174.2 (4)	N(2)−Re(1)−O	118.33 (18)
Re(2)−N(3)	175.0 (4)	N(2)−Re(1)−C(1)	101.5 (2)
Re(2)−N(4)	174.3 (5)	C(1)−Re(1)−O	78.72 (18)
N(1)−C(2)	140.7 (7)	C(1)−Re(1)−Re(2)	125.03 (16)
		O−Re(1)−Re(2)	46.39 (10)
		Re(1)−N(1)−C(2)	169.5 (4)
		Re(1)−N(2)−C(14)	162.1 (4)
		Re(2)−N(3)−C(27)	170.2 (4)
		Re(2)−N(4)−C(39)	170.2 (4)

(17) Herrmann, W. A.; Roesky, P. W.; Wang, M.; Scherer, W. *Organometallics* **1994**, *13*, 4531.

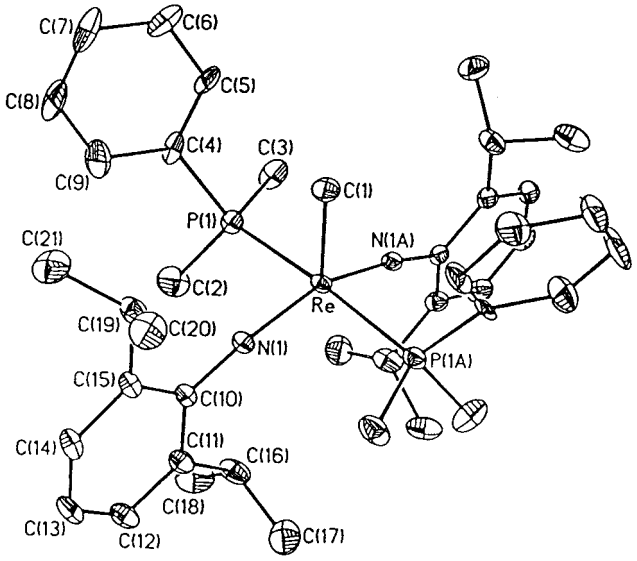

Figure 3. ORTEP view of the molecular structure of $MeRe(NAr)_2(PMe_2Ph)_2$ (**3a**) with thermal ellipsoids at 30% probability level.

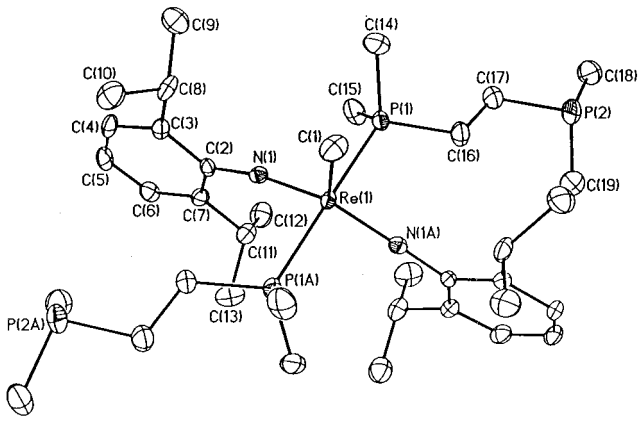

Figure 4. ORTEP view of the molecular structure of $MeRe(NAr)_2(Me_2PCH_2CH_2PMe_2)_2$ (**3j**) with thermal ellipsoids at 40% probability level.

ligands. The rhenium lies in the plane defined by the C1 carbon and the two nitrogen atoms. The two aromatic rings of the imido ligands lie perpendicular to the plane defined by C1−P1−Re−P1′. As a result, the isopropyl groups on the same aromatic ring are not equivalent because rotation about the N−C bond is hindered by the phosphine ligands.

Variable-Temperature NMR Studies. As reported in an earlier section, the ^{1}H resonances of **3a** in C_6D_6 are broad at room temperature. The broad singlet at δ 2.38 ppm at 298 K changes to a triplet with a coupling constant $^3J_{P-H}$ 4.8 Hz upon cooling to 283 K. Other multiplets sharpened as well when the temperature was decreased, as shown in Figure 5a. On the other hand, all the signals were broadened at $T > 298$ K. Thus the spectrum of **3a** shows that the septet resonances for the methine protons of the two inequivalent isopropyl groups disappeared into the baseline. The ^{31}P resonance of coordinated PMe_2Ph also sharpened at 283 K, whereas it was too broad to be observed at 313 K, Figure 5b. Over this range of temperature, the methyl resonance of the other product, $Me_2PhP{=}O$, remained as a sharp doublet. As T increased over that range, however, the signal from free PMe_2P lost its coupling and became a broad singlet.

