$COCH_3$), 101.2 (s, CH acac), 188.9 (s, CO acac), 231.8 (d, $^2J_{CP}$ = 18 Hz, CO), 257.7 (d, $^2J_{CP}$ = 9 Hz, $COCH_3$).

This complex may also be obtained by bubbling carbon monoxide through a solution of $Mo(\eta^2\text{-}C(O)CH_3)(acac)CO(PMe_3)_2$ in THF for ca. 20 min. The solution changed from red to yellow, and from the resulting reaction mixture the dicarbonyl complex was isolated in ca. 80% yield.

$Mo(CH_3)(CH_3C(O)CHC(O)CH_3)CO(PMe_3)_3$. IR (THF solution, 20 °C, cm^{-1}): 1742 (s) (ν(CO)). ^1H NMR ($C_6D_5CD_3$, 20 °C): δ −3.48 (td, $^3J_{HP}$ = 9.9, 1.3 Hz, Mo–CH_3), 1.00 (d, $^2J_{HP}$ = 7.6 Hz, PMe_3), 1.20 (d, $^2J_{HP}$ = 8.9 Hz, 2 PMe_3), 2.08 (s, 2 CH_3 acac), 5.23 (s, CH). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, 20 °C): δ 42.5 (d, $^2J_{PP}$ = 20 Hz, 2 PMe_3), 8.0 (t, PMe_3). $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, 20 °C): δ 15.7 (d, $^1J_{CP}$ = 24 Hz, 2 PMe_3), 15.9 (d, $^1J_{CP}$ = 17.6 Hz, PMe_3), 28.0 (s, CH_3 acac), 98.9 (s, CH acac), 185.3 (s, CO acac), 219.5 (m, CO). The ^{13}C resonance due to the Mo-bound methyl group could not be located under these conditions.

X-ray Structure Determinations of 1c and 3b. A summary of the fundamental crystal data is given in Table I. A crystal of **1c** was sealed in a glass capillary, while for **3b** the chosen single crystal was coated with an epoxy resin. Both were mounted in a Kappa diffractometer. The cell dimensions were refined by least-squares fitting of the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo, S, and P were taken from ref 20. The structures were solved by Patterson and Fourier methods. An empirical absorption correction[21] was applied at the end of the isotropic refinement.

Compound **1c** crystallizes in the space group $P\bar{1}$. After several cycles of mixed refinement, H(31), H(32), and H(33) were located in a difference synthesis calculated with reflections having $(\sin \theta)/\lambda < 0.5$ Å^{-1} as the highest peaks of the map. In order to prevent bias on ΔF vs F_o or $(\sin \theta)/\lambda$, the last steps of the refinement were carried out with $w = 1/(a + b|F_o|^2)$, where $a = 2.06$, $b = -0.16$ if $|F_o| < 12$ and $a = 0.29$, $b = 0.01$ if $|F_o| > 12$, calculated by PESOS.[22] Final refinement with fixed isotropic factors and coordinates for H atoms, except for H(31), H(32), and H(33), for which the corresponding coordinates were refined, led to final values of $R = 0.035$ and $R_w = 0.051$.

Similar refinement for complex **3b**, whose space group is $C2/c$, led to final values of $R = 0.026$ and $R_w = 0.027$.

The final values of the positional parameters are given in Table II for complex **1c** and Table III for complex **3b**.

Most of the calculations were carried out with the X-Ray 80 system.[23]

Acknowledgment. We thank the Dirección General de Investigación Cientifica y Técnica (Grants No. PB 90-0890 and PB 87-0201) and Junta de Andalucía for support of this research. L.C. and A.P. thank the Spanish Ministerio de Educacion y Ciencia and Junta de Andalucía for the award of research fellowships. Thanks are also due to the University of Sevilla for free access to its analytical and NMR facilities.

Supplementary Material Available: Tables of H atom coordinates and thermal parameters for **1c** and **3b** (4 pages). Ordering information is given on any current masthead page.

