Synthesis, Structure, and Exchange Reactions of Rhenium Alkoxide and Aryloxide Complexes. Evidence for both Proton and Hydrogen Atom Transfer in the Exchange Transition State

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A series of rhenium(I) aryloxide and alkoxide complexes have been prepared. The aryloxide complexes may be prepared by treatment of the methyl complex $(CO)_3(PPh_3)_2ReCH_3$ (**1**) with *p*-cresol, affording $(CO)_3(PPh_3)_2ReOC_6H_4CH_3$ (**3a**). The PPh_3 ligands may be displaced by a number of other ligands (PMe_3, 1,2-(dimethylarsino)benzene (diars), or *t*-BuNC), providing a route to substituted cresolate complexes. Alkoxide complexes of the type $(CO)_3(L)_2ReOR$ (R = CH_3 (**6**), CH_2CH_3 (**7**), $CH(CH_3)_3$ (**8**); L, L_2 = PMe_3, diars, depe, or (*S,S*)-bdpp) may be prepared by treatment of the triflate complexes $(CO)_3(L)_2ReOSO_2CF_3$ with the sodium salt of the appropriate alcohol. These alkoxide complexes are quite stable and do not decompose by β-hydride elimination. The coordinated alkoxide ligands exchange rapidly with added alcohols in solution, while the exchange of aryloxide ligands with added phenols is much slower. The alkoxide complexes may be converted into the aryloxide complexes by addition of the desired phenol and heating to 44 °C. This reaction proceeds via the intermediacy of a hydrogen-bonded adduct formed by coordination of the phenol O–H proton to the alkoxide oxygen atom. The hydrogen bonds are quite strong, and the adducts may be isolated if desired. One of the hydrogen-bonded adducts of **7e** and *p*-cresol, $(CO)_3(depe)ReOCH_2CH_3\cdots HOC_6H_4CH_3$, has been structurally characterized. The O–O distance is 2.532(5) Å, a value commonly observed for strong hydrogen bonds. The rates of conversion of a series of these complexes $(CO)_3(diars)ReOCH_3\cdots HOC_6H_4X$ (**6b**$\cdots HOC_6H_4X$) to $(CO)_3(diars)ReOC_6H_4X$ (**3b**) and methanol were studied. The rate of this reaction was found to be cleanly first order in the hydrogen-bonded complex **6b**$\cdots HOC_6H_4X$ and was unaffected by the addition of excess phenol and added bases. The rate was found to increase when the substituent X either lowers the O–H bond dissociation energy or increases the acidity of the phenol, indicating that the transition state for this reaction can have either proton or hydrogen atom transfer character.

Introduction

Low-valent metal alkoxide complexes of groups 6, 7, and 8 have been postulated as intermediates in a number of important homogeneous processes, such as the water-gas shift reaction,[1] organic carbonyl reductions,[2a] catalytic conversion of nitroaromatics to carbamates,[2b] and reduction of CO.[3] Among the most thoroughly investigated group of compounds in this class are the anionic group 6 pentacarbonyl complexes $M(CO)_5OR^-$ (M = Cr, Mo, W.; R = C_6H_5, $CH(CF_3)_2$) prepared by Darensbourg and co-workers.[4-6] In this group of compounds, the simple alkoxide complexes could not be prepared because of their proclivity to decompose by β-hydride elimination. With the exception of the triply bridging carbonyl anions[7] $(CO)_3Re(\mu\text{-}OR)_3Re(CO)_3^-$ and higher order manganese clusters,[8] the alkoxides and aryloxide complexes of Re(I) and Mn(I) have only recently been prepared.[9,10]

As part of our interest in the chemistry of metal–heteroatom bonds, we have developed synthetic routes to monomeric Re(I) aryloxide, fluoroalkoxide, and alkoxide complexes.[10] The structures of several of these complexes have been determined by X-ray diffraction studies. The mechanisms of the exchange reactions of $(CO)_3(L)_2ReOR$ and $(CO)_3(L)_2ReOAr$ with phenols and alcohols have been investigated. These octahedral Re(I) metal centers are well suited for mechanistic studies of exchange reactions because they are coordinatively saturated[11] and lack ligands capable of variable hapticity such as cyclopentadienyl and nitrosyl.[11,12]

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(9) Rhenium(I) amido complexes have been prepared: Chiu, K. W.; Howard, C. G.; Rzepa, H. S.; Sheppard, R. N.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 441–451.

(10) While this work was in progress, the syntheses of *fac*-$(CO)_3$(dppe)ReOR and *fac*-$(CO)_3$(dppe)MnOR were reported: (a) Mandal, S. K.; Ho, D. M.; Orchin, M. *Inorg. Chem.* **1991**, *30*, 2244–2248. See also: (b) Mandal, S. K.; Ho, D. M.; Orchin, M. J. *J. Organomet. Chem.* **1992**, *439*, 53.

(11) For oxidative addition reactions that convert coordinatively unsaturated to saturated (group 9) metal alkoxides, see: Thompson, J. S.; Bernard, K. A.; Rappoli, B. J.; Atwood, J. D. *Organometallics* **1990**, *9*, 2727.

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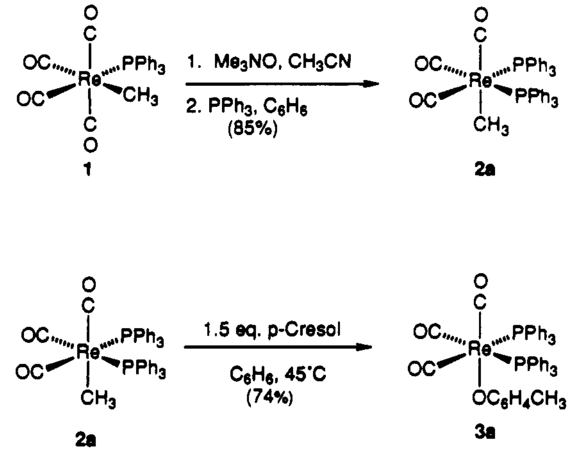
Scheme I



Results

Synthesis of Aryloxide and Alkoxide Complexes. Synthesis of rhenium aryloxide complexes was accomplished as shown in Scheme I. Treatment of *cis*-$(CO)_4(PPh_3)ReCH_3$ with trimethylamine *N*-oxide in acetonitrile resulted in oxidative decarbonylation, affording the acetonitrile solvate *fac*-$(CO)_3(PPh_3)(NCCH_3)ReCH_3$.[13] The labile acetonitrile ligand was readily displaced by PPh_3 to yield the bis(triphenylphosphine)-substituted complex $(CO)_3(PPh_3)_2ReCH_3$ (**2a**). Reaction of **2a** with a slight excess of *p*-cresol in benzene at 45 °C resulted in the formation of methane and the cresolate complex *fac,cis*-$(CO)_3(PPh_3)_2ReOC_6H_4CH_3$ (**3a**) in 74% isolated yield. The FAB mass spectrum of this complex in a *p*-nitrophenyl octyl ether matrix shows a peak at *m/e* 903 (M + 1) consistent with the formulation of the bis(triphenylphosphine) adduct. No peaks at higher mass, which could result from the formation of dimeric structures, were observed. The base peak observed in the spectrum appeared at 795 amu and corresponds to $(CO)_3(PPh_3)_2Re^+$, formed by loss of $CH_3C_6H_4OH$ from the complex. The IR spectrum shows three strong carbonyl stretching bands at 2015, 1930, and 1891 cm^{-1}, characteristic of a facial arrangement of carbonyl ligands about the Re center. The carbonyl resonances are severely broadened in the $^{13}C\{^1H\}$ NMR spectrum, and P–C couplings could not be resolved even at low temperatures. The ipso carbon of the cresolate ligand appears as a 1:2:1 triplet at 166.4 ppm with a P–C coupling of 4.6 Hz.

The structure of this compound was confirmed by a single-crystal X-ray diffraction study. Clear colorless crystals were grown by slow cooling of a toluene/pentane solution. The complex crystallizes in space group $Pbc2_1$ and contains two crystallographically independent molecules in the unit cell. An ORTEP diagram with atom labels is shown in Figure 1. Data collection parameters are given in Tables I and II; selected bond lengths and bond angles are given in Tables III and IV. The structure confirms the fac,cis coordination of the rhenium center. The rhenium center is extremely crowded by the presence of the cis-PPh_3 ligands. The P_1–Re–P_2 angle is 96.9°, a substantial deviation from an idealized octahedral geometry. All of the Re–carbonyl distances are quite similar, ranging from 1.920(3) to 1.942(3) Å. The Re–O distance is 2.143(9) Å. The Re–O–C_{ipso} angle is 131.7°.

The formation of **3a** apparently requires the transient formation of an open coordination site on the rhenium center. Qualitatively, the reaction is slowed by added triphenylphosphine. The nonlabile alkyl complexes such as $(CO)_4(PPh_3)ReCH_3$ and $(CO)_3(dppe)ReCH_2CH_3$ do not react with *p*-cresol under all conditions attempted. The most plausible mechanism for formation of **3a** is reversible dissociation of a PPh_3 ligand from **2a** to form a coordinately unsaturated complex. Coordination of the cresol to the metal can then lead to either O–H oxidative addition or protonation of the metal center to form a Re(III) intermediate, followed by loss of methane and reassociation of phosphine to form the observed products.

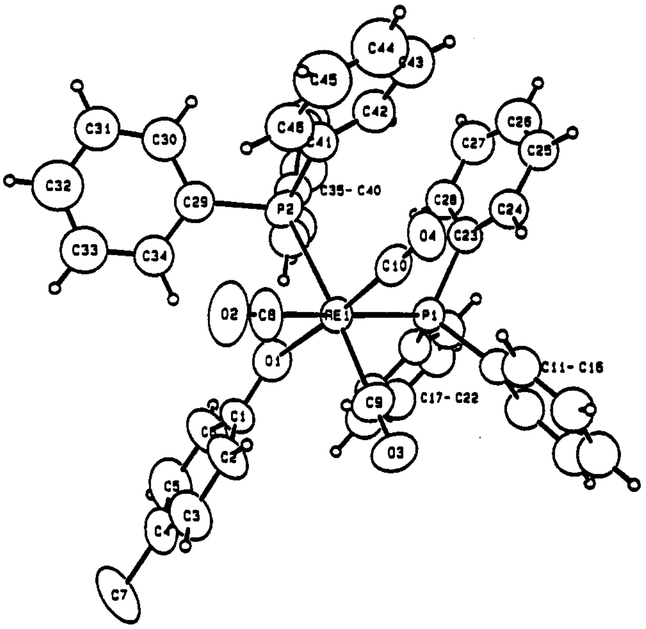


Figure 1. ORTEP diagram of $(CO)_3(PPh_3)_2ReOC_6H_4CH_3$. Only one of the crystallographically unique molecules in the unit cell is shown.

Table I. Crystal Parameters for Compounds 3a, 11b, and 7e···$HOC_6H_4CH_3$

	3a[a,b]	**11b**[b,c]	**7e···$HOC_6H_4CH_3$**[b,d]
formula	$C_{46}H_{37}P_2O_4Re$	$C_{16}H_{17}As_2F_6O_4Re$	$C_{25.5}H_{37}O_5P_2Re$
fw	902.0	723.3	671.1
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$Pbc2_1$	$P2_1/c$	$P2_1/n$
a, Å	19.0169 (16)	12.868 (2)	11.4604 (20)
b, Å	20.6117 (25)	8.708 (2)	11.4617 (20)
c, Å	20.4698 (22)	19.477 (2)	22.098 (5)
α, deg	90.0	90.0	90.0
β, deg	90.0	95.943 (13)	98.156 (16)
γ, deg	90.0	90.0	90.0
V, Å³	8023.6 (25)	2170.8 (12)	2873.3 (17)
Z	8	4	4
size, mm	0.15 × 0.33 × 0.44	0.40 × 0.50 × 0.70	0.30 × 0.34 × 0.38
color	colorless	colorless	colorless
d(calc), g cm^{-3}	1.49	2.21	1.55
μ(calc), cm^{-1}	31.9	87.6	44.3

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components, 24 reflections with 2θ between 28 and 30°. [b] In this and all subsequent tables the esd's of all parameters are given in parentheses, to the right of the least significant digit(s) of the reported value. [c] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components, 24 reflections with 2θ between 26 and 32°. [d] Unit cell parameter and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components, 25 reflections with 2θ between 28 and 34°.

The triphenylphosphine ligands of **3a** are easily displaced by a variety of less sterically demanding ligands; therefore, it is a useful starting material for other substituted complexes (Scheme II). The ligand substitution

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Table II. Data Collection Parameters for Compounds 3a, 11b, and 7e···$HOC_6H_4CH_3$

	3a[a]	11b[a]	7e···$HOC_6H_4CH_3$[b]
temp, K	298	191	178
diffractometer	Enraf-Nonius CAD-4		
monochromator	highly oriented graphite (2θ = 12.2)		
2θ or ω range, deg	3–45	3–45	3–50
scan width ($\Delta\theta$)	0.70 + 0.35 tan θ	0.65 + 0.35 tan θ	0.60 + 0.35 tan θ
scan type	ω fixed counter	θ–2θ	ω
scan speed, deg/min	1.05–6.70 (ω)	constant, 6.70	5.49–5.49 (ω)
vert aperture (mm)	3.0	3.0	4.0
horiz aperture (mm)	2.0 + 1.0 tan θ	2.0 + 1.0 tan θ	2.0 + 1.0 tan θ
data collcd	$+h,+k,+l$	$+h,+k,\pm l$	$+h,+k,\pm l$
bkgd	measd over 0.25($\Delta\omega$) added to each end of the scan		
no. of rflns collected	5795	3200	5337
no. of unique rflns	5417	2835	5052
no. of obsd rflns	4286 ($F^2 > 3\sigma F^2$)	2486 ($F^2 > 3\sigma F^2$)	3763 ($F^2 > 3\sigma F^2$)
abs cor	empirical	empirical	empirical
min/max transmissn	0.455/0.995	1.000/0.553	0.774/0.999
no. of params refined	494	132	465
$R(F)$, %	3.07	4.1	2.47
$R_w(F)$, %	3.55	5.5	2.66
R_{all}, %	6.80	4.9	4.41
goodness of fit	1.57	2.76	1.098
p factor	0.03	0.03	0.03

[a] Radiation: Mo Kα (λ = 0.709 26 Å). [b] Radiation: Mo Kα (λ = 0.710 73 Å).

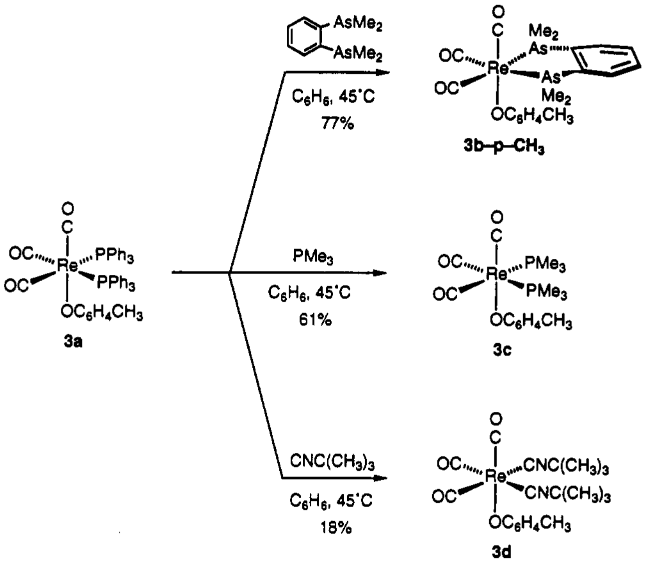
Table III. Selected Intramolecular Distances (Å) for *fac,cis*-$(CO)_3(PPh_3)_2ReOC_6H_4CH_3$ (3a)

Re_1–P_1	2.547(3)	Re_2–P_3	2.498(3)
Re_1–P_2	2.497(6)	Re_2–P_4	2.542(3)
Re_1–O_1	2.143(9)	Re_2–O_5	2.120(7)
Re_1–C_8	1.963(12)	Re_2–C_{58}	1.907(16)
Re_1–C_9	1.954(16)	Re_2–C_{59}	1.908(11)
Re_1–C_{10}	1.913(15)	Re_2–C_{60}	1.969(19)
O_1–C_1	1.341(20)	O_5–C_{51}	1.340(14)
C_1–C_2	1.38(3)	C_{51}–C_{52}	1.377(16)
C_1–C_6	1.36(3)	C_{51}–C_{56}	1.400(17)
C_2–C_3	1.38(3)	C_{52}–C_{53}	1.37(3)
C_3–C_4	1.36(3)	C_{53}–C_{54}	1.340(24)
C_4–C_5	1.41(3)	C_{54}–C_{55}	1.35(3)
C_4–C_7	1.573(19)	C_{54}–C_{57}	1.537(15)
C_5–C_6	1.37(3)	C_{55}–C_{56}	1.405(18)
C_8–O_2	1.124(14)	C_{58}–O_6	1.174(18)
C_9–O_3	1.111(17)	C_{59}–O_7	1.142(13)
C_{10}–O_4	1.148(14)	C_{60}–O_8	1.158(22)

Table IV. Selected Intramolecular Angles (deg) for *fac,cis*-$(CO)_3(PPh_3)_2ReOC_6H_4CH_3$ (3a)