Table 4. Selected Bond Lengths (pm) and Bond Angles (deg) for $MeRe(NAr)_2(PMe_2Ph)_2$ (3a, Ar = 2,6-diisopropylphenyl)

Re−N(1)	180.94 (18)	N(1)−Re−C(1)	103.23 (6)
Re−C(1)	213.9 (3)	N(1)−Re−N(A)	153.54 (12)
Re−P(1)	243.27 (6)	N(1)−Re−P(1)	90.87 (6)
N(1)−C(10)	137.7 (2)	N(A)−Re−P(1)	88.13 (6)
		C(1)−Re−P(1)	92.190 (15)
		P(1)−Re−P(A)	175.62 (3)
		C(10)−N(1)−Re	171.02 (15)

Table 5. Selected Bond Lengths (pm) and Bond Angles (deg) for $MeRe(NAr)_2(Me_2PCH_2CH_2PMe_2)_2$ (3j, Ar = 2,6-diisopropylphenyl)

Re−N(1)	179.9 (4)	N(1)−Re−C(1)	103.31 (11)
Re−C(1)	213.3 (6)	N(1)−Re−N(A)	153.4 (2)
Re−P(1)	242.95 (12)	N(1)−Re−P(1)	90.85 (11)
N(1)−C(2)	138.4 (5)	N(A)−Re−P(1)	88.63 (11)
		C(1)−Re−P(1)	91.11 (3)
		P(1)−Re−P(A)	177.78 (6)
		C(2)−N(1)−Re	168.3 (3)

The exchange between free PMe_2P and **3a** occurs more slowly than the NMR time scale at 283 K. Even at 203 K, exchange between free $P(OMe)Ph_2$ and **3b** is not slow enough to give sharp ^{31}P resonances for either species. With $P(OMe)_2Ph$ and **3c**, sharp resonances are seen for samples cooled to 253 K. Addition of PMe_2Ph to a solution of **3b** or **3c** resulted in the immediate formation of **3a**. Likewise, $P(OMe)_2Ph$ will replace $P(OMe)Ph_2$, causing the conversion of **3b** into **3c**.

Kinetics. The kinetics of reaction between **1** and PMe_2Ph was studied by monitoring the formation of **3a** at 630 nm (ϵ 1.2 × 10^4 L mol^{-1} cm^{-1}) in the presence of a large excess of phosphine. The initial rate (v_i) method was used, because the reaction is so slow; in such experiments the initial concentration of each reagent was varied. The rate was first-order with respect to each reagent. Accordingly, the plot of v_i against the product $[PMe_2Ph] \times [\mathbf{1}]$ is linear, as presented in Figure 6; its slope gives the second-order rate constant as $k = (2.15 \pm 0.02) \times 10^{-4}$ L mol^{-1} s^{-1}. The same method was used to study other comparably slow reactions of PMe_3, PEt_3, and dmpe. On the other hand, the reactions of other $P(OR)_nPh_{3-n}$ compounds, $n = 1-3$, proved much more rapid. The entire kinetic profile was collected and analyzed by pseudo-first-order kinetics; values of k_ψ vary linearly with the concentration of the phosphorus reagent, as shown in Figure 7. Among this set of compounds a considerable variation in rate constant was found; for example, $P(OMe)_2Ph$ is ∼100-fold more reactive than $P(OMe)_3$. The rate constants for all the compounds are summarized in Table 6, where k corresponds to the rate constant for the following equation:

$$-\frac{d[\mathbf{1}]}{dt} = k[\mathbf{1}] \times [P(OR)_nPh_{3-n}] \qquad (6)$$

Experiments were carried out on the reactions between 0.13 mM **1** and 3−9 mM $P(OMe)_3$ and $P(OEt)Ph_2$ with 34 mM $(MeO)_3P{=}O$ added. No difference in rate was found. This rules out a significant interaction between **1** and the phosphate product. To explore the role of ligands in the reactivity, experiments were carried out with added pyridine and bromide, both of which are ligands that bind tightly to Re(V) compounds such as MeRe(O)(mtp)L (mtp = dianion of