OM9204447

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Electrophilic Cleavage of Rhenium–Oxygen Bonds by Brønsted and Lewis Acids

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Received May 19, 1992

The rhenium–oxygen bond in complexes of the type $(CO)_3(L)_2ReOR$ (**1** (R = CH_3) or **2** (R = CH_2CH_3)) may be cleaved by a number of Brønsted and Lewis acids. When an acid X–H is added to **1** or **2**, one observes the formation of the exchanged rhenium product $(CO)_3(L)_2ReX$ and the free alcohol (L = 1,2-bis(dimethylarsino)benzene (diars, a), 1,2-bis(diethylphosphino)ethane (depe, b), PMe_3 (c), (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane (bdpp, d), or 1,2-bis(diphenylphosphino)ethane (dppe, e)). For the reactions with Brønsted acids, the reaction is reversible when aniline and certain other amines are added to **1** or **2**, but the reaction may be driven to the right by the removal of the alcohol from the reaction mixture. Using this technique, the arylamido complex $(CO)_3(depe)ReNHC_6H_5$ (**13b**) has been synthesized and its structure determined by a single-crystal X-ray diffraction study. Irreversible exchange occurs upon reaction with other acids such as R_2PH, RPH_2, H_2S, and $CpW(CO)_3H$. The terminal phosphido complexes are fluxional in solution, undergoing phosphorus inversion at temperatures much lower than the free phosphines. The alkoxides do not react cleanly with carbon acids, but the alkoxide ligands may be removed using alkyl- and alkenylboranes, leading to alkenylrhenium complexes.

Introduction

The coordination chemistry of alkoxides is dominated by examples from the left side of the periodic table in which the metal is in a high oxidation state. These complexes are believed to have strong M–O bonds because of π-donation of the heteroatom's lone pairs to vacant orbitals on the metal center.[1] There are far fewer examples of similar complexes for metals in low oxidation states. It is believed that this is due to an unfavorable interaction between the "hard" alkoxide ligand with the "soft" metal center, resulting in inherently weak bonds. The pioneering

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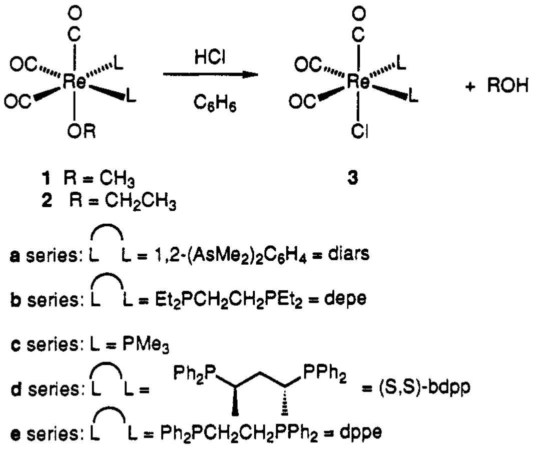
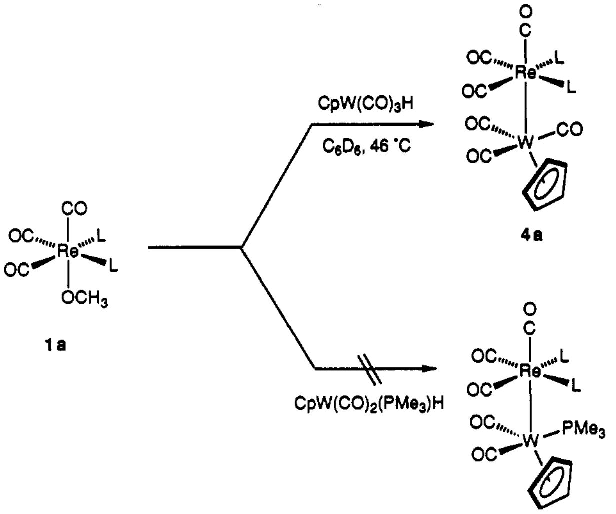
Scheme I