P_1–Re_1–P_2	96.9(2)	P_3–Re_2–P_4	95.81(9)
P_1–Re_1–O_1	92.3(2)	P_3–Re_2–O_5	83.9(2)
P_1–Re_1–C_8	172.9(4)	P_3–Re_2–C_{58}	88.0
P_1–Re_1–C_9	86.9(4)	P_3–Re_2–C_{59}	90.5(3)
P_1–Re_1–C_{10}	87.6(3)	P_3–Re_2–C_{60}	175.5(4)
P_2–Re_1–O_1	85.3(2)	P_4–Re_2–O_5	91.5(2)
P_2–Re_1–C_8	86.5(5)	P_4–Re_2–C_{58}	172.7(4)
P_2–Re_1–C_9	176.2(4)	P_4–Re_2–C_{59}	88.6(3)
P_2–Re_1–C_{10}	90.3(3)	P_4–Re_2–C_{60}	88.5(4)
O_1–Re_1–C_8	94.1(4)	O_5–Re_2–C_{58}	95.2(4)
O_1–Re_1–C_9	94.6(4)	O_5–Re_2–C_{59}	174.4(3)
O_1–Re_1–C_{10}	175.5(4)	O_5–Re_2–C_{60}	97.5(4)
C_8–Re_1–C_9	89.7(5)	C_{58}–Re_2–C_{59}	85.0(5)
C_8–Re_1–C_{10}	86.2(5)	C_{58}–Re_2–C_{60}	87.6(5)
C_9–Re_1–C_{10}	89.9(5)	C_{59}–Re_2–C_{60}	88.1(4)
Re_1–O_1–C_1	131.5(11)	Re_2–O_5–C_{51}	131.7(7)
Re_1–C_8–O_2	174.9(11)	Re_2–C_{58}–O_6	174.0(11)
Re_1–C_9–O_3	177.7(10)	Re_2–C_{59}–O_7	176.2(9)
Re_1–C_{10}–O_4	176.3(9)	Re_2–C_{60}–O_8	178.1(10)
Re_1–P_1–C_{11}	111.2(3)	Re_2–P_3–C_{61}	117.5(4)
Re_1–P_1–C_{17}	119.3(4)	Re_2–P_3–C_{67}	107.8(3)
Re_1–P_1–C_{23}	114.3(3)	Re_2–P_3–C_{73}	120.2(4)
Re_1–P_2–C_{29}	115.4(5)	Re_2–P_4–C_{79}	120.9(3)
Re_1–P_2–C_{35}	119.0(5)	Re_2–P_4–C_{88}	115.2(3)
Re_1–P_2–C_{41}	106.2(4)	Re_2–P_4–C_{91}	110.4(4)

Scheme II



reactions proceed rapidly at 45 °C to provide the substituted complexes in good yield. The electronic nature of the incoming ligand has little effect on the reaction. Good σ-donor ligands (PMe_3) substitute as readily as good π-acceptor ligands (t-BuNC). When monitored by ^1H NMR, these reactions proceed in very high yield; however, the substituted aryloxides are often difficult to separate from the liberated PPh_3, so the isolated yields are sometimes quite low.

This reaction sequence could not be applied to the synthesis of alkoxide complexes. Reaction of **2a** with alcohols (even activated alcohols such as $(CF_3)_2CHOH$ and CF_3CH_2OH) resulted only in decomposition. However, the alkoxides may be prepared in good yield by reaction of the metal triflates **5** with an excess of the sodium salts of the alcohols (Schemes III and IV). The triflate complexes were conveniently prepared by reaction of the corresponding chlorides with triflic acid in refluxing methylene chloride.[14] The triflate complexes obtained by this route appear quite clean by ^1H, ^{13}C, and ^{19}F NMR; however, they consistently failed to give correct elemental analyses. This may be due to the formation of hydrates. The inability to give proper analyses did not seem to affect the reactivity of these compounds in subsequent transformations. Formation of the triflates is essential; the

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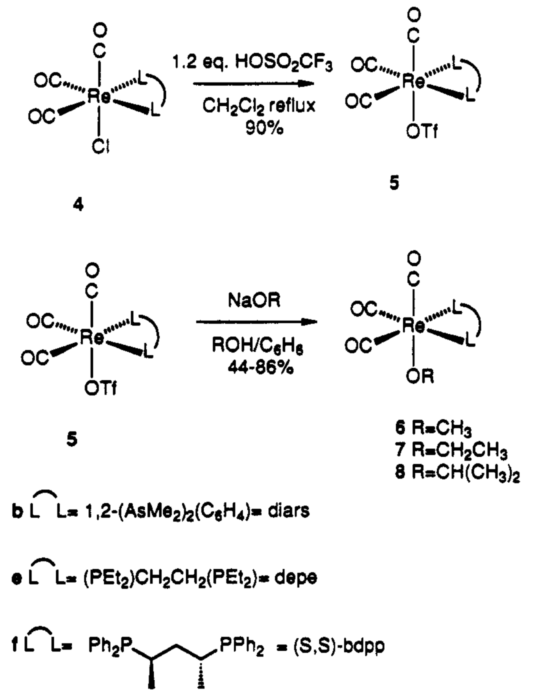
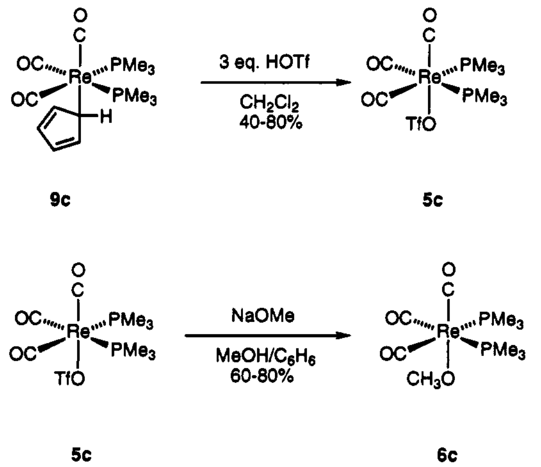
[14] Beck, W.; Olgemöller, B.; Oldgemöller, L. In *Inorganic Synthesis*; Angelici, R. J., Ed.; Wiley: New York, 1990; Vol. 28, pp 27–29.

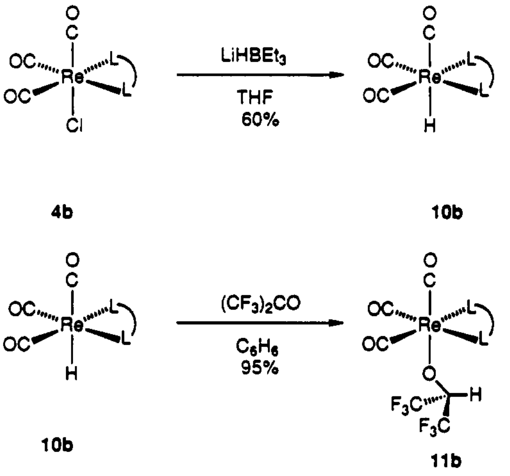
Scheme III



Scheme IV



Scheme V



chlorides were recovered unchanged when treated with alkali-metal alkoxide salts under a variety of conditions.

This synthetic route is extremely general, as long the rhenium bears a chelating ligand. All attempts to prepare methoxide complexes without chelating ligands failed except for the synthesis of the bis-PMe_3-substituted complex **6c** (Scheme IV). Treatment of the triflate **5c**, prepared by protonation of the η^1-C_5H_5 ligand of **9**[15] with triflic acid, with an excess of NaOMe in a mixed benzene/methanol solvent system afforded a 60–80% yield of the methoxide complex **6c**. As observed for **3a**, the carbonyl ligand resonances are broadened in the $^{13}C\{^1H\}$ NMR spectra and the P–C couplings cannot be resolved at temperatures as low as −70 °C. The coordinated methoxide resonance appears as a 1:2:1 triplet at δ 68.2 ppm with a P–C coupling of 4.9 Hz, a typical value for a three-bond P–C coupling. The $^{31}P\{^1H\}$ NMR spectrum is broad at room temperature and narrows as the sample is cooled, becoming sharp at −70 °C. No coalescence of the coordinated PMe_3 signals is observed when **6c** is heated with added PMe_3, demonstrating that this fluxional process does not involve phosphine dissociation. The nature of the fluxionality of this compound has not been determined. The broadened carbonyl resonances are also observed when the complex has a chelating ligand.

Alkoxide complexes were prepared with the following chelating ligands (Scheme III): 1,2-(dimethylarsino)benzene (diars) (**b** series), 1,2-bis(diethylphosphino)ethane (depe) (**e** series), and (−)-(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane ((*S*,*S*)-bdpp) (**f** series). In complexes bearing the chiral phosphine ligand, the two phosphorus nuclei are chemically inequivalent and the protons of the methylene group in the ethoxide ligand are diastereotopic. Also in the isopropoxide complexes, two diastereotopic methyl groups are observed in the ^1H NMR spectrum.

Other alkoxide salts can also be used in this reaction. Both primary and secondary alkoxides (Scheme III) may be used, but addition of KO-*t*-Bu does not produce the *tert*-butoxide complex. The aryloxide complexes can also be prepared by treatment of the triflate complexes with the potassium salt of the appropriately substituted phenol.

Another less general synthesis of hexafluoroisopropoxide complexes has been developed (Scheme V). Treatment of the hydride $(CO)_3$(diars)ReH with anhydrous hexafluoroacetone in benzene at room temperature leads to formation of the complex $(CO)_3$(diars)$ReOCH(CF_3)_2$ (**10b**), formed by insertion of the activated carbonyl into the metal–hydrogen bond.[16,17] While this reaction works well with this very electrophilic ketone, it cannot be applied to the synthesis of other alkoxide complexes. No reaction was observed when **10b** was treated with all other organic carbonyls, even aldehydes. The hexafluoroisopropoxide can also be prepared by treatment of **7b** with an excess of $(CF_3)_2CHOH$ in C_6H_6 at 44 °C.

The insertion of the activated ketone into the Re–H bond is the microscopic reverse of the well-known β-hydride elimination reaction, one of the principal pathways for the decomposition of metal alkoxides. The fact that formation of alkoxide complexes by carbonyl insertion into the Re–H bond only proceeds with the highly activated ketone $(CF_3)_2CO$ is consistent with previous work on the stability of metal alkoxides toward decomposition by β-hydride elimination. The presence of an electron-withdrawing group imparts unusually high stability to the alkoxide complex relative to the all-carbon analogues.

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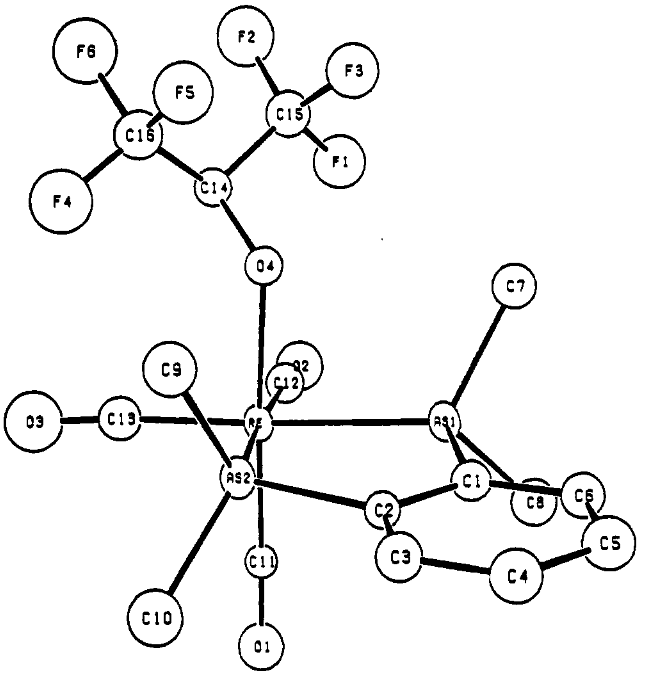


Figure 2. ORTEP diagram of $(CO)_3(diars)ReOCH(CF_3)_2$.

Table V. Selected Intramolecular Distances (Å) for *fac*-$(CO)_3(diars)ReOCH(CF_3)_2$ (11b)

Re–As_1	2.539(1)	C_{11}–O_1	1.169(7)
Re–As_2	2.530(1)	C_{12}–O_2	1.161(8)
Re–O_4	2.125(4)	C_{13}–O_3	1.169(8)
Re–C_{11}	1.882(6)	C_{14}–O_4	1.371(7)
Re–C_{12}	1.936(7)	C_{14}–C_{15}	1.517(9)
Re–C_{13}	1.881(7)	C_{14}–C_{16}	1.512(10)

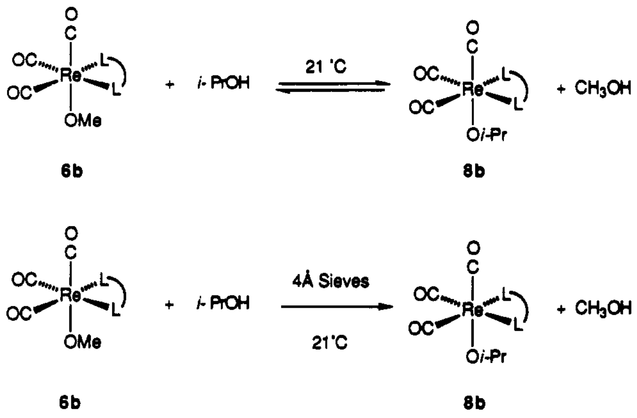
Table VI. Selected Intramolecular Angles (deg) for *fac*-$(CO)_3(diars)ReOCH(CF_3)_2$ (11b)

As_1–Re–As_2	81.43(2)	O_4–Re–C_{13}	93.39(23)
As_1–Re–O_4	82.20(11)	C_{11}–Re–C_{12}	91.1(3)
As_1–Re–C_{11}	93.20(19)	C_{11}–Re–C_{13}	90.8(3)
As_1–Re–C_{12}	93.10(19)	C_{12}–Re–C_{13}	91.9(3)
As_1–Re–C_{13}	173.58(22)	Re–C_{11}–O_1	176.6(5)
As_2–Re–O_4	83.67(12)	Re–C_{12}–O_2	176.6(6)
As_2–Re–C_{11}	90.54(19)	Re–C_{13}–O_3	176.2(6)
As_2–Re–C_{12}	174.37(20)	Re–O_4–C_{14}	123.4(4)
As_2–Re–C_{13}	93.49(22)	O_4–C_{14}–C_{15}	109.4(5)
O_4–Re–C_{11}	173.07(22)	O_4–C_{14}–C_{16}	107.1(5)
O_4–Re–C_{12}	94.33(22)	C_{15}–C_{14}–C_{16}	112.2(6)

This compound has been crystallographically characterized; an ORTEP diagram is shown in Figure 2. It crystallizes in space group $P2_1/c$. As seen in the cresolate complex **3a**, there is little variation in the Re–CO distances. The Re–O distance is 2.125(4) Å, and the Re–O–CH angle is 123.4(4)°. Data collection parameters are given in Tables I and II, and bond lengths and angles are given in Tables V and VI.

Stabilities of Aryloxide and Alkoxide Complexes. With the exception of the nonchelated complexes **3a** and **6c**, both the alkoxide and aryloxide complexes exhibit surprisingly high thermal stability. Complexes **3b** and the fluorinated alkoxide complex **10b** can be recovered unchanged after being heated in C_6D_6 solution at 140 °C for several days. The methoxide complex **7b** is somewhat less thermally stable; decomposition products were observed after heating C_6D_6 solutions of **7b** at 100 °C for 12 h. Examination of the decomposition products by ^1H NMR shows no formation of the hydride **10b**, the expected product from β-hydride elimination from the methoxide ligand. Because this result was unexpected, we demonstrated that the hydride is stable to the reaction conditions and that spiking C_6D_6 solutions of **7b** with **10b** does not lead to different decomposition products. These experiments indicate that the major decomposition pathway for the methoxide complexes is not β-hydride elimination. When **6c** or **3a** is thermolyzed, the major product observable by $^{31}P\{^1H\}$ NMR is the free ligand PPh_3 or PMe_3, respectively. Again no hydride resonances are observed.

Scheme VI



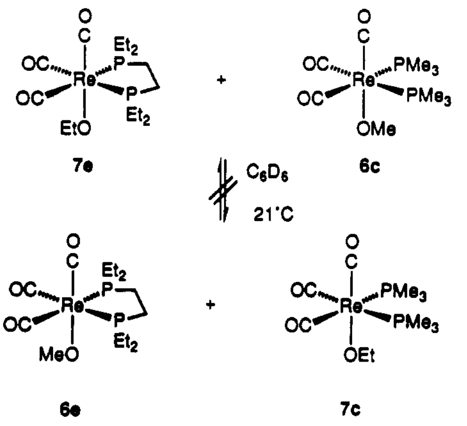
Exchange Reactions of Alkoxide Complexes with Alcohols. Addition of 1 equiv of 2-propanol to a C_6D_6 solution of the diars-substituted methoxide complex **6b** at 21 °C resulted in a presumably equilibrium mixture of **6b** and the isopropoxide **8b** (Scheme VI). This reaction occurs very rapidly at room temperature, with both complexes observed immediately upon mixing. The ^1H NMR chemical shifts of the added and released alcohols were shifted very little from those of the free alcohols without the metal alkoxides present. When 4-Å molecular sieves are added to this reaction mixture, the equilibrium can be driven to the side of the isopropoxide **8b**. The reaction is rapid on the chemical but not the NMR time scale: mixing methoxide **6b** with added methanol produces no coalescence of NMR resonances even at 90 °C in toluene.

This reaction is very sensitive to the steric environment about the metal center. With the less sterically demanding ligand depe, the isopropoxide for ethoxide exchange occurred readily at room temperature, while alkoxide exchange in the (*S,S*)-bdpp substituted complex **7f** required heating to 80 °C for the exchange to proceed. The fact that the bulkier ligand apparently retards the approach of the incoming alcohol to the coordinated oxygen is consistent with an associative mechanism for alkoxide exchange.