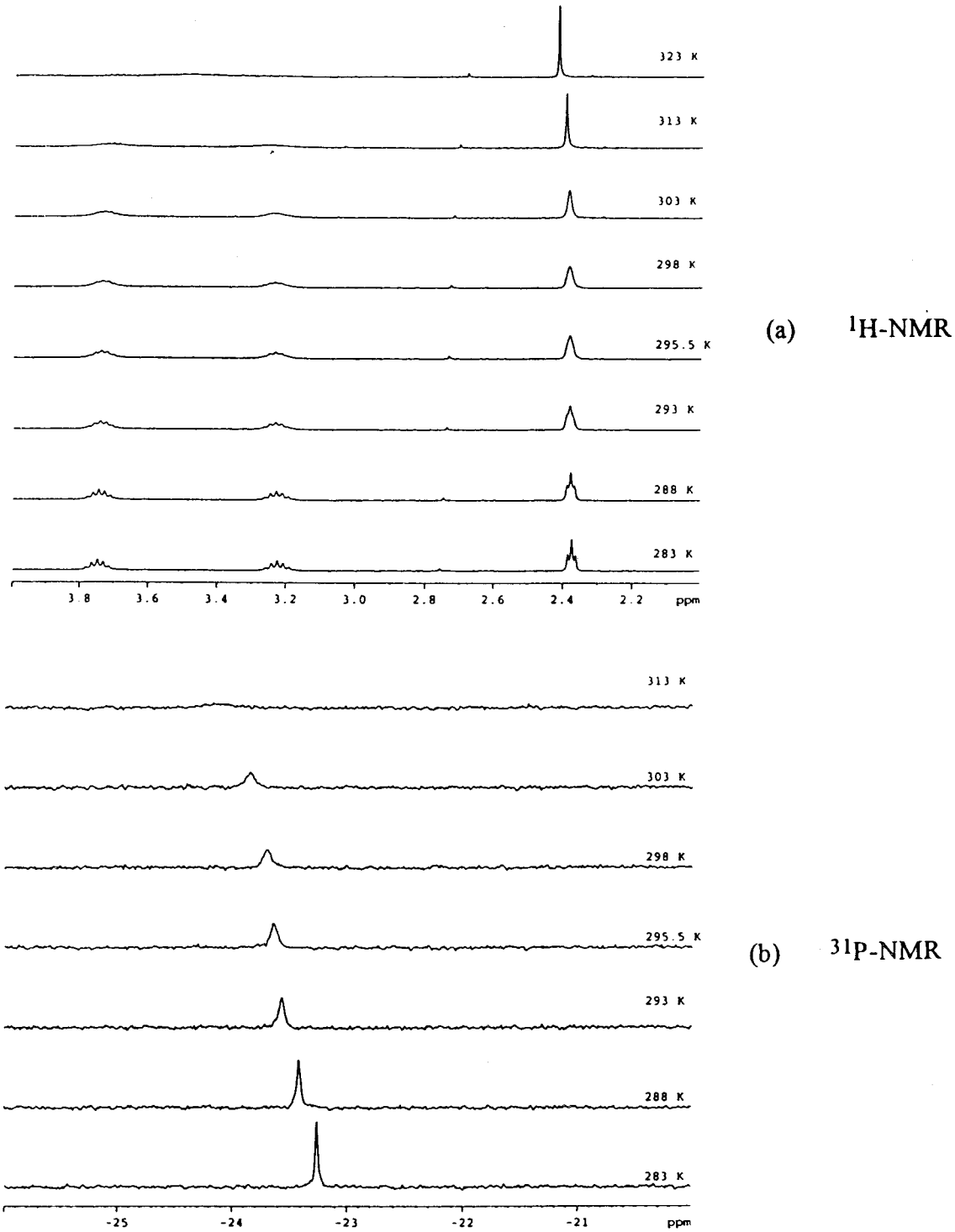

Figure 5. ^{1}H and ^{31}P NMR spectra of MeRe(NAr)$_2$(PMe$_2$Ph)$_2$ (**3a**) in C_6D_6.

2-mercaptomethylthiophenol). There was no difference in the rate of reaction between P(OMe)$_3$ and **1** when 50 mM pyridine or 4 mM tetra-*n*-butylammonium bromide was added.