Scheme II



thermochemical studies of Bryndza and Bercaw have shown that this is a misconception.[2,3] Reports of low-valent transition-metal alkoxide and amides have subsequently increased in the literature.[4-39]

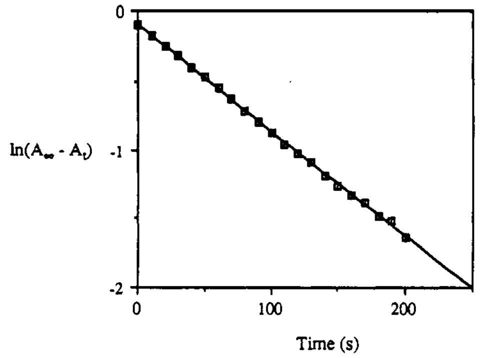


Figure 1. Representative first-order plot for the formation of the dimer $(CO)_3(diars)ReW(CO)_3Cp$ from $(CO)_3(diars)ReOCH_3$ and $CpW(CO)_3H$.

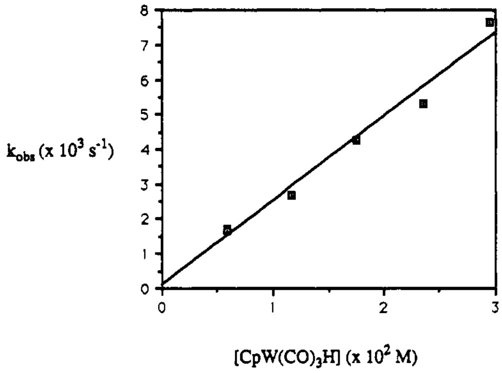


Figure 2. Dependence of k_{obs} for the formation of **4a** on the concentration of added $CpW(CO)_3H$.

Table I. Rate Constants for Formation of $CpW(CO)_3Re(diars)(CO)_3$

$[CpW(CO)_3H]$ ($\times 10^2$ M)	$CpW(CO)_3H^a$ (equiv)	k_{obs} ($\times 10^3$ s^{-1})^b	k_2 ($\times 10^2$ M^{-1} s^{-1})^b
0.587	9.2	1.71	2.91
0.587	9.2	1.66	2.82
1.17	18.4	2.68	2.29
1.76	27.6	4.28	2.43
2.35	36.8	5.31	2.25
2.94	47.0	7.65	2.60

^{a} All experiments were performed at 40 °C in toluene. The $[(CO)_3(diars)ReOCH_3]$ for each run was 6.38×10^{-4} M. ^{b} The error limits each rate constant is taken to be the reproducibility of each measurement, ±0.05 s^{-1}.

We have recently prepared Re(I) alkoxide complexes of the type $(CO)_3(L_2)ReOR$ where L is a phosphine or arsine

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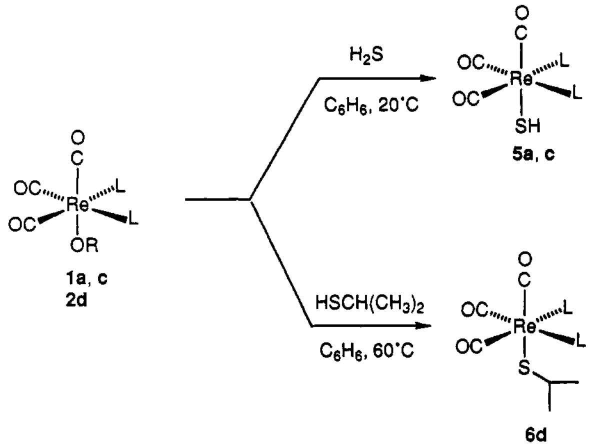
Scheme III



ligand.[40] In this paper, we wish to report the reactions of these alkoxide complexes with both Brønsted and Lewis acids, which result in the cleavage of the Re–O bond, and a description of the compounds derived from these reactions.