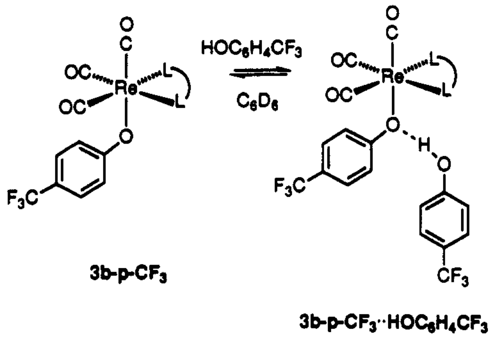
Intermolecular Exchange Reactions. When two different alkoxide complexes were mixed together in C_6D_6 at room temperature, no exchange of alkoxide ligands was observed (Scheme VII). However, the intermolecular exchange of alkoxide ligands can be catalyzed by added alcohol. When a C_6D_6 solution of **6c** and **7e** was treated with 0.05 equiv of CH_3OH, exchange was observed. The mechanism of this exchange is undoubtedly identical with that discussed for the exchange with added alcohol, except that in this case the exchange produces varying mixtures of the two alcohols in solution.

Interaction of Aryloxide Complexes with Phenols: Observation of Intermediate Hydrogen-Bonded Complexes. The exchange of coordinated aryloxides with external phenols also occurs, but the reaction does not occur as readily as the alkoxide-for-alkoxide exchange. The ^1H NMR chemical shifts of the added phenol and the aryloxide complex are different from those of the pure

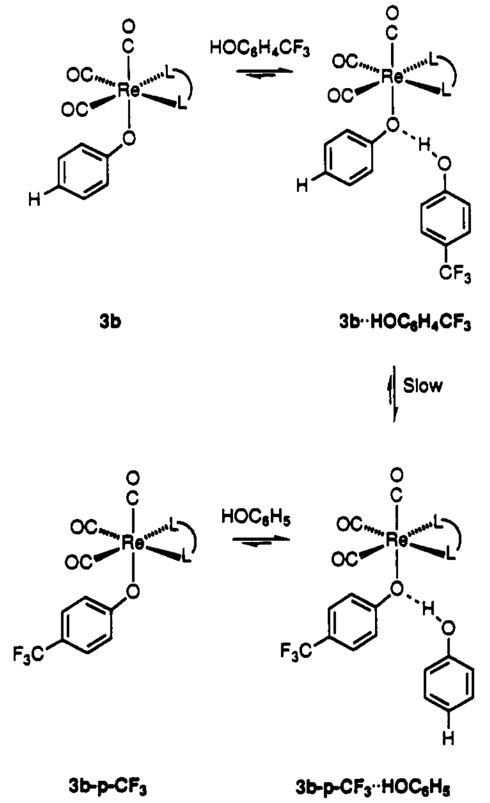
Scheme VII



Scheme VIII



Scheme IX



compounds under the same conditions. We believe that this behavior is caused by the formation of a hydrogen-bonded complex between the metal aryloxide and the added phenol (Scheme VIII).[18-27] When a toluene-d_8 solution of **3b**-p-CF_3 was treated with 1.0 equiv of HOC_6H_4-CF_3 at room temperature, two distinct sets of para-substituted aryl protons were present at 20.9 °C. The OH proton resonance was seen as a broad peak at δ 4.38 ppm. As the temperature was raised, the chemical shift of the phenol and aryloxide complex aromatic protons changed very little. However, the chemical shift of the OH proton moved upfield by 0.39 ppm and the resonance sharpened. Again, no coalescence of the aryl proton resonances was observed. This behavior demonstrates that in spite of the formation of a hydrogen-bonded complex, the rhenium-bond aryloxide ligand does not undergo degenerate exchange with the hydrogen-bonded phenol rapidly on the NMR time scale.

Exchange of unsubstituted aryloxides with more acidic phenols also does not occur rapidly. For example, upon addition of $CF_3C_6H_4OH$ to a C_6D_6 solution of $(CO)_3$(diars)-$ReOC_6H_5$, the NMR spectrum showed only the formation of hydrogen-bonded complex **3b**···$HOC_6H_4CF_3$ at room temperature (Scheme IX). The resonances of the added phenol are shifted slightly relative to those of the free compound. The most marked difference is the hydroxyl proton. It appears as a broad peak at δ 5.12 ppm in the room-temperature spectrum (21 °C), a downfield shift of 0.98 ppm relative to that of the free phenol. Only one fluorine-containing species is seen in the ^{19}F NMR spectrum. After 24 h at 21 °C, the NMR spectrum shows a 1:2 mixture of **3b**···$HOC_6H_4CF_3$:**3b**-p-CF_3···HOC_6H_5. The OH resonance is severely broadened and could not be observed. Complete exchange to **3b**-p-CF_3···HOC_6H_5 was not observed even after 10 days at room temperature.

Exchange Reactions of Alkoxide Complexes with Phenols. As discussed in the description of the syntheses of these compounds, the alkoxide complexes can be converted into the aryloxide complexes **3** by adding the phenol and then heating to 44 °C. If the initial phenol and **3** mixture is monitored by ^1H NMR, one can detect the formation of the hydrogen-bonded complexes **6**···HO-C_6H_4X or **7**···HOC_6H_4X (Scheme X). These adducts are stable in solution at room temperature and appear to be more robust than the hydrogen-bonded complexes between the aryloxides and phenols. If the solvent is removed, added phenol cannot be pumped off even when the complex has not crystallized. Addition of solvent and examination of the residue by ^1H NMR demonstrates that the hydrogen-bonded complex is still intact. The most conspicuous feature of these complexes is the low-field shift of the phenolic hydrogen. A resonance between δ 14 and 8 ppm is commonly observed, but the chemical shift varies greatly depending upon the solvent, temperature,

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(18) Several groups have recently observed the formation of hydrogen bonds between alcohols and phenols and the M–O bond.[19-26] The association of δ-valerolactam with a W(II) fluoride has also been reported.[27]

(19) Osakada, K.; Ohshiro, K.; Yamamoto, A. *Organometallics* **1991**, *10*, 404–410.

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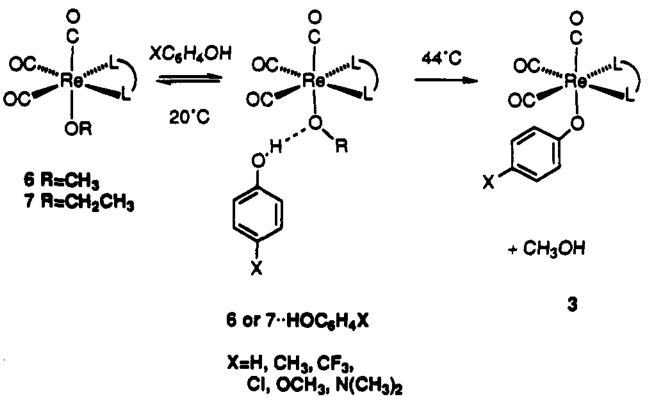
Scheme X



and concentration of the sample.[28] It is important to stress that these hydrogen bonds persist in solution as well as in the solid state. A detailed description of the spectroscopic characteristics of $(CO)_3(depe)ReOCH_2CH_3{\cdots}HOC_6H_4CH_3$ (**7e**$\cdots HOC_6H_4CH_3$) follows.

Adding 1 equiv of *p*-cresol to a toluene/pentane solution of $(CO)_3(depe)ReOCH_2CH_3$ followed by cooling to −40 °C for 7 days leads to a 65% yield of the hydrogen-bonded complex $(CO)_3(depe)ReOCH_2CH_3{\cdots}HOC_6H_4CH_3$. The complex is a white, moderately air-stable solid. It is indefinitely stable under a nitrogen atmosphere at −40 °C. The room-temperature ^1H NMR spectrum displays the characteristics of a hydrogen-bonded complex (Figure 3); the hydrogen-bonded proton appears as a broad singlet at δ 12.23 ppm. The chemical shift of this resonance is very dependent upon both the temperature at which the spectrum is recorded and the concentration of the sample. The $^{13}C\{^1H\}$ NMR spectrum of **7e**$\cdots HOC_6H_4CH_3$ is consistent with the proposed structure and demonstrates that the compound is not the cresolate $(CO)_3(depe)ReOC_6H_4CH_3$. The methylene carbon of the ethoxide ligand resonance occurs as a triplet at δ 72.8 ppm with $J_{PC} = 3.2$ Hz. The identity of this resonance was also conformed by a DEPT135 experiment. The P–C coupling constant is quite similar to the value of a three-bond cis P–C coupling but is slightly smaller than the 4.5-Hz value in the parent complex. This reduction in coupling constant may be caused by several factors, such as a distortion of the C–O–Re–P bond angles or a lengthening of the Re–O bond length. The resonance is shifted 2.4 ppm upfield from that of the non-hydrogen-bonded complex. Both of the carbonyl resonances are much sharper than those of **7e**. The carbonyl ligand trans to the hydrogen-bonded ethoxide appears as a 1:2:1 triplet at δ 192.3 ppm with $J_{PC} = 5.1$ Hz. The resonance for the cis carbonyls is at δ 196.0 ppm. It is split into a doublet of doublets due to coupling to the two magnetically inequivalent phosphine ligands with $J_{PcisC} = 10.7$ Hz and $J_{PtransC} = 60.8$ Hz. The coupling constants of the carbonyl ligand to the phosphine ligands have never been observed in any of the previously prepared alkoxide or aryloxide complexes.

Solution Behavior of the Alkoxide···Phenol Hydrogen-Bonded Complexes. Presumably the geometries of the hydrogen-bonded complexes in solution are similar to those in the solid state. The IR spectra of the compound **7e**$\cdots HOC_6H_4CH_3$ in solution and the solid state were quite similar.

Addition of an excess of *p*-(trifluoromethyl)phenol to **6b** in C_6D_6 gave only a single set of phenolic resonances in both the ^1H and ^{19}F NMR spectra, due to formation of the hydrogen-bonded complex **6b**$\cdots HOC_6H_4CF_3$. This demonstrated that the hydrogen-bonded phenol can exchange with external phenol and that this exchange equilibrium was occurring rapidly on the NMR time scale (Scheme XI). All of the chemical shifts were slightly shifted relative to those of the hydrogen-bonded complex derived from addition of a single equivalent of phenol.

Crystal Structure of *fac*-$(CO)_3(depe)ReOCH_2CH_3{\cdots}HOC_6H_4CH_3$ (7e$\cdots HOC_6H_4CH_3$). To further study the structure of this complex, a single-crystal X-ray diffraction study was undertaken. Large, clear, colorless crystals were grown by layering a cooled toluene solution of **7e**$\cdots HOC_6H_4CH_3$ with pentane for 7 days at −40 °C. Data collection parameters are given in Tables I and II and in the Experimental Section. The structure consists of molecules of **7e**$\cdots HOC_6H_4CH_3$ (Figure 4) and disordered toluene molecules of solvation. These are packed in the unit cell with no particularly close contacts between molecules. The hydrogen atoms were located and refined. The bond lengths and angles are given in Tables VII and VIII. The O–O distance is quite short, 2.532(5) Å, a value which is typically observed for strong hydrogen bonds. The O_5–H distance is 0.77(5) Å, while the O_4–H distance is 1.77(5) Å.[20,22-26] The O_5–H–O_4 angle is nearly linear, 172.3°. The Re–O bond length of 2.154(3) Å is quite similar to the Re–O bond distances in other structurally characterized compounds discussed in this paper. A comparison of the O···H–O bond angle and O–O distances of this complex and other crystallographically characterized hydrogen bonds between alcohols or phenols and M–O bonds is given in Table IX.

Substituent Effects on the Interchange of Hydrogen-Bonded Phenol for Methoxide. The hydrogen-bonded complexes were found to undergo phenol/aryloxide exchange by a first-order process in C_6D_6 at 44 °C. This process could be conveniently monitored by ^1H NMR spectrometry. For example, the rate of conversion of **6b**$\cdots HOC_6H_4CH_3$ to **3b**-*p*-CH_3 and methanol (Scheme X) was measured by following the disappearance of the Re–OCH_3 signal and the hydrogen-bonded *p*-cresol methyl group, as well as the appearance of Re–$OC_6H_4CH_3$ and free CH_3OH. All of these first-order rate constants k_{obs} were identical within experimental error. In order to further probe the mechanism of the exchange reaction, we measured rate constants for the interchange of methoxide for several para-substituted phenols. The first-order rate constants are listed in Table X. The rate constants were cleanly first order in alkoxide and were unaffected by addition of excess phenol. Also, the rate was not affected by the additions of trace amounts (0.1 equiv) of bases such as Proton Sponge.

The most striking feature of these rate constants is that they show so little dependence on the nature of the para substituent. The rates of the reaction were virtually the same for the conversion of **6b**$\cdots HOC_6H_4OCH_3$ and **6b**$\cdots HOC_6H_4CF_3$. When the logarithms of these data were plotted against the substituent constant σ_p, the resulting Hammett plot showed that k_{obs} is highest at the two extremes.

Discussion

Synthesis and Structures. The results described above provide synthetic routes to a wide variety of monomeric Re(I) alkoxide and aryloxide complexes. The alkoxide group is considered to be an exceptionally good

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[28] Silverstein, R. M.; Bassler, G. C.; Morill, T. C. *Spectroscopic Identification of Organic Compounds*, 4th ed.; Wiley: 1981; pp 186.

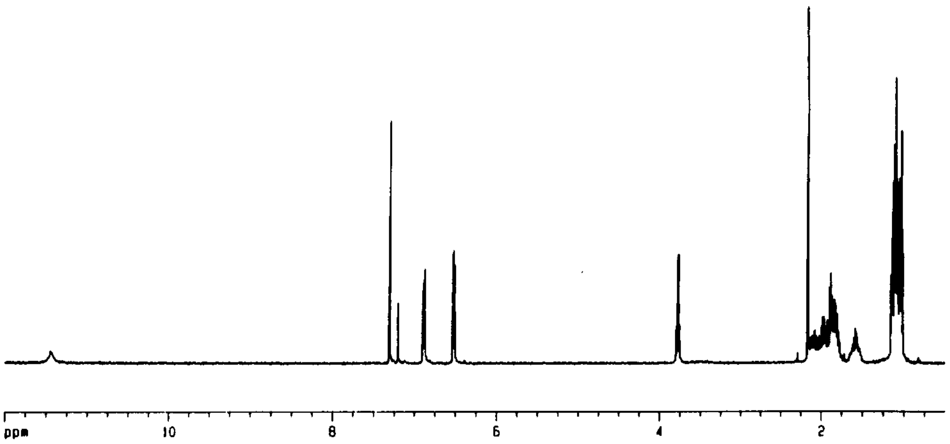
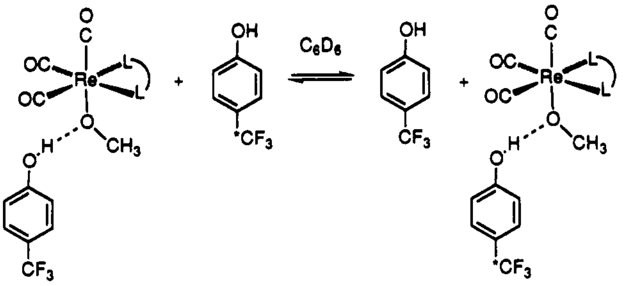


Figure 3. ^{1}H NMR spectrum of $(CO)_3(depe)ReOCH_2CH_3\cdots HOC_6H_4CH_3$ in C_6D_6 at 20 °C.

Scheme XI



6b··HOC₆H₄CF₃

$HOC_6H_4{}^*CF_3$=added $CF_3C_6H_4OH$

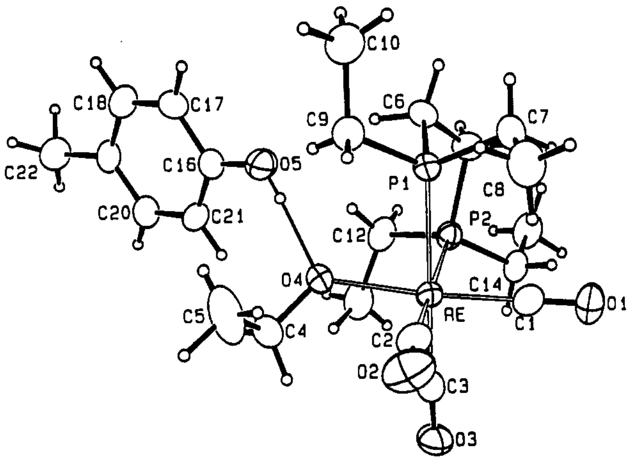


Figure 4. ORTEP diagram of $(CO)_3(depe)ReOCH_2CH_3\cdots HOC_6H_4CH_3$. The hydrogen-bonded proton was located.

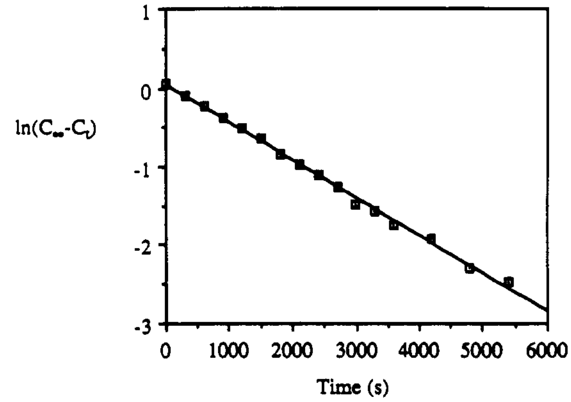


Figure 5. A representative first-order plot for the conversion of the hydrogen-bonded complex $(CO)_3(diars)ReOCH_3\cdots HOC_6H_4CF_3$ to $(CO)_3(diars)ReOC_6H_4CF_3$ and CH_3OH.