Several of the reactions were followed as a function of temperature in the range 283−313 K to allow the determination of the activation parameters. The values of $\Delta S^{\ddagger}$/J K^{-1} mol^{-1} are −154 for P(OMe)$_3$ and P(OMe)$_2$Ph and not far from those for PMe$_3$ (−146) and PMe$_2$Ph (−140). Values of $\Delta H^{\ddagger}$ are small but variable, in the range 16.4−52.4 kJ mol^{-1} for the four compounds cited. These data are presented in Table 7.

Discussion

Ligand Exchange of 3. The ^{1}H NMR spectrum of **3a** at 283 K is consistent with its structure in the solid state, in that two sets of resonances for the isopropyl groups could clearly be observed, Figure 5a. The triplet pattern of the methyl group bound to rhenium arises from coupling to phosphorus, which establishes that the two phosphine ligands remain coordinated to rhenium in solution. Even at 298 K the two isopropyl groups on a single aryl group remain different by NMR, showing that the rotational barrier along the N1−C10 bond is reasonably large. The *Me*−Re resonance loses its cou-

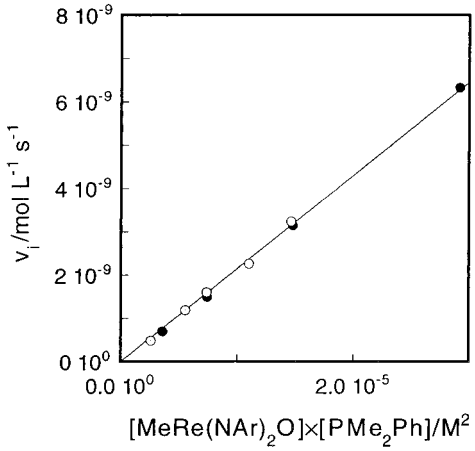

Figure 6. Plot of the initial rates against the product of the concentrations of $MeRe(NAr)_2O$, **1**, and PMe_2Ph, with 0.18−1.5 mM **1** and 20−80 mM PMe_2Ph in benzene at 298 K. Solid circles are shown for data with constant [$MeRe(NAr)_2O$], and solid triangles are for data collected at constant [PMe_2Ph].

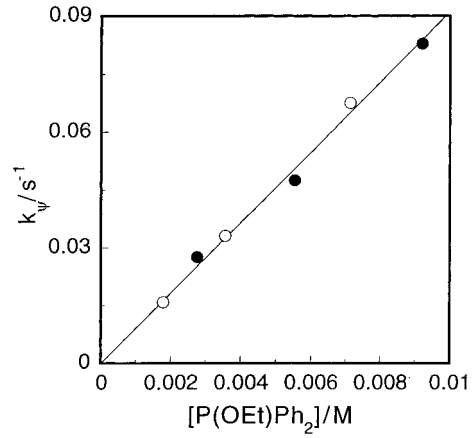

Figure 7. Plot of the pseudo-first-order rate constants against the concentration of $P(OEt)Ph_2$, showing the lack of effect of added $(MeO)_3P{=}O$. Circles are with 34 mM phosphate added, and triangles without it being added; in C_6H_6 at 298 K.

pling to phosphorus at 298 K; this result suggests that exchange between coordinated and free phosphine may have become more rapid than the NMR time scale at 298 K. Because the ^1H NMR resonance of free PMe_2Ph broadens with temperature, whereas that of $Me_2PhP{=}O$ remains sharp, the exchange process does not involve the phosphine oxide. It is feasible, but not established, that exchange occurs by a pseudorotation mechanism.

Considerations of Electronic, Steric, and Basicity Effects. Let PY_3 represent any of the compounds encompassed by the formulas $P(OR)_nPh_{3-n}$ and PR_nPh_{3-n}, $n = 0-3$. There is nothing in the data to support a concerted reaction ($Re{=}O + PY_3 \rightarrow Re + Y_3P{=}O$). Such a simplified scheme would suggest an undocumented correlation between rate constant and properties that represent the nucleophilicity or Lewis basicity of PR_3. We consider certain parameters that have been summarized in Table 6. For example, k decreases in this order: PMe_3 (pK_a 8.6) > PMe_2Ph (pK_a 6.5) > $PMePh_2$ (pK_a 4.6). However, the reaction of **1** with PCy_3 (pK_a 9.7) is *much* slower than that with PMe_2Ph. Steric effects appear to play little role, at least when the cone angle