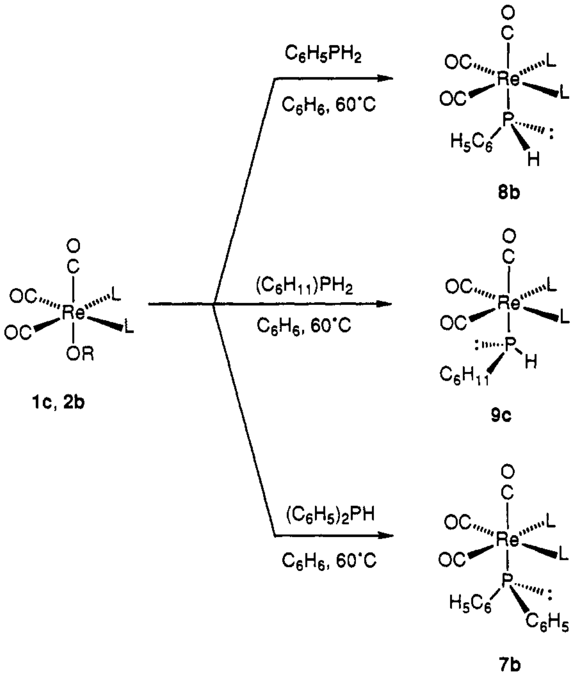
Results

Irreversible Exchange Reactions. Addition of HCl to alkoxide complex **2b** results in cleavage of the metal–oxygen bond and formation of the corresponding chloride in 90% yield (by integration against an internal standard) and the free alcohol (Scheme I). Similar reactions have been carried out with several of the other alkoxides illustrated in Scheme I. These reactions occur readily at room temperature and are not reversible. The methanol generated during the reaction does not need to be removed in order to drive the reaction to completion. When methanol is added to the products obtained from the protonation reactions they are recovered unchanged.

Addition of CpW(CO)$_3$H to C$_6$H$_6$ solutions of (CO)$_3$(diars)ReOCH$_3$ results in the immediate development of a bright yellow color and the formation of the metal-metal-bonded complex CpW(CO)$_3$Re(CO)$_3$(diars) (**4a**, Scheme II) in 76% yield.

The IR spectrum shows a complicated carbonyl region with several absorptions, but no bands from 1850 to 1700 cm^{-1}, the region where bridging carbonyl stretches are commonly observed. The ^{13}C{^{1}H} spectrum shows four resonances at δ 196.5, 190.9, 188.4, and 186.5 ppm, again consistent with a structure with only terminal carbonyls. The ^{183}W satellites could not be resolved so the resonances could not be assigned. When **1a** was added to the substituted tungsten hydride CpW(CO)$_2$(PMe$_3$)H, no reaction was observed even at elevated temperatures.

Scheme IV



Kinetic studies on this reaction were conducted. Using at least a 10-fold excess of CpW(CO)$_3$H, the rate of formation of the dimer **4a** was monitored using UV/Vis spectrophotometry at 40 °C in THF. A large increase in absorbance at 410 nm corresponding to the formation of **4a** was observed during the course of the reaction. Under these conditions, the accompanying first-order plot of ln $(A_\infty - A_t)$ versus time (Figure 1) gave the pseudo-first-order rate constant k_{obs}. These rate constants were found to increase with the concentration of added tungsten hydride (Table I). A plot of k_{obs} vs [CpW(CO)$_3$H] is linear, as shown in Figure 2. The second-order rate constant for the reaction of **1a** with CpW(CO)$_3$H was found to be 0.23 M^{-1} s^{-1} in THF at 40 °C.