Table VII. Selected Intramolecular Distances (Å) for *fac*-$(CO)_3(depe)ReOCH_2CH_3\cdots HOC_6H_4CH_3$ ($7e\cdots HOC_6H_4CH_3$)

$Re-P_1$	2.449(1)	C_3-O_3	1.163(6)
$Re-P_2$	2.445(1)	C_4-O_4	1.417(6)
$Re-O_4$	2.154(3)	C_4-C_5	1.508(9)
$Re-C_1$	1.893(5)	$O_4\cdots O_5$	2.532(5)
$Re-C_2$	1.949(6)	$O_4\cdots H(O)$	1.77(5)
$Re-C_3$	1.935(5)	$H(O)-O_5$	0.77(5)
C_1-O_1	1.157(6)	O_5-C_{16}	1.351(6)
C_2-O_2	1.162(6)		

Table VIII. Selected Intramolecular Angles (deg) for *fac*-$(CO)_3(depe)ReOCH_2CH_3\cdots HOC_6H_4CH_3$ ($7e\cdots HOC_6H_4CH_3$)

P_1-Re-P_2	81.24(4)	C_1-Re-C_2	88.53(23)
P_1-Re-O_4	85.31(9)	C_1-Re-C_3	90.31(21)
P_1-Re-C_1	90.85(16)	C_2-Re-C_3	92.96(21)
P_1-Re-C_2	93.50(15)	$Re-C_1-O_1$	178.9(5)
P_1-Re-C_3	173.46(16)	$Re-C_2-O_2$	175.8(5)
P_2-Re-O_4	85.71	$Re-C_3-O_3$	177.0(4)
P_2-Re-C_1	89.85(16)	$Re-O_4-C_4$	119.9(3)
P_2-Re-C_2	174.49(15)	$Re-O_4\cdots H(O)$	126.6(17)
P_2-Re-C_3	92.33(16)	$C_4-O_4\cdots H(O)$	111.2(18)
O_4-Re-C_1	174.52(17)	$O_4-C_4-C_5$	112.0(5)
O_4-Re-C_2	95.54(18)	$O_4\cdots H(O)-O_5$	172.3(60)
O_4-Re-C_3	93.07(16)	$H(O)-O_5-C_{16}$	119.1(42)

cis-labilizing ligand,[4,29,30] a property that has been used to explain the formation of clusters when syntheses of the pentacarbonyl derivatives of the type $(CO)_5ReOR$ were attempted.[8,9,31] The formation of clusters containing bridging alkoxide ligands was avoided in our systems by using metal centers substituted with two phosphine or arsine ligands.

The aryloxide complexes can be prepared by treatment of the methyl complex $(CO)_3(PPh_3)_2ReCH_3$ with *p*-cresol or by metathesis using the triflate complexes **5**. Even though **2a** reacts with alcohols, stable alkoxide complexes could not be prepared in the bis-PPh_3-substituted systems. The alkoxide complexes may be prepared in good yields using the triflate displacement reaction. The alkoxides are remarkably stable and show no tendency to decompose by β-hydride elimination. Complexes bearing chelating ligands were found to be more thermally stable than those without. This trend has also been observed to be true for

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(29) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366–373.

(30) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160–3165.

(31) The attempted synthesis of $(CO)_5ReF$ by reaction of $(CO)_5ReBr$ with AgF resulted in the formation of a tetramer of $\{(CO)_3Re(\mu_3\text{-}F)\}$: Horn, E.; Snow, M. R. *Aust. J. Chem.* **1981**, *34*, 81–85.

Table IX. O–H⋯O Distances in Structurally Characterized Hydrogen-Bonded Transition-Metal Alkoxide Complexes

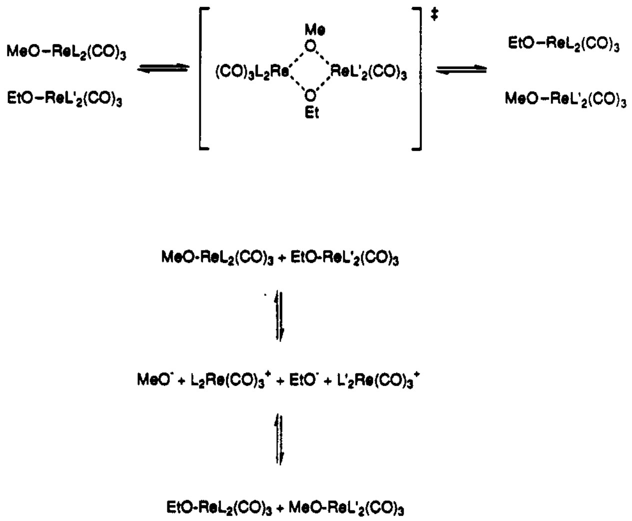
complex	O–H⋯O (Å)	ref
$(PMe_3)_3RhOC_6H_4CH_3\cdots HOC_6H_4CH_3$	2.62	19
trans-$(PC_6H_{11})_2Pd(H)(OC_6H_5)\cdots HOC_6H_5$	2.64	21
trans-$(PC_6H_{11})_2Pd(H)(OC_6F_5)\cdots HOC_6F_5$	2.59	22
trans-$(PMe_3)_2Pd(CH_3)(OC_6H_5)\cdots HOC_6H_5$	2.593(4)	23
trans-$(PMe_3)_2Ni(CH_3)(OC_6H_5)\cdots HOC_6H_5$	2.602(8)	23
trans-$(PMe_3)_2Pd(CH_3)(OC_6H_5)\cdots HOCH(CF_3)(C_6H_5)$	2.601(4)	23
cis-$(PMe_3)_2Pt(CH_3)(OCH(CF_3)_2)\cdots HOCH(CF_3)_2$	2.63(4)	24
trans-$(PCH_2C_6H_5)_2Ni(H)(OC_6H_5)\cdots HOC_6H_5$	2.544(10)	25
fac-$(CO)_3(depe)ReOCH_2CH_3\cdots HOC_6H_4CH_3$	2.532(5)	this work

Table X. Rate Constants for the Conversion of $(CO)_3(diars)ReOCH_3\cdots HOC_6H_4X$ to $(CO)_3(diars)ReOC_6H_4X$ and CH_3OH at 44 °C in C_6D_6

X	[**6b**], M	$[HOC_6H_4X]$, M	amt of HOC_6H_4X, equiv	k_{obs}, 10^4 s^{-1} [a]
H	0.0225	0.0225	1.0	3.6
CH_3	0.0225	0.0225	1.0	2.8
OCH_3	0.0225	0.0225	1.0	5.8
OCH_3	0.0268	0.0268	1.0	5.4
CF_3	0.0225	0.0225	1.0	4.8
CF_3	0.0225	0.113	5.0	4.9
Cl	0.0225	0.0225	1.0	1.6
$N(CH_3)_2$	0.0268	0.0268	1.0	9.9
$N(CH_3)_2$ [b]	0.0268	0.0268	1.0	9.7

[a] The largest variation found in the reproducibility of k_{obs} was ±0.4 s^{-1}. [b] 0.1 equiv of Proton Sponge was added.

Scheme XII



Pt(II) alkoxide complexes.[32] The alkoxide complexes can be converted to the aryloxide complexes by treatment of the alkoxides **6**–**8** with a variety of substituted phenols. The reaction is not reversible, and the aryloxide complexes **3b**,**c** do not react with alcohols to re-form the alkoxides. Because of the high kinetic stability of the aryloxides, it seem likely that part of the driving force for this reaction is due to formation of a stronger M–O bond in the aryloxides. However, part of the driving force could also arise from the formation of a stronger O–H bond. The bond energy of the O–H bond in methanol has been measured to be 102 kcal/mol,[33] while the O–H bond energy in *p*-cresol is only 88.7 kcal/mol.[34]

The structures of several of these complexes have been determined by X-ray diffraction studies. The Re–O distances show very little variation. The Re–O distance in **3a** is 2.143(9) Å, a value quite similar to that found in other Re(I) aryloxide complexes which have been structurally characterized. It is longer than the Re–O bond lengths in the complex *trans*-$(PMe_3)_2Re(OC_6H_5)_4$.[35] There is very little trans influence by the coordinated alkoxide or aryloxide on the Re–CO distances.

From a mechanistic point of view, the alkoxide for aryloxide exchange reaction is a perplexing transformation. As shown in Scheme VII, uncatalyzed intermolecular exchange of alkoxide ligands between rhenium centers does not occur. With the exception of the PPh_3-substituted cresolate complex **3a**, no dative ligand (CO, phosphine, or arsine) exchange reactions are observed for any of the alkoxide or aryloxide complexes. This strongly suggests that the observed alkoxide exchange reactions do not require an open coordination site at another position on the metal center. These observations greatly limit the likelihood of several potential mechanisms for external exchange of ligands.

One potential mechanism is a concerted, associative exchange between two different alkoxide complexes (Scheme XII). This pathway has been suggested to occur during alkoxide transfer reactions between coordinatively unsaturated metal centers.[36] Another mechanism involves ion pairs, in which the coordinated alkoxide or aryloxide ligand reversibly dissociates from the metal center to give an oxygen anion and a rhenium cation, and exchange could be effected by the free ions in solution (Scheme XII). Since no intermolecular exchange of alkoxide ligands was observed, it seems unlikely that these processes are occurring.

If the addition is performed at low temperatures, below 30 °C, the hydrogen-bonded complexe $\mathbf{6}\cdots HOC_6H_4X$ or $\mathbf{7}\cdots HOC_6H_4X$ are formed and may be isolated. The structure of $\mathbf{7e}\cdots HOC_6H_4CH_3$ has been determined by a X-ray diffraction study. The hydrogen atoms were refined on this structure, so it is possible to determine that there is a hydrogen bond between the *p*-cresol and the ethoxide. The O–O distance is quite short (2.532(5) Å), as is the O⋯H distance (1.77(5) Å). The O⋯H–O angle is nearly linear (173.2(60)°). These parameters put this hydrogen bond in the "strong" category.

Mechanism of Alkoxide for Aryloxide Exchange. In a number of previously described systems, aryloxide–phenol association constants were measured by a variety of techniques. We made several attempts to determine K_{eq} for hydrogen bond formation between **6b** and phenols using the method of Scatchard. However, the results were not accurate because of uncertainties in the measurement of the chemical shift of the H–O proton.[37] Using the O–O distance as a measure of the strength of the hydrogen bond, it is not unreasonable to assume that the association

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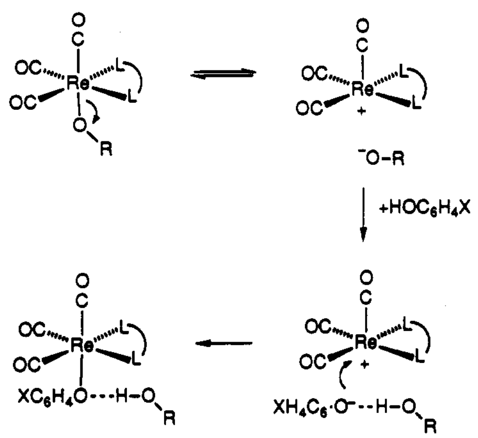
Scheme XIII



constant K_{eq} is very large. That this is qualitatively the case is indicated by the fact that the hydrogen bond persists even in dilute solution. The chemical shift of the hydrogen-bonded O–H is observed at low field even at temperatures where the alkoxide for aryloxide exchange reaction occurs.

Arnett and co-workers have measured the enthalpies of association for the reaction of *p*-fluorophenol and a number of neutral bases.[38] Some typical values (in kcal/mol) are as follows: FC_6H_5OH···anisole, $\Delta H = -3.13$; FC_6H_5OH···THF, $\Delta H = -5.75$; FC_6H_5OH···triethylamine, $\Delta H = -8.92$. The hydrogen bonds between phenols and metal alkoxides which have been measured have values of −11.4 kcal/mol for the O–H···O bond in the rhodium system[20] and −4.1 to −5.9 kcal/mol for palladium and platinum systems.[24,25]

In all of these previously mentioned cases, the metal center to which the alkoxide is coordinated has all of its bonding orbitals occupied. π back-donation of the alkoxide's lone pair would have to be placed into a metal antibonding orbital.[39] To avoid this unfavorable interaction, the coordinated oxygen is much more basic than "normal" oxygen linkage. A more appropriate model for the hydrogen bonding in this system may be charged complexes such as $C_6H_5O^-$···HOC_2H_5. The enthalpy of the hydrogen bond in this complex has been measured to be $\Delta H = -19.3$ kcal/mol in the gas phase.[40] The strong hydrogen bonds between alkoxide complexes and phenols (**6**···HOC_6H_4X or **7**···HOC_6H_4X), compared to those formed between aryloxide complexes and phenols, is expected since the oxygen center in the alkoxide complexes is more electron rich. An electron-rich hydrogen bond acceptor has been shown to contribute to the formation of strong hydrogen bonds.[41]

These hydrogen bonds between the alkoxides and phenols are exceptional, given the large difference in pK_B's between RO^- and $XC_6H_4O^-$.[42] The rates of proton transfer from HOR to HO^- typically have extremely fast (diffusion-controlled) rate constants.[43-45] If the rate-limiting step in the exchange reaction is the ionization of RO^- from the alkoxide complex (Scheme XIII), then all of the exchange reactions would proceed at the same rate, assuming that recoordination of the phenolate anion to the rhenium cation is fast and that the change of the para substituent does not cause a change in the exchange mechanism. This high barrier for proton transfer suggests that even though the Re–OR bond is highly polarized toward oxygen, it still contains a great deal of covalent character.

Table XI. Comparison of Rate Constants for Interchange of $(CO)_3$(diars)$ReOCH_3$···HOC_6H_4X with Phenol pK_A and BDE

X	k_{obs}, 10^4 s^{-1}	BDE, kcal/mol[a]	pK_A(DMSO)[a]
$N(CH_3)_2$	9.8	80.3	19.8
OCH_3	5.8	84.6	19.1
CH_3	2.8	88.7	18.9
H	3.6	89.8	18
Cl	1.6	90.3	16.7
CF_3	4.8	95.3	15.2
NO_2	very fast	94.7	10.8

[a] Data are taken from: Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 1736–1743.

The unusual stability of the hydrogen bond in these complexes allows for the measurement of the first-order rate constants (k_{obs}) for the interconversion of the hydrogen-bonded methoxide complexes **6**···HOC_6H_4X to the substituted phenols **3b**-*p*-X. All of the measured rate constants are remarkably similar, and there is very little change caused by the para substituent.

During the course of these studies, Bordwell and Cheng[34] conducted a thorough investigation of pK_a's and bond dissociation energies of a number of para-substituted phenols. Their results along with our rate constants are listed in Table XI. Two distinct trends are evident from the data. The first is that electron-withdrawing groups in the para position decrease the pK_a's of the phenols and increase the O–H bond dissociation energies, while electron-donating groups decrease the bond dissociation energies and increase the pK_a's. We propose that the exchange rate is increased by a decrease in the phenol pK_a as well as by a decrease in O–H BDE. If this is the case, the small dependence of the rate on the substituent may be due to the fact that these two effects operate in opposite directions for the substituents listed in Table X.

To test this hypothesis, the acidity and/or the BDE of the hydrogen-bonded phenol must be changed independently. Bordwell's data suggest that this can be done with the *p*-$N(CH_3)_2$ and *p*-NO_2 substituents. Substitution of an $N(CH_3)_2$ group for the OCH_3 group results in a change in pK_a from only 19.1 (OCH_3) to 19.8 ($N(CH_3)_2$), while the BDE decreases from 84.6 (OCH_3) to 80.3 kcal/mol ($N(CH_3)_2$). Upon this substitution, the exchange rate constant increases from $k_{obs}(OCH_3) = 5.8 \times 10^{-4}$ s^{-1} to $k_{obs}(N(CH_3)_2) = 9.8 \times 10^{-4}$ s^{-1}. On the "low pK_a" end of the scale, substitution of a NO_2 group for the *p*-CF_3 group changes the pK_a quite dramatically (pK_a(CF_3) = 15.2, pK_a(NO_2) = 10.8) while perturbing the O–H BDE very little (BDE(CF_3) = 95.3, BDE(NO_2) = 94.7). The result is again an increase in rate: $k_{obs}(CF_3) = 4.8 \times 10^{-}$ s^{-1}, while exchange of Re–OCH_3 for $OC_6H_4NO_2$ occurs upon mixing **6b** and $HOC_6H_4NO_2$ at room temperature (we estimate conservatively that $k_{obs} \geq 10$ s^{-1}).

We suggest that the exchange transition state can be stabilized by both a decrease in the phenol's O–H BDE as well as an increase in the phenol's acidity. These divergent trends cause a Hammett plot of k_{obs} vs σ_p to be "bowl shaped" rather than linear. These results suggest that the transition state for M–OR to M–OAr interchange has both hydrogen atom transfer and proton transfer character (Scheme XIV).