Table 6. Cone Angles, pK_a Values, and Electronic Parameters for PY_3 and Rate Constants for Their Reaction with 1

L	θ, deg[a]	pK_a[b]	χ/cm^{-1} [a]	k_{298}/L mol^{-1} s^{-1}
$P(OMe)_3$	107	2.60	24.1	0.72 ± 0.011
$P(OMe)_2Ph$	120	(2.64)	19.45	72 ± 2.6
$P(OMe)Ph_2$	132	(2.69)	16.3	21.7 ± 0.63
$P(OEt)_3$	109	3.31	21.6	0.57 ± 0.01
$P(OEt)_2Ph$	121	(3.1)	18.1	37.0 ± 0.47
$P(OEt)Ph_2$	133	(2.91)	15.60	9.4 ± 0.11
PMe_3	118	8.65	8.55	$(1.46 \pm 0.04) \times 10^{-3}$
PMe_2Ph	122	6.5	10.6	$(2.15 \pm 0.02) \times 10^{-4}$
PEt_3	132	8.69	6.30	$(1.01 \pm 0.05) \times 10^{-3}$
dmpe	107	−	−	$(1.85 \pm 0.033) \times 10^{-3}$
PCy_3	170	9.70	1.40	$<5 \times 10^{-6}$

[a] Refs 19, 20. [b] Ref 18.

Table 7. Activation Parameters for the Oxo-Transfer Reactions between Oxo−Metal Complexes and Phosphorus(III) Compounds

metal−oxo	L	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}
$MeRe(NAr)_2O$	$P(OMe)_3$	27.9 ± 2.5	-154 ± 8
$MeRe(NAr)_2O$	$P(OMe)_2Ph$	16.4 ± 1.0	-154 ± 3
$MeRe(NAr)_2O$	PMe_3	45.7 ± 2.9	-146 ± 9.9
$MeRe(NAr)_2O$	PMe_2Ph	52.4 ± 4.7	-140 ± 16
$[MoO_2(mnt)_2]^{2-}$ [a]	$P(OMe)_3$	41.8 ± 4.2	-134 ± 4
$[WO_2(mnt)_2]^{2-}$ [a]	$P(OMe)_3$	58.6 ± 4.2	-138 ± 8
$[MoO_2(mnt)_2]^{2-}$ [a]	$P(OMe)_2Ph$	34.3 ± 1.7	-138 ± 4
$[WO_2(mnt)_2]^{2-}$ [a]	$P(OMe)_2Ph$	46.0 ± 4.2	-159 ± 8
$[HCpz_3)ReOCl_2]^{+}$ [b]	PPh_3	56.1 ± 2.1	-79 ± 8
$(HBpz_3)ReOCl_2$[b]	PPh_3	71.6 ± 0.54	-82 ± 2

[a] Ref 8. [b] Ref 30.

is <132°. For instance, PMe_3 ($\theta = 118°$) and PEt_3 ($\theta = 132°$) have essentially the same rate constant; at the extreme, however, steric interactions might intrude, possibly accounting for PCy_3 ($\theta = 170°$). Perhaps there is a *threshold*, beneath which any variation is not felt but above which the given interaction manifests itself. The existence of steric thresholds for reaction enthalpies and rate constants of ligand substitution reactions has been presented by Giering and co-workers.[18] It should be noted that parallel electronic effects have been noted in reactions of $[Mo(O)_2(mnt)_2]^{2-}$ and PEt_nPh_{3-n}.