Addition of H$_2$S to **1a** and **c** results in rapid formation of the monomeric thiol complexes (CO)$_3$(L$_2$)ReSH **5a** and **c** (Scheme III). In the diars substituted system, the S–H resonance appears as a sharp singlet at δ −2.6 ppm in the ^{1}H NMR spectrum. In complex **5c**, the S–H proton's resonance is now split into a 1:2:1 triplet at δ −2.6 ppm with J_{PH} = 9.3 Hz. In both of these complexes, the resonances for the carbonyl ligands in the ^{13}C{^{1}H} NMR spectrum were not observed, even at low temperature. Similar broadening has been observed in the alkoxides and many other heteroatom substituted rhenium complexes.[40] The presence of a facial arrangement of carbonyl ligands has been confirmed by the presence of three strong carbonyl stretches in the IR spectra.

Alkanethiols also react with the alkoxide complexes. Addition of 2-propanethiol to the ((*S*,*S*)-bdpp) substituted ethoxide **2d** affords the thioisopropoxide **6d**. The conditions needed to effect this transformation are more vigorous than those required to form the Re–SH complexes. The greater steric requirements of both the 2-propanethiol and the ((*S*,*S*)-bdpp) ligand probably contribute to the slower reaction times. Unlike the thiols, this complex is yellow in solution and in the solid state, displaying a weak absorption at λ = 363 nm (ϵ = 596 M^{-1} cm^{-1}).

As illustrated in Scheme IV, diphenylphosphine also reacts irreversibly with **2b** to form the phosphido complex (CO)$_3$(depe)ReP(C$_6$H$_5$)$_2$ (**7b**). The reaction is very slow, requiring 3 days at 60 °C to effect complete conversion to

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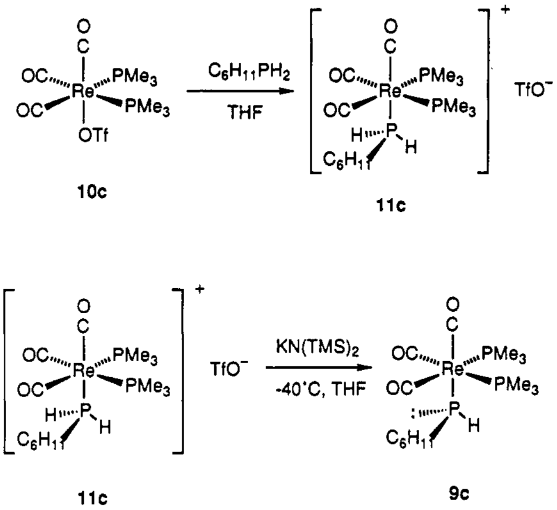
Scheme V



7b. The complex was isolated as yellow crystals in 31% yield after recrystallization from toluene/pentane. The $^{31}P\{^1H\}$ NMR spectrum displays two resonances in a 2:1 ratio. The downfield resonance (δ = 20.60 ppm) is a broad doublet with J_{PP} = 27.64 Hz and is assigned to the two equivalent ^{31}P nuclei of the depe ligand. The upfield resonance (δ = −47.38 ppm) is a sharp triplet with the same coupling constant. In THF-d_8 solution both signals sharpen upon cooling to −50 °C. In the $^{13}C\{^1H\}$ NMR spectrum, the ipso carbon of the $P(C_6H_5)_2$ ligand appears as a doublet of triplets at δ 149.7 ppm, with $^1J_{PC}$ = 28.38 Hz and $^3J_{PC}$ = 3.70 Hz. The carbonyl resonances are broadened and were not observed. The facial arrangement of carbonyls was confirmed by the characteristic IR spectrum, displaying three strong bands at 1996, 1917, and 1893 cm^{-1}. This complex is bright yellow, displaying a broad absorbance at 361 nm (ϵ = 13 000 M^{-1} cm^{-1}). The exchange reaction also proceeds when the alkoxide complexes are allowed to react with phenyl- and cyclohexylphosphine, forming the phosphido complexes $(CO)_3(L)_2RePHC_6H_5$ (**8b**) and $(CO)_3(L)_2RePHC_6H_{11}$ (**9c**).