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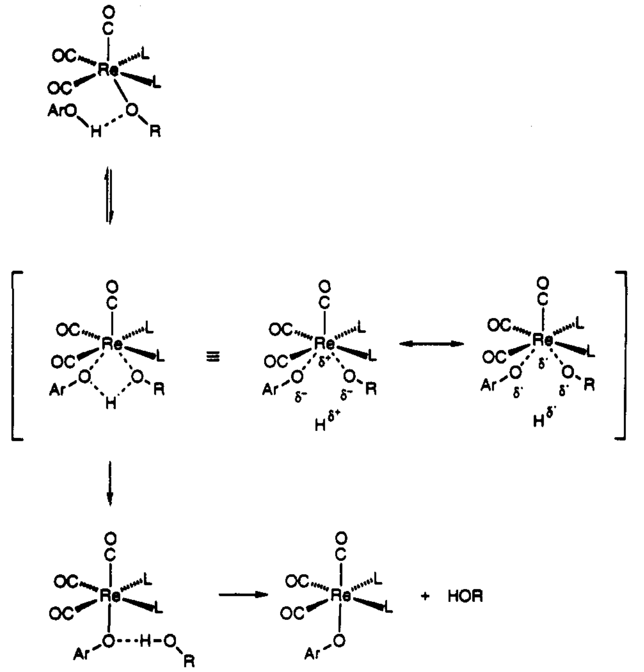
Scheme XIV



Summary. Rhenium alkoxide and aryloxide complex complexes of the general formula $(CO)_3(L)_2ReOR$ may be synthesized by a variety of techniques. The alkoxide complexes are prepared by the displacement of coordinated triflate, while the aryloxide complexes may be prepared by the reaction of an alkyl complex with phenol, the displacement of coordinated triflate by a phenoxide anion, or reaction of the alkoxide complexes with phenol. In general, the aryloxide complexes are thermally more stable than the corresponding alkoxide complexes. The Re–O bond in these complexes is highly polarized, making the oxygen atom much more basic than those in organic ethers. This is demonstrated by the ability of the alkoxide complexes to form strong hydrogen bonds to phenols. These complexes are intermediates in the alkoxide for phenol exchange. Mechanistic studies on this process reveal that the transition state of the exchange reaction is stabilized by a decrease in both phenol pK_a and O–H BDE.

Experimental Section

General Considerations. Unless otherwise stated, all reactions and manipulations were accomplished in dry glassware under nitrogen or argon atmospheres in a Vacuum Atmospheres HE-553-2 Dri-Lab with an attached MO-40 Dri-Train. The amount of oxygen in the drybox atmosphere was monitored by a Teledyne Model 316 trace oxygen analyzer, and the H_2O level in the atmosphere was monitored by an E & H Ondyne Model 1400 hygrometer.

All ^1H, $^{13}C\{^1H\}$, ^{19}F, and $^{31}P\{^1H\}$ spectra were recorded on a Bruker AMX spectrometer at 400, 100, 376, or 162 MHz, respectively, or on a 300-MHz instrument assembled by Mr. Rudi Nunlist at the University of California, Berkeley (UCB), NMR Facility, operating at 300, 75.5, and 121.5 MHz, respectively. Assignments of ^{13}C chemical shifts were made using standard DEPT pulse sequences. For second-order spin systems (AXX′), the value listed is the sum of the one-bond and three- or four-bond coupling constants in the spin system. For the PMe_3 ^1H resonances, the value listed as the coupling constant ("J_{PH}") is the separation in hertz of the two outer lines and is listed as an method for identification and not meant to represent the actual coupling constant. Infrared spectra were recorded on a Nicolet 510 FT-IR interfaced to a 620 Data Processor. Mass spectroscopic analyses were obtained at the UCB mass spectrometry facility on AEI MS-12 or Kratos MS-50 mass spectrometers. Elemental analyses were obtained from the UCB Microanalytical Laboratory.

Benzene, toluene, Et_2O, pentane, hexanes, and THF were distilled from sodium/benzophenone. Acetonitrile and methylene chloride were distilled from CaH_2. Benzene-d_6, toluene-d_8, and THF-d_8 were vacuum-transferred from sodium/benzophenone. $CDCl_3$ and CD_2Cl_2 were vacuum-transferred from CaH_2. The compounds 1,[46] **4b**,[47] **9c**,[15] and $Re(CO)_5Cl$[48] were prepared by literature methods. Trimethylamine *N*-oxide was dried by azeotropic distillation of a DMF solution of the dihydrate and then crystallization. Triphenylphosphine and *p*-nitrophenol were recrystallized from EtOH. Phenol, *p*-cresol, *p*-(trifluoromethyl)phenol, and *p*-chlorophenol were first dried by azeotropic distillation with benzene and then distilled under vacuum. *p*-Methoxyphenol was recrystallized from C_6H_6. *p*-(Dimethylamino)phenol was synthesized by the procedure of Sekiya, Tomie, and Leonard and distilled prior to use.[49] Trimethylphosphine was purchased from Strem Chemical Co. and vacuum-transferred from a Na/K mirror. *tert*-Butyl isocyanide was purchased from Aldrich and vacuum-transferred from P_2O_5. *o*-Phenylenebis(dimethylarsine) (diars) was purchased from Quantum Design and used as received. Bis(diethylphosphino)ethane (depe) was synthesized from the tetrachloride using the literature procedure.[50] Trifluoromethanesulfonic acid (triflic acid) was used as received from Aldrich and stored at −10 °C under Ar. Methanol, ethanol, and 2-propanol were distilled from magnesium turnings. Unless otherwise noted, all other reagents were used as received. Flash chromatography was performed using the procedure of Still, Khan, and Mitra.[51] A "bomb" refers to a cylindrical glass vessel sealed to a Kontes high-vacuum stopcock. Reactions with gases involved condensation of a calculated pressure of gas from a bulb of known volume into a reaction flask cooled to −196 °C (liquid N_2). The pressure of the added gas was measured by the use of an MKS Baratron gauge. Sealed NMR tubes were prepared using Wilmad 505-PP tubes attached to a vacuum line via Cajon adapters fitted with Kontes vacuum stopcocks.[52]

$(CO)_3(PPh_3)_2ReCH_3$ (2a). In the drybox a flask was charged with 750 mg (1.48 mmol) of *cis*-$(CO)_4(PPh_3)ReCH_3$ (1) and 20 mL of CH_3CN. A vial was charged with 116 mg (1.55 mmol, 1.05 equiv) of trimethylamine *N*-oxide and 2 mL of CH_3CN. This solution was added via pipet to the stirred solution of 1, and then the flask was stoppered and the mixture stirred at room temperature for 2 h. At this time an aliquot was removed and examined by IR. It showed complete disappearance of the carbonyl absorptions of 1 and formation of the previously reported[13] complex *fac*-$(CO)_3(PPh_3)(NCCH_3)ReCH_3$ (ν_{CO} 2017, 1909, 1878 cm^{-1}). The acetonitrile was removed with the aid of a vacuum pump in the box and the remaining off-white residue dissolved in 10 mL of C_6H_6. Triphenylphosphine (408 mg, 1.55 mmol, 1.05 equiv) was dissolved in 3 mL of C_6H_6 and added via pipet to the reaction mixture. The mixture was stirred at room temperature overnight. The benzene was then removed by lyophilization to yield a white powder. This was collected on a glass frit and washed with hexanes to remove the excess PPh_3. Recrystallization from toluene/pentane afforded 1.02 g (1.26 mmol, 85% yield) of analytically pure **2a**. ^1H NMR ($CDCl_3$): 7.29 (m, 12H, PPh_3 ortho), 7.16 (m, 18H, PPh_3 meta and para),

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-0.558 (t, J_{PH} = 8.0 Hz, Re–CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 195.6 (AXX′, $J_{PC} + J_{P'C}$ = 89.3 Hz, CO cis to CH_3), 194.2 (t, J_{PC} = 7.9, CO trans to CH_3), 134.0 (AXX′, $J_{PC} + J_{P'C}$ = 70.9, PPh_3 ipso), 133.9 (vt, J_{PC} = 5.3, PPh_3 ortho or meta), 129.8 (PPh_3 para), 128.0 (vt, J_{PC} = 4.5, PPh_3 ortho or para), -20.8 (t, J_{PC} = 9.1, Re–CH_3) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): 8.0 ppm. IR (KBr): ν_{CO} 2030 (sh), 2002 (s), 1919 (s), 1877 (s) cm^{-1}. Anal. Calcd for $C_{40}H_{33}O_3P_2Re$: C, 59.30; H, 4.11. Found: C, 58.97; H, 4.12.

$(CO)_3(PPh_3)_2ReOC_6H_4CH_3$ (3a). In the drybox, a bomb was charged with 748 mg (0.923 mmol) of **2a**, 200 mg (1.85 mmol, 2 equiv) of p-cresol, and 20 mL of C_6H_6. The colorless solution was heated at 46 °C for 12 h. After this time the colorless solution had turned lemon yellow. The bomb was removed from the bath and cooled to room temperature, and the volatile materials were removed on a vacuum line. The resulting yellow residue was exposed to vacuum overnight to remove the excess cresol. The bomb was taken into the drybox, and the residue was washed with hexanes. The residue was extracted with toluene (3 × 2 mL), and the toluene extracts were evaporated using a vacuum pump. The resulting yellow oil was extracted into 3:1 Et_2O:toluene. This solution was cooled to −40 °C for 3 days. The resulting off-white powder was collected on a sintered glass frit, washed with hexanes, and exposed to high vacuum for 12 h to yield 620 mg (0.690 mmol, 74%) of $(CO)_3(PPh_3)_2ReOC_6H_4CH_3$ (**3a**). ^1H NMR (CD_2Cl_2): 7.32 (m, 12H, PPh_3 ortho), 7.14 (m, 18H, PPh_3 meta and para), 6.86 (d, 2H, J = 8.2 Hz, $OC_6H_4CH_3$), 6.37 (d, 2H, J = 8.2, $OC_6H_4CH_3$), 2.20 (s, 3H, $OC_6H_4CH_3$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 192.3 (b, CO), 166.4 (t, J_{PC} = 4.5 Hz, $OC_6H_4CH_3$ ipso bearing oxygen), 134.5 (vt, J_{PC} = 5.3, PPh_3 ortho or meta), 133.0 (AXX′, $J_{PC} + J_{P'C}$ = 42.0, PPh_3 ipso), 130.5 ($OC_6H_4CH_3$ arom CH), 129.8 ($OC_6H_4CH_3$ arom CH), 128.5 (vt, J_{PC} = 4.8, PPh_3 ortho or meta), 122.6 (PPh_3 para), 120.0 ($OC_6H_4CH_3$ ipso bearing methyl), 20.4 ($OC_6H_4CH_3$) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 6.0 ppm. IR (KBr): ν_{CO} 2015, 1919, 1891 cm^{-1}. Anal. Calcd for $C_{46}H_{37}O_4P_2Re$: C, 61.26; H, 4.13. Found: C, 61.09; H, 3.98. FAB mass spectrum (*p*-nitrophenyl octyl ether matrix, *m/e*): M + H^+ 903; base peak 795; $(CO)_3(PPh_3)_2ReOC_6H_4CH_3 - HOC_6H_4CH_3$.

Crystal Structure Determination of 3a. Clear, colorless, blocklike crystals of **3a** were obtained by slow cooling of a toluene/pentane solution to −40 °C. Fragments cleaved from some of these crystals were mounted on glass fibers using polycyanoacrylate cement and then coated with the same to protect the crystal from moisture. Preliminary Laue photographs determined crystal quality.

The crystal used for data collection was then transferred to our Enraf-Nonius CAD-4 diffractometer and centered in the beam. Automatic peak search and indexing yielded an orthorhombic reduced primitive unit cell. The final cell parameters and specific data collection parameters for this data set are given in Tables I and II.

The 5795 unique raw intensity data were converted to structure factor amplitudes and their standard esd's by correction for scan speed, background, and polarization effects. Inspection of the intensity standards revealed a reduction of 4% of the original intensity. The data were corrected for this decay. Inspection of the azimuthal scan data showed the variation I_{min}/I_{max} = 0.64 for the average curve. An empirical correction based on the observed variation was applied to the data. Inspection of the systematic absences indicated possible space groups *Pbcm* and $Pbc2_1$ (an alternative setting of No. 29, $Pca2_1$). The choice of the noncentric $Pbc2_1$ was determined by the Patterson map and by the successful solution and refinement of the structure. Removal of systematically absent data left 5417 unique data in the final data set.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. Since there were too few data to refine all atoms with anisotropic thermal parameters, only Re, P, carbonyl, and cresolate atoms were refined anisotropically. Hydrogen atoms were included (except for the cresolate methyl group) in idealized locations, and values of B_{iso} were approximately 1.2 times the B_{eqv} value of the atoms to which they were attached. They were included in the structure factor calculations but not refined. Testing of the enantiomorph of the crystal structure revealed that the sample was probably twinned. The best residuals were obtained with the imaginary term of the scattering factors set to zero.

The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The analytical forms of the scattering factor tables for the neutral atoms were used, and all scattering factors were corrected for the real component of anomalous dispersion.

Inspection of the residuals ordered in ranges of $(\sin\theta)/\lambda$, $|F_o|$, and parity and value of the individual indexes showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 1.32 e/Å^3 and a lowest excursion of -0.37 e/Å^3. There was no indication of secondary extinction in the low-angle data.

The crystal structure consists of two crystallographically independent molecules of the compound packed in the unit cell. There are no particularly close intermolecular contacts.

In each molecule the three carbonyl ligands are *fac*, with the plane of the tosylate ligand approximately bisecting the angle between the two CO's which are in the same plane as the PPh_3 ligands. Each cresolate coordinates to the Re with a C–O–Re angle of about 132°, and Re is in the plane of the cresolate ligand. As reported, the two independent molecules are approximately enantiomorphic to each other. Since both enantiomorphs of each molecule are present in the cell, the two can be regarded as nearly identical. Minor differences in orientation, bond angles, and torsion angles do exist between the two molecules.

When such close correspondence of crystallographically independent molecules exists, there is always the suspicion that the solution is in the wrong space group and that the true space group relates the two molecules by symmetry. After careful inspection it appears that the symmetry elements which might relate the two molecules are all local symmetry rather than global (space group) symmetries.

The positional parameters, thermal parameters, and anisotropic thermal parameters of non-hydrogen atoms and their estimated standard deviations are available as supplementary material.

$(CO)_3(PMe_3)_2ReOC_6H_4CH_3$ (3c). Method A. In the drybox, a bomb was charged with 250 mg (0.279 mmol) of **3a** in 10 mL of C_6H_6. It was removed from the box and attached to a vacuum line equipped with an MKS Baratron gauge. PMe_3 (0.692 mmol, 2.5 equiv) was condensed into the bomb at −196 °C. The bomb was closed and heated to 45 °C overnight. After this time the reaction mixture was examined by $^{31}P\{^1H\}$ NMR spectrometry. This showed complete disappearance of **3a** (δ 6.0) and new peaks for **3c** (δ −31.5), free PPh_3 (δ −4.85), and PMe_3 (δ −62.0). The benzene solution was concentrated to ~1 mL, and hexanes (10 mL) was added, which caused a white solid to form immediately. The white solid was collected on a sintered-glass frit and washed with 3 × 10 mL of hexanes. It was dissolved in a minimum volume of toluene and the resulting solution layered with pentane and cooled to −40 °C overnight. After the mixture stood overnight, white needles had formed. These were collected on a frit, washed with hexane (2 × 10 mL), and exposed to high vacuum for 12 h to yield 90 mg (0.17 mmol, 61% yield) of **3c**.

Method B. In the drybox, a Schlenk flask was charged with 120 mg (1.11 mmol, 1.11 equiv) of *p*-cresol and 221 mg (1.11 mmol, 1.11 equiv) of $KN(TMS)_2$. The flask was removed from the drybox and attached to a Schlenk line. THF (30 mL) was added via syringe, and the resulting solution was stirred at room temperature for 20 min. This solution was transferred via cannula to a Schlenk flask containing 571 mg (1.0 mmol) of **5c**. The resulting solution was stoppered and stirred for 2 days at room temperature. After this time, the volatile materials were removed using a vacuum line. The white residue was dissolved in 30 mL of toluene and filtered through a piece of Whatman filter paper (No. 1) wrapped around the bottom of a cannula. The toluene was removed on a vacuum line to yield 450 mg (0.835 mmol, 84%) of a white solid. ^1H NMR ($CDCl_3$): 7.15 (d, 2H, J = 8.3 Hz, $OC_6H_4CH_3$), 6.01 (d, 2H, J = 8.3, $0C36H_4CH_3$), 2.28 (s, 3H, $OC_6H_4CH_3$), 1.22 ($A_9A_{9'}XX'$, 18H, "J_{HP}" = 8.22, $P(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C): 197.4 (b, CO), 168.9 (t, J_{PC} = 2.7

Hz, $OC_6H_4CH_3$ ipso bearing oxygen), 130.2 ($OC_6H_4CH_3$ arom *C*H), 122.5 ($OC_6H_4CH_3$ ipso bearing methyl), 119.6 ($OC_6H_4CH_3$ arom *C*H), 20.7 ($OC_6H_4CH_3$), 15.8 (AXX′, $^1J_{PC} + {}^3J_{PC} = 30.1$, $P(CH_3)_3$) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −31.5 ppm. IR (KBr): ν_{CO} 2010 (s), 1921 (s), 1887 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{24}O_4P_2Re$: C, 36.79; H, 4.76. Found: C, 36.44; H, 4.73.

Preparation of $(CO)_3(diars)ReOC_6H_4CH_3$ (3b-*p*-CH_3) by Ligand Substitution (Method A). In the drybox, 300 mg (0.333 mmol) of **3a** was dissolved in 5 mL of C_6H_6. *o*-Phenylenebis(dimethylarsine) (diars; 123 mg, 0.430 mmol, 1.3 equiv) was added via syringe and the bomb stoppered and placed in a 46 °C bath for 12 h. After this time, examination of the mixture by $^{31}P\{^1H\}$ NMR spectrometry showed the disappearance of **3a** (δ 6.0 ppm) and formation of free PPh_3 (δ −4.85 ppm). The benzene was removed on a vacuum line and the bomb taken into the drybox. The white powder was washed with hexanes (3 × 3 mL) to yield 170 mg (0.26 mmol, 77%) of analytically pure **3b**-*p*-CH_3.