Neither the steric effect nor the basicity can account for the reactivity order of alkoxy phosphines. This can be illustrated with one pair of compounds, PMe_2Ph and $P(OMe)_2Ph$, having similar cone angles, 122° and 120°, with the first considerably more basic, the pK_a values being 6.5 and 2.6. Nonetheless the alkoxy compound is more reactive than PMe_2Ph by a factor of 3×10^5. To our knowledge, a kinetic enhancement of this magnitude, upon replacing two methyl groups by methoxy groups, has not been realized previously. The rate constant for the reaction of $[Mo(O)_2(mnt)_2]^{2-}$ with $P(OMe)_2Ph$ is only 40-fold larger than with PEt_3.[8,9]

Extensive correlations of kinetic, thermodynamic, and spectroscopic (NMR, IR) data for reactions of PY_3 have been made with certain quantities such as pK_a, cone angles, and χ values. The latter are derived from the correlation between the frequencies of the A_1 carbonyl band of $Ni(CO)_3(PY_3)$. From that, a quantity χ can be obtained for each PY_3 that combines its σ-donor ability (pK_a) and π-acceptor property.[19,20] The insufficiency of

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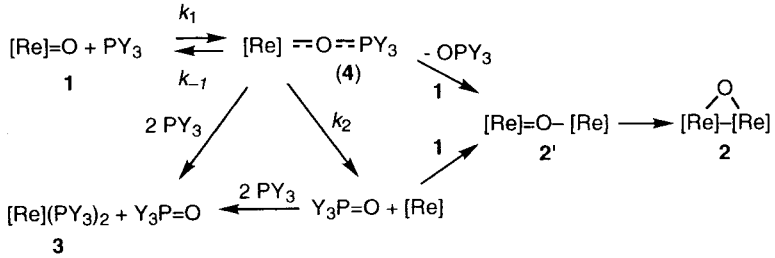
Scheme 1



pK_a alone was stated previously, and it seems that the modified electronic parameter χ is not sufficient to correlate the rate constants for reactions between **1** and PY_3. Although the reactivity order of PY_3 toward the carbon center of halocarbons correlates with the basicity of phosphines,[21] the orders toward hydrogen peroxide[22] and nitroalkanes do not correlate with basicity.[23]

A Role for Coordination? We also considered the likelihood of intervention of a species featuring simple coordination of the phosphorus atom to Re(VII). Such effects seem unlikely in this reaction. For one thing, the lack of inhibiting effect of added bromide, pyridine, or phosphine oxides suggests that coordination equilibria are not pertinent. For another, **1** is approximately modeled by $MeReO_3$, which is a weak Lewis acid toward soft donors; it shows moderate interaction with pyridine,[24] bromide,[25] and triphenylphosphine oxide but no detectable coordination of phosphine.[26] It seems unlikely that coordination of phosphine would in any event be productive: no intramolecular oxo-transfer occurs with $[(bpy)_2Ru(O)(PEt_3)]^{2+}$.[27] The inferred reaction scheme is presented in Scheme 1.

The kinetic data suggest that the interpretation of the kinetic data rests upon the balance between the steps designated by the rate constants k_1, k_{-1}, and k_2. If intermediate **4** reacts with PY_3 to give **3**, then that step must be relatively rapid, since the order with respect to $[PY_3]$ remains at unity. With the steady-state approximation made for [**4**], the reaction rate is given as

$$-\frac{d[\mathbf{1}]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2}[\mathbf{1}] \times [PY_3] \qquad (7)$$

Depending on the relative values of k_{-1} and k_2, the experimental rate constant will, at each limit, represent either k_1 or the composite quantity k_1k_2/k_{-1}. The bonding interactions implied in Scheme 1 suggest considerable stabilization of **4** when an alkoxy group is present.

The Reaction Intermediate. The π-network involves the Re atom, the oxo group, and the pendant PY_3. The oxo group acts as a π-donor to the other two, as allowed by the competitive Lewis π-acidity of each. Since alkoxy groups are known to make PY_3 molecules into better π-acids, it comes as no surprise that they provide the greatest stabilization of the transition state and are thus much more reactive. The values of k/L mol^{-1} s^{-1} in this work for two series are

$P(OMe)_2Ph$ (72) > $P(OMe)Ph_2$ (22) > $P(OMe)_3$ (0.7) > PMe_3 (0.0015) > PMe_2Ph (0.0002)

$P(OEt)_2Ph$ (37) > $P(OEt)PPh_2$ (9.4) > $P(OEt)_3$ (0.6) > PEt_3 (0.0010)

For both the methyl and ethyl series, $P(OR)_3$ is less reactive than $P(OR)_2Ph$ and $P(OR)Ph_2$. The reason for this irregularity is unclear. However, this trend has been observed in the deoxygenation of nitro compounds by phosphines and is believed[23] to be consistent with the nucleophilicity order.