Preparation of diars-Substituted Aryloxide Complexes by Exchange of Methoxide (Method B). $(CO)_3(diars)ReOC_6H_4CH_3$ (3b-*p*-CH_3). In the drybox, a bomb was charged with 58.0 mg (0.10 mmol) of **6b**, 11.0 mg (0.10 mmol, 1.01 equiv) of *p*-cresol, and 3 mL of C_6H_6. It was removed from the drybox and heated at 44 °C for 10 h. The bomb was then removed from the bath, and the volatile materials were removed in vacuo. The resulting white powder was dissolved in a minimum amount of toluene (~0.5 mL), layered with 5 mL of Et_2O, and cooled to −40 °C for 2 days. The resulting white powder was collected on a sintered-glass funnel and washed with pentane. Residual solvent was removed under high vacuum to yield 62 mg (93% yield, 0.093 mmol) of **3b**-*p*-CH_3. ^1H NMR ($CDCl_3$): 7.80 (m, 2H, diars, C*H*), 7.63 (m, 2H, diars C*H*), 6.83 (d, 2H, *J* = 8.3 Hz, $OC_6H_4CH_3$), 6.36 (d, 2H, *J* = 8.3 Hz, $OC_6H_4CH_3$), 2.17 (s, 3H, $OC_6H_4CH_3$), 1.79 (s, 6H, diars CH_3), 1.59 (s, 6H, diars CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 194.0 (*C*O cis to $OC_6H_4CH_3$), 191.5 (*C*O trans to $OC_6H_4CH_3$), 167.3 ($OC_6H_4CH_3$ ipso bearing oxygen), 139.8 (diars ipso), 131.4 (arom *C*H), 130.3 (arom *C*H), 129.4 (arom *C*H), 122.3 ($OC_6H_4CH_3$ ipso bearing methyl), 118.6 (arom *C*H), 20.2 ($OC_6H_4CH_3$), 12.8 (diars *C*H_3), 8.7 (diars *C*H_3) ppm. IR (KBr): ν_{CO} 2014, 1913, 1881 cm^{-1}. Anal. Calcd for $C_{20}H_{23}As_2O_4Re$: C, 36.21; H, 3.49. Found: C, 36.35; H, 3.39.

$(CO)_3(diars)ReOC_6H_4OCH_3$ (3b-*p*-OCH_3). Employing the above procedure on a 0.10-mmol scale resulted in a 71% yield of pale yellow crystals. ^1H NMR ($CDCl_3$): 7.68 (m, 2H, diars, C*H*), 7.50 (m, 2H, diars C*H*), 6.83 (AA′BB′, 2H, *J* = 9.0 Hz, $OC_6H_4OCH_3$), 6.36 (AA′BB′, 2H, *J* = 9.0 Hz, $OC_6H_4OCH_3$), 3.57 (s, 3H, $OC_6H_4OCH_3$), 1.67 (s, 6H, diars CH_3), 1.48 (s, 6H, diars CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 194.1 (*C*O cis to $OC_6H_4OCH_3$), 191.4 (*C*O trans to $OC_6H_4OCH_3$), 164.3 ($OC_6H_4OCH_3$ ipso), 149.0 ($OC_6H_4OCH_3$ ipso), 139.8 (diars ipso), 131.4 (diars *C*H), 130.3 (diars *C*H), 118.6 ($OC_6H_4OCH_3$ *C*H), 115.0 ($OC_6H_4OCH_3$ *C*H), 56.0 ($OC_6H_4OCH_3$ *C*H_3), 20.2 ($OC_6H_4CH_3$), 12.8 (diars *C*H_3), 8.7 (diars *C*H_3) ppm. IR (KBr): ν_{CO} 2014, 1910, 1892 cm^{-1}.

$(CO)_3(diars)ReOC_6H_4CF_3$ (3b-*p*-CF_3). Employing the above procedure on a 0.10-mmol scale resulted in a 95% yield of white crystals. ^1H NMR ($CDCl_3$): 7.69 (m, 2H, diars C*H*), 7.55 (m, 2H, diars, C*H*), 6.83 (d, 2H, *J* = 8.7 Hz, $OC_6H_4CF_3$), 6.36 (d, 2H, *J* = 8.7 Hz, $OC_6H_4CF_3$), 1.71 (s, 6H, diars CH_3), 1.45 (s, 6H, diars CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 193.6 (*C*O cis to $OC_6H_4CF_3$), 191.1 (*C*O trans to $OC_6H_4CF_3$), 172.2 ($OC_6H_4CF_3$ ipso bearing oxygen), 139.5 (diars ipso), 131.6 (diars *C*H), 130.3 (diars *C*H), 126.3 (q, J_{FC} = 3.6 Hz, $OC_6H_4CF_3$ *C*H ortho to CF_3), 125.6 (q, J_{FC} = 269.9 Hz, *C*F33), 118.7 ($OC_6H_4CF_3$*C*H ortho to O), 115.1 ($OC_6H_4CF_3$ ipso bearing CF_3), 12.8 (diars *C*H_3), 8.9 (diars *C*H_3) ppm. ^{19}F NMR ($CDCl_3$): −60.3 ppm. IR (KBr): ν_{CO} 2019, 1921, 1891 cm^{-1}. Anal. Calcd for $C_{20}H_{20}As_2F_3O_4Re$: C, 33.48; H, 2.81. Found: C, 33.37; H, 2.85.

$(CO)_3(diars)ReOC_6H_5$ (3b). Employing the above procedure on a 0.10-mmol scale resulted in a 90% yield of white crystals. ^1H NMR ($CDCl_3$): 7.69 (m, 2H, diars C*H*), 7.51 (m, 2H, diars C*H*), 6.91 (vt, 2H, "*J*" = 7.2, OC_6H_5 ortho), 6.32 (m, 3H, OC_6H_5 meta and para), 1.68 (s, 6H, diars CH_3), 1.47 (s, 6H, diars CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 193.9 (*C*O cis to OC_6H_5), 191.3 (*C*O trans to OC_6H_5), 169.5 (OC_6H_5 ipso bearing oxygen), 139.8 (diars ipso), 131.4 (arom *C*H), 130.3 (arom *C*H), 129.9 (arom *C*H), 119.1 (arom *C*H), 113.7 (arom *C*H), 20.2 ($OC_6H_4CH_3$), 12.8 (diars *C*H_3), 8.8 (diars *C*H_3) ppm. IR (KBr): ν_{CO} 2015, 1932, 1889 cm^{-1}.

$(CO)_3(diars)ReOC_6H_4Cl$ (3b-*p*-Cl). Employing the procedure on a 0.10-mmol scale resulted in an 81% yield of white powder. ^1H NMR ($CDCl_3$): 7.67 (m, 2H, diars, C*H*), 7.53 (m, 2H, diars C*H*), 6.82 (d, 2H, *J* = 8.8 Hz, OC_6H_4Cl), 6.22 (d, 2H, *J* = 8.8 Hz, OC_6H_4Cl), 1.69 (s, 6H, diars CH_3), 1.46 (s, 6H, diars CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 168.3 (OC_6H_4Cl ipso bearing oxygen), 139.6 (diars ipso), 131.5 (diars *C*H), 130.3 (diars *C*H), 128.5 (OC_6H_4Cl *C*H), 119.9 (CO_6H_4Cl *C*H), 117.8 (OC_6H_4Cl ipso bearing chlorine), 12.8 (diars *C*H_3), 8.8 (diars *C*H_3) ppm. The resonances for the carbonyl ligands were not observed. IR (KBr): ν_{CO} 2017, 1917, 1884 cm^{-1}. Anal. Calcd for $C_{19}H_{20}As_2ClO_4Re$: C, 33.37; H, 2.95. Found: C, 33.51; H, 2.95.

$(CO)_3(diars)ReOC_6H_4N(CH_3)_2$ (3b-*p*-$N(CH_3)_2$). Employing the above procedure on a 0.10-mmol scale resulted in a 93% yield of bright yellow crystals. ^1H NMR ($CDCl_3$): 7.80 (m, 2H, diars C*H*), 7.63 (m, 2H, diars C*H*), 6.83 (d, 2H, *J* = 8.3 Hz, $OC_6H_4CH_3$), 6.36 (d, 2H, *J* = 8.3, $OC_6H_4CH_3$), 2.17 (s, 3H, $OC_6H_4CH_3$), 1.79 (s, 6H, diars CH_3), 1.59 (s, 6H, diars CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): 194.0 (*C*O cis to $OC_6H_4CH_3$), 191.5 (*C*O trans to $OC_6H_4CH_3$), 163.8 ($OC_6H_4N(CH_3)_2$ ipso bearing oxygen), 142.2 (arom ipso), 140.3 (arom ipso), 131.0 (diars *C*H), 130.3 (diars *C*H), 119.2 ($OC_6H_4N(CH_3)_2$ *C*H), 117.5 ($OC_6H_4N(CH_3)_2$ *C*H), 43.3 ($OC_6H_4N(CH_3)_2$ *C*H_3), 12.1 (diars *C*H_3), 8.3 (diars *C*H_3) ppm. IR (KBr): ν_{CO} 2014, 1913, 1881 cm^{-1}.

$(CO)_3(diars)ReOC_6H_4NO_2$ (3b-*p*-NO_2). The compound was prepared using the same procedure, except that excess $HOC_6H_4NO_2$ was removed by sublimation at 45 °C. The compound was crystallized by layering a CH_2Cl_2 solution of **3b**-*p*-NO_2 (2 ML) with 5 mL of hexanes for 2 days at room temperature. ^1H NMR ($CDCl_3$): 7.95 (d, 2H, *J* = 9.3 Hz, $OC_6H_4NO_2$ C*H*), 7.87 (m, 2H, diars C*H*), 7.67 (m, 2H, diars C*H*), 6.34 (d, 2H, *J* = 9.2, $OC_6H_4NO_2$), 1.84 (s, 6H, diars CH_3), 1.55 (s, 6H, diars, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 193.1 (*C*O cis to $OC_6H_4NO_2$), 190.8 (*C*O trans to $OC_6H_4NO_2$), 176.5 ($OC_6H_4NO_2$ ipso bearing oxygen), 139.1 (diars ipso), 135.6 ($OC_6H_4NO_2$ ipso bearing NO_2), 131.8 (diars *C*H), 130.4 (diars *C*H), 126.4 ($OC_6H_4NO_2$ *C*H), 118.5 ($OC_6H_4NO_2$ *C*H, 12.8 (diars *C*H_3), 9.1 (diars *C*H_3) ppm. IR (KBr): ν_{Co} 2021 (s), 1926 (s), 1893 (s) cm^{-1}; ν_{NO} 1300 (s) cm^{-1}.

$(CO)_3(t\text{-}BuNC)_2ReOC_6H_4CH_3$ (3d). In the drybox, a bomb was charged with 181 mg (0.202 mmol) of **3a** and 10 mL of C_6H_6. *tert*-Butyl isocyanide (0.582 mmol, 3.5 equiv) was vacuum-transferred into the bomb at −196 °C. After thawing, it was heated to 46 °C for 18 h. Analysis of the reaction mixture by $^{31}P\{^1H\}$ NMR spectrometry showed only free PPh_3. The benzene was removed by lyophilization to yield an off-white powder. This residue was taken into the drybox and the residue slurried in hexanes, collected on a glass frit, and washed with 2 × 10 mL of hexanes. The residue was dissolved in 1 mL of toluene, the resulting solution layered with pentane, and the mixture cooled to −40 °C for 2 days. After this time, white needlelike crystals had deposited on the bottom of the vial. These were collected on a sintered-glass frit and washed with hexanes. The residue was redissolved in 0.5 mL of toluene, layered with pentane, and cooled to −40 °C for 3 days. The resulting white crystals were collected on a frit. ^1H and $^{31}P\{^1H\}$ NMR analysis showed no remaining PPh_3. The white crystals were exposed to high vacuum for 12 h overnight to yield 20 mg (0.036 mmol, 18%) of **3d**. ^1H NMR (C_6D_6): 7.11 (m, 4H, $OC_6H_4CH_3$), 2.32 (s, 3H, $OC_6H_4CH_3$), 0.76 (s, 18H, $CNC(CH_3)_3$) ppm. $^{13}C\{^1H\}$ (CD_2Cl_2): 190.2 (*C*O cis to $OC_6H_4CH_3$), 188.3 (*C*O trans to $OC_6H_4CH_3$), 170.3 ($CO_6H_4CH_3$ ipso bearing oxygen), 136.3 (1:1:1 t, J_{NC} = 19.0 Hz, *C*$NC(CH_3)_3$), 134.2 ($OC_6H_4CH_3$ *C*H), 133.9 ($OC_6H_4CH_3$ *C*H), 121.3 ($OC_6H_4CH_3$ ipso bearing methyl), 58.2 (1:1:1 t, J_{NC} = 5.2, CN*C*$(CH_3)_3$), 30.4 ($CNC(CH_3)_3$), 20.4 ($C_6H_4CH_3$) ppm. IR (KBr): ν_{CO} 2008, 1927, 1902 cm^{-1}. FAB mass spectrum (18-crown-6 matrix): calcd for $C_{17}H_{25}N_2O_4{}^{185}Re + H^+/C_{17}H_{25}N_2O_4{}^{187}Re + H^+$ 542.383 642/544.386 430 8, found 542.134 415/544.137 750 4. Repeated attempts at elemental analysis gave results which were ~2% low in carbon.

$(CO)_3(depe)ReCl$ (4e). In the drybox, a 250-mL Schlenk flask was charged with 723 mg (2.0 mmol) of $\mathrm{Re(CO)_5Cl}$, 412 mg (2.0 mmol, 1.0 equiv) of depe, and 50 mL of toluene. The flask was stoppered and removed from the box. It was attached to a Schlenk line, fitted with condenser, and allowed to reflux under $\mathrm{N_2}$ for 12 h. After this time, all the $\mathrm{Re(CO)_5Cl}$ had dissolved, yielding a clear, colorless solution. The mixture was cooled to room temperature, and the solvent was removed using a rotary evaporator. The white residue was purified using flash chromatography in air on $\mathrm{SiO_2}$ (7 × 25 cm) with 4:1 $\mathrm{CH_2Cl_2/Et_2O}$ as eluent. The fractions containing the product ($R_f = 0.53$) were evaporated using a rotary evaporator and residual solvent removed under high vacuum, yielding 610 mg (1.19 mmol, 62%) of **4e**. ^{1}H NMR ($\mathrm{CDCl_3}$): 2.15–1.66 (m, 12H, depe $\mathrm{C}H_2$), 1.17 (m, 12H, depe $\mathrm{C}H_3$) ppm. ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): 193.75 (d of d, $J_{\mathrm{PcisC}} = 10.7$ Hz, $J_{\mathrm{PtransC}} = 61.0$, CO cis to Cl), 190.09 (t, $J_{\mathrm{PC}} = 6.9$, CO trans to Cl), 23.25 (AXX′, $^1\mathrm{J}_{\mathrm{PC}} + {}^3J_{\mathrm{PC}} = 41.3$, depe $C\mathrm{H_2}$), 19.33 (AXX′, $^1J_{\mathrm{PC}} + {}^4J_{\mathrm{PC}} = 35.16$, depe $C\mathrm{H_2CH_3}$), 13.66 (AXX′, $^{J}{}_{\mathrm{PC}}$ + $^4J_{\mathrm{PC}} = 31.33$, depe $C\mathrm{H_2CH_3}$), 8.21 (depe $C\mathrm{H_3}$), 7.79 (depe $C\mathrm{H_3}$) ppm. ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$): 32.3 ppm. IR (KBr): ν_{CO} 2015, 1928, 1883 cm^{-1}. Anal. Calcd for $\mathrm{C_{13}H_{24}ClO_3P_2Re}$: C, 30.50; H, 4.73. Found: C, 30.56; H, 4.63.