The Rate-Controlling Step. These trends suggest to us that the k_2 reaction is the RCS. Alone, k_1 would not show such severe rate trends; stabilization of intermediate **4**, and not just its transition state, is needed. This assignment implicates the incipient formation of the free phosphine oxide, this being the point at which the π-acidity difference between the Re and phosphorus atoms is most strongly felt, as the greatest kinetic barrier. Not only does the trend in the rate constant values support that, but so does the chemical sense of the mechanism: rate control must logically reside in the step in which the Re−O bond is broken and the O−P bond made. These bonds being by far the two strongest interactions, they define the transition state for the overall reaction.

The values of $\Delta S^{\ddagger}$ for the reactions of **1** with PY_3 are nearly all the same, roughly −150 J K^{-1} mol^{-1}, largely independent of the phosphorus reagent used, Table 7. The rate differences along the series resides entirely in the systematic change of $\Delta H^{\ddagger}$ in the range 16−53 kJ mol^{-1}. This supports a mechanism that involves the stabilization of the key intermediate **4** by π-interactions, clearly an enthalpic effect. As to the values of $\Delta S^{\ddagger}$, one can see that −150 J K^{-1} mol^{-1} amounts to an considerable entropic barrier, $T\Delta S^{\ddagger} = 45$ kJ mol^{-1}. This points to considerable ordering in the transition state, in line with the model from the Re−O−PY_3 interaction in **4**.

The initial formation of $L_nM-O-PY_3$ compounds has been observed for both Ru(VI)[28,29] and Re(V).[30,31] Although such adducts have been characterized structurally for Re(III),[30] not all oxo-transfer systems give an observable or persistent intermediate. For example, a

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bound M−O−PY_3, M = W and Mo, has not been detected.

Phosphine Coordination to the Product. The equilibrium constants for phosphine dissociation reactions of **3** are pertinent to the clean formation of that product. The values of K_8 are sufficiently large that **5**

$$MeRe(NAr)_2PY_3\ (\mathbf{5}) + PY_3 \rightleftarrows MeRe(NAr)_2(PY_3)_2\ (\mathbf{3}) \quad (8)$$

cannot be detected in any reaction. The dimerization reaction, shown in Scheme 1, is of no importance in the kinetics of the oxo-transfer step provided an excess of PY_3 is used. Only when the alkoxyphosphine was taken in stoichiometrically deficient amount were **2′** and **2** obtained. This constitutes a distinction from many molybdenum oxo-transfer systems, where oxo-bridged dimer formation was important.[1,32] The absence of compounds **2′** and **2** during the reaction of **1** with PMe_3, which is a much better ligand toward Re^V than alkoxyphosphines, suggests that the competition reaction of **4** or $MeRe(NAr)_2$ with PMe_3 is favored over the dimerization reaction with **1**, Scheme 1.

Rate Comparisons. It is instructive to compare the data for **1** with these group VI compounds, $[Mo(O)_2(mnt)_2]^{2-}$ and $[W(O)_2(mnt)_2]^{2-}$, Table 7. For $P(OMe)_3$, for example, the rate constants relative to **1** = 100 are 4.1 (Mo) and 0.003 (W); for $P(OMe)_2Ph$, the relative reactivities are 0.5 (Mo) and 0.0003 (W). These differences undoubtedly arise from the change in the metal-oxo bond energy; the Mo═O bond is known to be much weaker than the W═O bond.[8] Kinetic data have also been reported[30] for two other oxorhenium compounds, as presented in Table 7.

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Conclusions

The alkoxy group shows a remarkable effect on the reactivity of PY_3 toward $MeRe(NAr)_2O$. Compound $P(OR)_nPh_{3-n}$ (n = 1−3) is much more reactive than the corresponding PR_nPh_{3-n}. The different reactivity between $P(OR)_nPh_{3-n}$ and PR_nPh_{3-n} is mainly due to the difference in the activation enthalpies of the oxo-transfer reactions. The basicities and cone angles are not the only factors governing the oxophilicity of PY_3 and may not even be the important factors in the reactions with $MeRe(NAr)_2O$. It seems that the π-acidity of PY_3 also plays an important role in the oxo-transfer reactions. Both the bond strengths of the starting M═O complex and the yielding P═O product will contribute to the kinetics of the oxo-transfer reactions.

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Supporting Information Available: Complete tables of crystal data and refinement details, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org

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