$\mathrm{(CO)_3}$((S,S)-bdpp)ReCl (4f). In the drybox, a bomb was charged with 246 mg (0.681 mmol) of $\mathrm{Re(CO)_5Cl}$, 300 mg (0.681 mmol, 1.0 equiv) of (S,S)-bdpp, and 15 mL of toluene. The bomb was stoppered, placed in a 100 °C bath, and maintained at that temperature for 10 h. After this time, all the $\mathrm{Re(CO)_5Cl}$ had dissolved, yielding a clear, colorless solution. The bomb was then removed from the bath and cooled to room temperature. It was then carefully opened in a hood (*Caution*! CO gas is evolved), and the toluene was removed using a rotary evaporator. The residue was recrystallized from hot ethanol in the air to yield 452 mg (0.063 mmol, 88%) of analytically pure **4f**. ^{1}H NMR ($\mathrm{C_6D_6}$): 7.78 (m, 2H, (S,S)-bdpp $\mathrm{C_6H_5}$ ortho), 7.63–7.15 (m, 18H, (S,S)-bdpp aromatics), 3.51 (bm, 1H, (S,S)-bdpp $\mathrm{C}H$), 3.19 (bm, 1H, (S,S)-bdpp $\mathrm{C}H$), 2.25 (m, 1H, (S,S)-bdpp $\mathrm{C}H_2$), 1.85 (m, 1H, (S,S)-bdpp $\mathrm{C}H_2$), 1.29 (d of d, $J_{\mathrm{HH}} = 7.4$ Hz, $J_{\mathrm{PH}} = 14.0$, 3H, (S,S)-bdpp $\mathrm{C}H_3$), 0.922 (d of d, $J_{\mathrm{HH}} = 7.1$, $J_{\mathrm{PH}} = 11.1$, (S,S)-bdpp $\mathrm{C}H_3$) ppm. ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): 191.0 (d of d, $J_{\mathrm{PcisC}} = 9.8$ Hz, $J_{\mathrm{PtransC}} = 56.2$, CO cis to Cl), 190.2 (t, $J_{\mathrm{PC}} = 6.5$, CO trans to Cl), 189.0 (d of d, $J_{\mathrm{PcisC}} = 8.4$, $J_{\mathrm{PtransC}} = 59.7$, CO cis to Cl), 136.2 (d, $J_{\mathrm{PC}} = 10.7$, (S,S)-bdpp $\mathrm{C_6H_5}$ ortho or meta), 135.5 (d, $J_{\mathrm{PC}} = 44.6$, (S,S)-bdpp $\mathrm{C_6H_5}$ ipso), 134.8 (d, $J_{\mathrm{PC}} = 10.2$, (S,S)-bdpp $\mathrm{C_6H_5}$ ortho or meta), 134.4 (d of d, $J_{\mathrm{PC}} = 4.0$, $J_{\mathrm{PC}} = 33.7$, (S,S)-bdpp $\mathrm{C_6H_5}$ ipso), 132.9 (d of d, $J_{\mathrm{PC}} = 3.1$, part of the signal due to this carbon is buried under the neighboring resonance, (S,S)-bdpp $\mathrm{C_6H_5}$ ipso), 132.4 (d, $J_{\mathrm{PC}} = 8.0$, (S,S)-bdpp $\mathrm{C_6H_5}$ ortho or meta), 132.2 (d, $J_{\mathrm{PC}} = 9.3$, (S,S)-bdpp $\mathrm{C_6H_5}$ ortho or meta), 130.9 (d, $J_{\mathrm{PC}} = 2.1$, (S,S)-bdpp $\mathrm{C_6H_5}$ para), 130.4 (d, $J_{\mathrm{PC}} = 2.2$, (S,S)-bdpp $\mathrm{C_6H_5}$ para), 130.2 (d, $J_{\mathrm{PC}} = 1.8$, (S,S)-bdpp $\mathrm{C_6H_5}$ para), 129.6 (d, $J_{\mathrm{PC}} = 1.9$, (S,S)-bdpp $\mathrm{C_6H_5}$ para), 128.5 (d, $J_{\mathrm{PC}} = 8.9$, (S,S)-bdpp $\mathrm{C_6H_5}$ ortho or meta), 128.2 (d, $J_{\mathrm{PC}} = 9.9$, (S,S)-bdpp $\mathrm{C_6H_5}$ ortho or meta), 127.8 (d, $J_{\mathrm{PC}} = 9.1$, (S,S)-bdpp $\mathrm{C_6H_5}$ ortho or meta), 127.6 (d, $J_{\mathrm{PC}} = 9.6$, (S,S)-bdpp $\mathrm{C_6H_5}$ ortho or meta), 127.1 (d, $J_{\mathrm{PC}} = 41.4$, (S,S)hbdpp $\mathrm{C_6H_5}$ ipso), 37.26 (vt, $J_{\mathrm{PC}} = 6.7$, (S,S)-bdpp $\mathrm{C_6H_5}$ CH), 32.69 (d, $J_{\mathrm{PC}} = 22.7$, (S,S)hbdpp $\mathrm{C_6H_5}$ CH), 18.17 (d, $J_{\mathrm{PC}} = 6.5$, (S,S)-bdpp $\mathrm{C_6H_5}$ $C\mathrm{H_3}$), 17.44 (vt, $J_{\mathrm{PC}} = 19.3$, (S,S)-bpdd $\mathrm{C_6H_5}$ $C\mathrm{H_2}$), 17.32 (d, $J_{\mathrm{PC}} = 2.2$, (S,S)-bdpp $\mathrm{C_6H_5}$ $C\mathrm{H_3}$) ppm. ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$): 5.09 (d, $J_{\mathrm{PP}} = 30.9$ Hz), −6.34 (d, $J_{\mathrm{PP}} = 30.9$). IR (KBr): ν_{CO} = 2026, 1948, 1933, 1910, 1902 cm^{-1}. Anal. Calcd for $\mathrm{C_{32}H_{30}ClO_3P_2Re}$: C, 51.51; H, 4.05. Found: C, 51.75; H, 4.02.

$\mathrm{(CO)_3(PMe_3)_2ReOSO_2CF_3}$ (5c). In the drybox, a Schlenk flask was charged with 2.15 g (4.41 mmol) of $\mathrm{(CO)_3(PMe_3)_2Re(\eta^1\text{-}C_5H_5)}$. The flask was removed from the box, and $\mathrm{CH_2Cl_2}$ (150 mL) was added. The pale yellow solution was stirred at room temperature under Ar. Triflic acid (117.0 μL, 13.23 mmol, 3.0 equiv) was added via syringe. The solution immediately turned dark brown, and it was stirred at room temperature for 30 min. The solution was then filtered in the air through a bed of Celite, and the $\mathrm{CH_2Cl_2}$ was removed on a rotary evaporator to yield a brown oil. This was dissolved in 10 mL of $\mathrm{CH_2Cl_2}$, filtered through a 4-cm bed of acidic $\mathrm{Al_2O_3}$ on a sintered-glass funnel, and eluted with 150 mL of $\mathrm{CH_2Cl_2}$ to yield a brown solution which turns green as it stands in the air. The $\mathrm{CH_2Cl_2}$ was removed on the rotary evaporator. Because the residue still contained colored impurities (blue-green), it was dissolved in 10 mL of $\mathrm{CH_2Cl_2}$. This solution was filtered through a bed of $\mathrm{SiO_2}$ (1 cm) on a bed of acidic $\mathrm{Al_2O_3}$, with $\mathrm{CH_2Cl_2}$ as eluent. A pale brown filtrate was obtained, and a bright green band remained on the $\mathrm{SiO_2}$. The solvent was removed on a rotary evaporator to yield a brownish solid, which was slurried in hexanes, collected on a sintered-glass frit, and washed with hexanes (3 × 10 mL), $\mathrm{Et_2O}$ (1 × 10 mL), methanol (1 × 5 mL), and hexanes (1 × 10 mL) to yield 1.25 g (2.19 mmol, 50%) of $\mathrm{(CO)_3(PMe_3)_2ReOSO_2CF_3}$. ^{1}H NMR ($\mathrm{CDCl_3}$): 1.64 ($\mathrm{A_9A_{9'}XX'}$, "$J_{\mathrm{PH}}$" = 7.5 Hz, $\mathrm{P(C}H_3)_3$) ppm. ^{13}C{^{H}} NMR ($\mathrm{CDCl_3}$): 191.9 (t, $J_{\mathrm{PC}} = 5.4$, CO trans to $\mathrm{OSO_2CF_3}$), 189.4 (AXX′, $^1J_{\mathrm{PC}} + {}^3J_{\mathrm{PC}} = 48.8$, CO cis to $\mathrm{OSO_2CF_3}$), 118.3 (q, $J_{\mathrm{CF}} = 389.0$, $\mathrm{OSO_2}C\mathrm{F_3}$), 17.0 (AXX′, $^1J_{\mathrm{PC}} + {}^3J_{\mathrm{PC}} = 32.9$, $\mathrm{P(}C\mathrm{H_3)_3}$) ppm. ^{19}F NMR ($\mathrm{CDCl_3}$): −76.9 ppm. ^{31}P{^{1}H} NMR ($\mathrm{CDCL_3}$): −28.7 ppm. IR (KBr): ν_{CO} 2035 (s), 1931 (s), 1915 (s) cm^{-1}. Repeated attempts failed to give satisfactory elemental analysis of this compound; results were consistently >2% low. This does not affect the reactivity of the material in subsequent transformations.

Representative Procedure for the Preparation of Triflate Complexes from Chlorides. $\mathrm{(CO)_3(diars)ReOSO_2CF_3}$ (5b). A 250–mL Schlenk flask was charged with 870 mg (1.47 mmol) of $\mathrm{(CO)_3(diars)ReCl}$. Methylene chloride (100 mL), freshly distilled from $\mathrm{CaH_2}$, was added to the flask, and the resulting solution was stirred under Ar. Triflic acid (320 μL, 3.67 mmol, 3 equiv) was added via syringe, and the reaction mixture was refluxed under Ar for 15 h. The $\mathrm{CH_2Cl_2}$ was removed on a vacuum line to yield a gray residue. Hexanes (20 mL) was added via cannula and then decanted off. This procedure was repeated with $\mathrm{Et_2O}$ (20 mL) and methanol (5 mL), and the resulting white residue was exposed to high vacuum for 12 h to yield 882 mg (1.25 mmol, 85%) of **5b**. ^{1}H NMR ($\mathrm{CDCl_3}$): 7.81 (m, 2H, diars $\mathrm{C}H$), 7.64 (m, 2H, diars $\mathrm{C}H$), 1.88 (s, diars $\mathrm{C}H_3$), 1.76 (s, diars $\mathrm{C}H_3$) ppm. ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): 191.2 (CO trans to $\mathrm{OSO_2CF_3}$), 189.4 (CO cis to $\mathrm{OSO_2CF_3}$), 138.8 (diars ipso), 132.0 (diars CH), 130.3 (diars CH), 118.6 (q, $J_{\mathrm{CF}} = 389.0$, $\mathrm{OSO_2}C\mathrm{F_3}$), 13.1 (diars $C\mathrm{H_3}$), 10.6 (diars $C\mathrm{H_3}$) ppm. ^{19}F NMR ($\mathrm{CDCl_3}$): −76.7 ppm. IR (KBr): ν_{CO} 2046 (s), 2038 (s), 1939 (s), 1910 (s) cm^{-1}. Repeated attempts failed to give satisfactory elemental analysis of this compound; results were consistently >2% low. This does not affect the reactivity of the material in subsequent transformations.

$\mathrm{(CO)_3(depe)ReOSO_2CF_3}$ (5e). Treatment of **4e** as described above gave a 65% yield of **5e**. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.10–1.76 (m, 12H, depe $\mathrm{C}H_2$'s), 1.24–1.17 (m 12H, depe $\mathrm{CH_3}$) ppm. ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): 192.3 (d of d, $J_{\mathrm{PcisC}} = 9.6$ Hz, $J_{\mathrm{PtransC}} = 57.5$, CO cis to $\mathrm{OSO_2CF_3}$), 191.3 (t, $J_{\mathrm{PC}} = 6.6$, CO trans to $\mathrm{OSO_2CF_3}$), 118.2 (q, $J_{\mathrm{CF}} = 318.7$, $\mathrm{OSO_2}C\mathrm{F_3}$), 23.5 (AXX′, $^1J_{\mathrm{PC}} + {}^3J_{\mathrm{PC}} = 41.3$, depe $4CH_2$), 18.5 (AXX′, $^1J_{\mathrm{PC}} + {}^4J_{\mathrm{PC}} = 34.8$, depe $C\mathrm{H_2CH_3}$), 14.7 (AXX′, $^1J_{\mathrm{PC}} + {}^4J_{\mathrm{PC}} = 30.4$, depe $C\mathrm{H_2CH_3}$), 8.1 (depe $C\mathrm{H_3}$), 7.42 (depe $C\mathrm{H_3}$) ppm. ^{19}F NMR ($\mathrm{CDCl_3}$): −77.0 ppm. ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$): 40.2 ppm. IR (KBr): ν_{CO} 2030 (s), 2016 (sh), 1944 (s), 1916 (sh), 1907 (s) cm^{-1}.

$\mathrm{(CO)_3}$((S,S)-bdpp)$\mathrm{ReOSO_2CF_3}$ (5f). Treatment of **4f** as described above gave a 99% yield of **5f**. ^{1}H NMR ($\mathrm{CDCl_3}$): 7.56–7.19 (m, 20H, (S,S)-bdpp $\mathrm{C_6}H_5$), 3.04 (m, 2H, (S,S)-bdpp $\mathrm{C}H$), 2.11–2.02 (m, 2H, (S,S)-bdpp $\mathrm{C}H_2$), 1.01–0.96 (m, 6H, (S,S)-bdpp $\mathrm{C}H_3$) ppm. ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): 191.9 (t, $J_{\mathrm{PC}} = 6.7$ Hz, CO trans to $\mathrm{OSO_2CF_3}$), 189.4 (d of d, $J_{\mathrm{PcisC}} = 9.3$, $J_{\mathrm{PtransC}} = 56.3$, CO cis to $\mathrm{OSO_2CF_3}$), 189.3 (d of d, $J_{\mathrm{PcisC}} = 9.2$, $J_{\mathrm{PtransC}} = 57.1$, CO cis to $\mathrm{OSO_2CF_3}$), 135.3 (d, $J_{\mathrm{PC}} = 10.6$, (S,S)-bdpp $\mathrm{C_6H_5}$ ortho or meta), 135.1 (d, $J_{\mathrm{PC}} = 10.6$, (S,S)-bdpp ortho or meta), 133.6 (d, $J_{\mathrm{PC}} = 48.1$, (S,S)-bdpp $\mathrm{C_6H_5}$ ipso), 134.4 (d of d, $J_{\mathrm{PC}} = 4.0$, $J_{\mathrm{PC}} = 33.7$, (S,S)-bdpp $\mathrm{C_6H_5}$ ipso), 132.6 (d, $J_{\mathrm{PC}} = 8.9$, (S,S)-bdpp $\mathrm{C_6H_5}$ ortho or meta), 131.8 (d, $J_{\mathrm{PC}} = 9.0$, (S,S)-bdpp $\mathrm{C_6H_5}$ ortho or meta), 131.1 (((S,S)-bdpp $\mathrm{C_6H_5}$ para), 131.0 (((S,S)-bdpp $\mathrm{C_6H_5}$ para), 130.5 (two (S,S)-bdpp $\mathrm{C_6H_5}$ para), 130.1 (d, $J_{\mathrm{PC}} = 44.3$, (S,S)-bdpp $\mathrm{C_6H_5}$ ipso), 129.5 (one wing of a doublet of a (S,S)-bdpp $\mathrm{C_6H_5}$ ipso), 128.9 (d, $J_{\mathrm{PC}} = 9.3$, (S,S)-bdpp $\mathrm{C_6H_5}$ ortho or meta), 128.6 (d, $J_{\mathrm{PC}} = 9.9$, (S,S)-bdpp $\mathrm{C_6H_5}$ ortho or meta), 128.6 (one wing of a doublet of a (S,S)-bdpp $\mathrm{C_6H_5}$ ipso), 128.2 (d, $J_{\mathrm{PC}} = 10.1$, two overlapping (S,S)-bdpp $\mathrm{C_6H_5}$ ortho or meta), 36.6 (t,

J_{PC} = 5.0, (*S,S*)-bdpp CH_2), 27.7 (d, J_{PC} = 23.6, (*S,S*)-bdpp CH), 23.6 (d, J_{PC} = 35.1, (*S,S*)-bdpp CH), 17.3 ((*S,S*)-bdpp CH_3), 17.7 ((*S,S*)-bdpp CH_3) ppm. ^{19}F NMR ($CDCl_3$): −76.9 ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 11.36 (d, J = 29.3 Hz), 3.82 (d, J = 29.3) ppm. IR (KBr): ν_{CO} = 2039 (s), 1955 (s), 1918 (s) cm^{-1}.

Representative Procedure for the Synthesis of Methoxide, Ethoxide, and Isopropoxide Complexes. In an inert-atmosphere box, a Schlenk flask was charged with 50 mg of freshly cut sodium metal, stoppered, and removed from the box. Benzene (10 mL) and methanol (4 mL) were added via syringe. The resulting solution was stirred until effervescence had stopped. This solution was transferred via cannula to a rapidly stirred slurry of trifluoromethanesulfonate **5b** (625 mg, 0.877 mmol) in benzene (20 mL). The resulting mixture was stirred under Ar for 12 h, after which time it became homogeneous. After this time the solvents were removed on a vacuum line and the resulting residue was extracted with 2 × 20 mL of toluene and filtered through a cannula wrapped with a piece of Watman filter paper (No. 1). The solvent was removed using a vacuum line to yield **6b** as a pale yellow powder (381 mg, 76%). A similar procedure was used for complexes **7** and **8**, except that ethanol or 2-propanol was used in place of methanol.

$(CO)_3$(diars)ReOCH_3 (6b). ^1H NMR (C_6D_6): 7.01 (m, 4H, diars CH), 4.29 (s, 3H, OCH_3), 1.29 (s, 6H, diars CH_3), 1.12 (s, 6H, diars CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 195.0 (CO cis to OCH_3), 191.3 (CO trans to OCH_3), 139.9 (diars ipso), 131.3 (diars CH), 130.4 (diars CH), 68.5 (OCH_3), 13.0 (diars CH_3), 8.0 (diars CH_3). IR (KBr): ν_{CO} 2003 (s), 1910 (s), 1880 (s), 1862 (sh), 1845 (sh). Anal. Calcd for $C_{14}H_{19}As_2O_4Re$: C, 28.63; H, 3.26. Found: C, 28.66; H, 2.96.

$(CO)_3(PMe_3)_2$ReOCH_3 (6c). The procedure for the synthesis of this compound is analogous to that for **7b** except benzene rather than toluene was used in the final extraction and not toluene. This compound begins to decompose in non-protic solvents but is stable as a solid as long it is kept cool. Higher yields of purer product are obtained if the benzene solution of **7c** is allowed to freeze on the vacuum line and then lyophilized off. This yields a fine white powder (86% yield). ^1H NMR (toluene-d_8, −70 °C): 4.60 (s, 3H, OCH_3), 0.90 ($A_9A_9'XX'$, 18H, "J_{PH}" = 7.43 Hz, $P(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (toluene-d_8, −70 °C): 193.8 (b, CO), 69.7 (t, J_{PC} = 4.9 Hz, OCH_3), 16.6 (AXX′, $^1J_{PC} + {}^3J_{PC}$ = 30.6, $P(CH_3)_3$). $^{31}P\{^1H\}$ (toluene-d_8): −28.3 ppm. IR (KBr): ν_{CO} 2012 (s), 1921 (s), 1801 (m), 1875 (s), 1800 (m) cm^{-1}. Elemental analysis of this compound could not be obtained because its instability in solution precluded attempts at recrystallization.

$(CO)_3$(depe)ReOCH_2CH_3 (7e). Recrystallization from pentane at −40 °C gave a 83% yield of **7e**. ^1H NMR (C_6D_6): 4.10 (q, 2H, J = 6.7 Hz, ReOCH_2CH_3), 1.87 (septet, "J" = 7.7, 4H, depe CH_2), 1.53–1.10 (m, 6H, depe CH_2), 1.24 (t, J = 6.7, 3H, ReOCH_2CH_3), 0.93–0.81 (m, 6H, depe CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): 75.16 (t, J_{PC} = 4.5 Hz, ReOCH_2CH_3), 23.75 (ReOCH_2CH_3), 22.54 (AAX′, $^1J_{PC} + {}^3J_{PC}$ = 40.4, depe CH_2), 18.74 (AXX′, $^1J_{PC} + {}^4J_{PC}$ = 34.5, depe CH_2), 13.02 (AXX′, $^1J_{PC} + {}^4J_{PC}$ = 33.8, depe CH_2), 8.41 (depe CH_3), 7.71 (depe CH_3) ppm. The carbonyl resonances were too broad to observe. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 36.54 (bs) ppm. IR (KBr): ν_{CO} 2000 (s), 1905 (s), 1865 (s) cm^{-1}. High resolution MS (EI, *m/e*): calcd for $^{185}Re/^{187}Re$ 520.1057/522.110, found 520.1070/522.1098.

$(CO)_3$((*S,S*)-bdpp)ReOCH$(CH_3)_2$ (8f). Recrystallization from toluene/pentane gave a 44% yield of **8f**. ^1H NMR ($CDCl_3$): 7.75–7.06 (m, 20H, (*S,S*)-bdpp C_6H_5), 3.54 (m, 1H, (*S,S*)-bdpp CH), 3.25 (septet, 1H, J = 4.5 Hz, $OCH(CH_3)_2$), 3.04 (m, 1H, (*S,S*)-bdpp CH), 2.16 (m, 1H, (*S,S*)-bdpp CH_2), 1.72 (m, 1H, (*S,S*)-bdpp CH_2), 1.32 (d of d, J_{HH} = 7.2, J_{PH} = 13.5, (*S,S*)-bdpp CH_2), 1.16 (d, J = 4.5, $OCH(CH_3)_2$), 1.06 (d, J = 4.5, $OCH(CH_3)_2$), 0.92 (d of d, J_{HH} = 7.2, J_{PH} = 10.7, (*S,S*)-bdpp CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 191.5 (b, CO), 136.2 (d, J_{PC} = 10.6 Hz, (*S,S*)-bdpp C_6H_5 ortho or meta), 135.3 (d of d, J_{PC} = 4.5, J_{PC} = 42.6, (*S,S*)-bdpp C_6H_5 ipso), 134.8 (d, J_{PC} = 10.2, (*S,S*)-bdpp C_6H_5 ortho or meta), 134.2 (d, J_{PC} = 42.1, (*S,S*)-bdpp C_6H_5 ipso), 133.5 (d, J_{PC} = 41.5, (*S,S*)-bdpp C_6H_5 ipso), 132.5 (d, J_{PC} = 9.2, (*S,S*)-bdpp C_6H_5 ortho or meta), 132.5 (d, J_{PC} = 8.5, (*S,S*)-bdpp C_6H_5 ortho or meta), 130.5 (d, J_{PC} = 2.1, (*S,S*)-bdpp C_6H_5 para), 130.1 (d, J_{PC} = 2.2, (*S,S*)-bdpp C_6H_5 para), 130.0 ((*S,S*)-bdpp C_6H_5 para), 129.3 (d, J_{PC} = 1.5, (*S,S*)-bdpp C_6H_5 para), 128.8 (d, J_{PC} = 41.2, (*S,S*)-bdpp C_6H_5 ipso), 128.5 (d, J_{PC} = 8.5, (*S,S*)-bdpp C_6H_5 ortho or meta), 127.8 (d, J_{PC} = 8.5, (*S,S*)-bdpp C_6H_5 ortho or meta), 127.6 (d, J_{PC} = 9.7, (*S,S*)-bdpp C_6H_5 ortho or meta), 127.5 (d, J_{PC} = 8.2, (*S,S*)-bdpp C_6H_5 ortho or meta), 74.8 (t, J_{PC} = 5.4, $OCH(CH_3)_2$), 37.1 (vt, J_{PC} = 5.4, (*S,S*)-bdpp CH), 30.8 (d, J_{PC} = 21.2, (*S,S*)-bdpp CH), 28.8 ($OCH(CH_3)_2$), 27.1 ($OCH(CH_3)_2$), 17.9 (d, J_{PC} = 6.8, (*S,S*)-bdpp CH_3), 16.7 ((*S,S*)-bdpp CH_3), 15.9 (d, J_{PC} = 22.5, (*S,S*)-bdpp CH_2) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): 6.13 (d, J_{PP} = 30.9 Hz), −6.56 (d, J_{PP} = 30.9). IR (KBr): ν_{CO} 2005 (s), 1910 (s), 1877 (s) cm^{-1}. Anal. Calcd for $C_{35}H_{37}O_4P_2Re$: C, 53.15; H, 5.00. Found: C, 53.35; H, 4.74.

$(CO)_3$(diars)ReH (10b). A 50-mL Schlenk flask was charged with 339 mg (0.609 mmol) of $(CO)_3$(diars)ReBr and 10 mL of THF. A 1.22-mL amount of Super-Hydride ($LiBEt_3H$, 1.0 M solution in THF, 1.22 mmol, 2.0 equiv) was added to the solution via syringe. The reaction mixture was stirred for 3 h at room temperature, over which time it turned yellow. The THF was then removed on a vacuum line, and the yellow residue was taken into the drybox. The oily residue was extracted with pentane (4 × 10 mL) to remove the excess BEt_3 and $LiBEt_3H$. The remaining oil was dissolved in 5 mL of C_6H_6, filtered through a 2 cm thick bed of SiO_2, and eluted with an additional 30 mL of C_6H_6. Removal of the solvent resulted in 175 mg of a white solid (60%, 0.27 mmol). ^1H NMR (C_6D_6): 7.07–7.05 (m, 4H, diars CH), 1.40 (s, 6H, diars CH_3), 1.14 (s, 6H, diars CH_3), −5.71 (s, 1H, Re–H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): 197.81 (CO cis to hydride), 194.3 (CO trans to hydride), 141.9 (diars ipso), 130.7 (diars CH), 129.3 (diars CH), 18.8 (diars CH_3), 15.6 (diars CH_3). IR (KBr): ν_{CO} 1992 (s), 1909 (s), 1886 (s) cm^{-1}; ν_{Re-H} 1863 (m) cm^{-1}. Anal. Calcd for $C_{13}H_{17}As_2O_3Re$: C, 28.01; H, 3.08. Found: C, 27.92; H, 3.14.

$(CO)_3$(diars)ReOCH$(CF_3)_2$ (11b). Method A. In the drybox, a bomb was charged with 72 mg (0.129 mmol) of **10b** and 7 mL of C_6H_6. The bomb was closed, removed from the drybox, and attached to a vacuum line equipped with an MKS Baratron gauge. It was evacuated, and hexafluoroacetone (0.646 mmol, 5 equiv) was condensed in at −196 °C. The bomb was thawed and allowed to stand for 40 min at room temperature. The volatile material was removed on a vacuum line, and the bomb was returned to the drybox. The resulting white solid was slurried in hexane and collected on a sintered-glass frit to yield 89 mg (95% yield, 0.122 mmol) of **11b**.

Method B. A bomb was charged with 40 mg (0.068 mmol) of **6b**, and 3 mL of C_6H_6 was added. The bomb was closed and removed from the box, and $(CF_3)_2CHOH$ (22 μL, 0.204 mmol, 3 equiv) was added via syringe. The colorless reaction mixture was heated at 44 °C overnight. The volatile materials were removed on a vacuum line, and the bomb was then returned to the drybox. The resulting white powder was dissolved in toluene (0.5 mL), layered with pentane (2 mL), and cooled to −40 °C. After 2 days a white powder had formed. This was collected on a glass frit, washed with hexanes, and exposed to high vacuum for 12 h to yield 30 mg (0.41 mmol) of **11b**. The spectral properties of **11b** prepared by the two methods are identical.

^1H NMR ($CDCl_3$): δ 7.77 (m, 2H, diars CH), 7.59 (m, 2H, diars CH), 4.16 (septet, 1H, J_{HF} = 6.6 Hz, $OCH(CF_3)_2$), 1.82 (s, 6H, diars CH_3), 1.60 (s, 6H, diars CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 140.0 (diars ipso), 131.5 (diars CH), 130.1 (diars CH), 125.7 (t, J_{FC} = 268.0 (the other lines of the multiplet were too weak to observe), $OCH(CF_3)_2$), 83.7 (quintet, J_{FC} = 29.4 (the other lines of the expected septet were too weak to observe), $OCH(CF_3)_2$), 13.0 (diars CH_3), 8.7 (diars CH_3) ppm. ^{19}F NMR ($CDCl_3$): −75.78 (d, J_{HF} = 6.5 Hz). IR (KBr): ν_{CO} 2023 (s), 2001 (sh), 1936 (s), 1918 (sh), 1910 (sh), 1869 (s), 1829 (sh) cm^{-1}. Attempts at elemental analysis were consistently off. The closest result is given. Anal. Calcd for $C_{16}H_{17}As_2F_6O_4Re$: C, 26.57; H, 2.37. Found: C, 27.15; H, 2.39. High-Resolution MS (EI; *m/e*): calcd for $^{185}Re/^{187}Re$ 721.899 000/723.901 960, found 721.899 272/723.902 060.

Crystal Structure Determination of 11b. Clear blocklike crystals of **11b** were grown from a toluene/pentane solution of

11b at −40 °C. A crystal was selected and mounted on glass fibers using polycyanoacrylate cement to protect them from the atmosphere. Data were collected as described for **3a**.

Only the Re and As atoms were refined anisotropically. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p factor, used to reduce the weight of the intense reflections, was set to 0.03. The analytical forms of the scattering factor tables for the neutral atoms were used, and all scattering factors were corrected for both real and imaginary components of anomalous dispersion. The positional parameters, thermal parameters, and anisotropic thermal parameters of non-hydrogen atoms and their estimated standard deviations are available as supplementary material.

$(CO)_3(depe)ReOCH_2CH_3\cdots HOC_6H_4CH_3$ (7e···$HOC_6H_4CH_3$). In the drybox, a vial was charged with 68.0 mg (0.130 mmol) of **7e** and 14.1 mg (0.130 mmol, 1.0 equiv) of *p*-cresol. The mixture was dissolved in ~0.7 mL of toluene and the solution concentrated to a final volume of ~0.4 mL, layered with pentane, and cooled to −40 °C for 7 days. After this time, large, colorless crystals of the hydrogen-bonded complex **7e**···$HOC_6H_4CH_3$ had formed. The crystals were isolated in 68% yield. Pumping on the crystals for 2 days at room temperature did not remove 0.2 equiv of toluene, confirmed by NMR and elemental analysis. ^1H NMR (C_6D_6): 12.21 (b, 1H, $\mathit{H}OC_6H_4CH_3$), 7.00 (d, 2H, J = 9.5 Hz, arom C*H*), 6.84 (d, 2H, J = 9.5, arom C*H*), 4.13 (q, 2H, J = 6.9, $OC\mathit{H}_2CH_3$), 2.17 (3H, $HOC_6H_4C\mathit{H}_3$), 1.92 (m, 2H, depe $C\mathit{H}_2$), 1.70–1.20 (m, 10H, depe $C\mathit{H}_2$'s), 1.34 (t, 3H, J = 6.9, $OCH_2C\mathit{H}_3$), 0.902 (m, 6H, depe $C\mathit{H}_3$), 0.79 (m, 6H, depe $C\mathit{H}_3$) ppm. $^{13}C\{^1H\}$ NMR: 196.0 (d of d, J_{PcisC} = 10.7 Hz, $J_{PtransC}$ = 60.7, *C*O cis to OCH_2CH_3), 192.3 (t, J_{PC} = 5.1, *C*O trans to OCH_2CH_3), 157.4 ($HOC_6H_4CH_3$ ipso bearing oxygen), 130.1 (arom *C*H), 125.6 ($HOC_6H_4CH_3$ ipso bearing methyl group), 116.5 (arom *C*H), 72.8 (t, J_{PC} = 3.2, $O\mathit{C}H_2CH_3$), 23.1 (AXX′, $^1J_{PC} + {^3J_{PC}}$ = 68.9, depe CH_2), 21.1 ($HOC_6H_4\mathit{C}H_3$), 20.59 ($OCH_2\mathit{C}H_3$), 13.28 (AXX′, $^1J_{PC} + {^4J_{PC}}$ = 31.8, depe $\mathit{C}H_2CH_3$), 13.78 (AXX′, $^1J_{PC} + {^4J_{PC}}$ = 25.1, depe $\mathit{C}H_2CH_3$), 8.17 (depe $\mathit{C}H_3$), 8.03 (depe $\mathit{C}H_3$) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): 36.7 ppm. IR (KBr): ν_{CO} 2006 (s), 1920 (s), 1874 (m), 1864 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{37}O_5P_2Re\cdot 0.2C_7H_8$: C, 43.37; H, 6.00. Found: C, 43.37; H, 5.84.

Crystal Structure Determination of $(CO)_3(depe)ReOCH_2CH_3\cdots HOC_6H_4CH_3$. Large, clear, blocklike crystals of **7e**···$HOC_6H_4CH_3$ were grown by slow diffusion of pentane into a toluene solution at −40 °C. A fragment was cleaved from one of these and mounted on a glass fiber using Paratone N hydrocarbon oil.

The procedure for data collection is described in the procedure for **3a**, and specific parameters are given in Table I.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. In a difference Fourier map calculated following the refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks were found corresponding to the positions of most of the hydrogen atoms. Hydrogen atoms were predicted at idealized locations and then refined with isotropic thermal parameters. Before the final cycles of refinement, six reflections which had abnormally large weighed residuals were given zero weights. The final residuals for the 465 variables refined against the 3763 accepted data for which $F^2 > 3\sigma(F^2)$ where R = 2.47%, R_w = 2.66%, and GOF = 1.098. The R value for all 5052 data was 4.41%. In the final cycles of refinement a secondary extinction parameter was included (maximum correction 5% on F).

Inspection of the residuals ordered in ranges of $(\sin\theta)/\lambda$, $|F_o|$, and parity and values of the individual indexes showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 0.91 e/Å^3. The largest positive peaks were all located near the Re atom.

The positional parameters, thermal parameters, and anisotropic thermal parameters of non-hydrogen atoms and their estimated standard deviations are available as supplementary material.

Kinetic Studies on the Exchange of Hydrogen-Bonded Complexes. The following is a typical procedure used for the kinetic investigations performed in this study. A stock solution was prepared by dissolving 132 mg (0.225 mmol) of **6b** in 10 mL of C_6D_6 in a volumetric flask ([**6b**] = 0.225 M). For each run, a stock solution of the desired phenol was prepared in C_6D_6 as follows. *p*-Methoxyphenol (31.6 mg, 0.255 mmol) was dissolved in 1.0 mL of C_6D_6 in a volumetric flask, resulting in a 0.225 M solution. Methylene chloride (~16 μL) was added as an internal standard. An oven-dried NMR tube was charged with 0.5 mL of the **6b** solution (measured with a gastight syringe). Using a gastight syringe, 44.3 μL of the *p*-methoxyphenol solution (0.0112 mmol, 1.0 equiv) was added to the NMR tube. It was then fitted with a gum rubber septum and wrapped with Parafilm. The tube was then removed from the drybox and placed into the NMR tube which had been warmed to 44 °C. The temperature of the probe was determined by comparing the difference in chemical shift between the *H*O and $C\mathit{H}_3$ resonances of methanol. After equilibration for 300 s, data points were measured at 300-s intervals. A single pulse was used for each experiment to avoid problems with differing relaxation times of the observed signals. Each spectrum was phased using the same phase corrections, and an automatic base line correction was applied. The integrals were positioned manually but were not phased. The first-order constants were obtained by plotting ln $(C_\infty - C_t)$, where C is the ratio of the integrations of the liberated methanol to the internal standard. Rate constants were also obtained by following the disappearance of the coordinated methoxide resonance. Both rate constants were found to be identical within experimental error.

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Supplementary Material Available: Tables of general temperature factor expressions (*B*'s), positional parameters and their estimated standard deviations, and root-mean-square amplitudes of anisotropic displacements for **3a**, **11b**, and **7e**···$HOC_6H_4CH_3$ (33 pages). This material is provided with the archival edition of the journal, available in many libraries. Alternatively, ordering information is given on any current masthead page.

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