An alternative route to these complexes employs the previously prepared triflate complexes $(CO)_3(L)_2ReOSO_2CF_3$.[40] Addition of $C_6H_{11}PH_2$ to $(CO)_3(PMe_3)_2ReOSO_2CF_3$ (**10c**) in THF (Scheme V) leads to the coordinated phosphine complex $[(CO)_3(PMe_3)_2RePH_2C_6H_{11}]^+CF_3SO_3^-$ (**11c**) in 91% yield. These salts may be isolated and crystallized or used directly in the next step. In contrast to the phosphido complexes, which are extremely reactive toward oxygen, **11c** is air stable in the solid state. The coordinated phosphine may be deprotonated using $KN(TMS)_2$ in THF at −40 °C, yielding the phosphido complex **9c** in 52% yield. This reaction is reversible as evidenced by addition of triflic acid to **9c** which regenerates the salt. The IR spectrum of $(CO)_3(PMe_3)_2RePH(C_6H_{11})$ has three carbonyl stretches at 1996, 1912, and 1897 cm^{-1}. They are shifted to a much lower wavenumber compared to the salt **11c**, where they are observed at 2034, 1970, and 1944 cm^{-1}. A weak, broad peak at 2245 cm^{-1} was assigned to the P–H stretch.

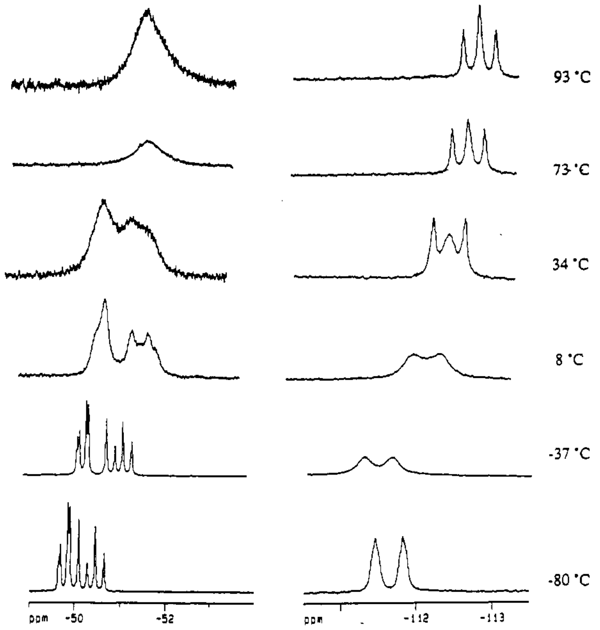


Figure 3. Temperature dependence of the $^{31}P\{^1H\}$ NMR spectrum of **9c**. The resonances on the left belong to the PMe_3 ligands, while those on the right are assigned to the coordinated $PH(C_6H_{11})$.

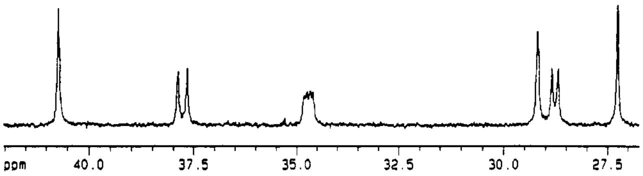


Figure 4. Cyclohexyl region of the $^{13}C\{^1H\}$ NMR spectrum of **9c**, taken at −56 °C in THF-d_8.

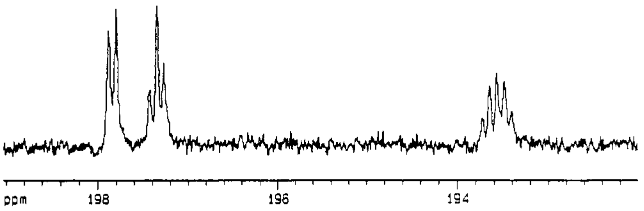
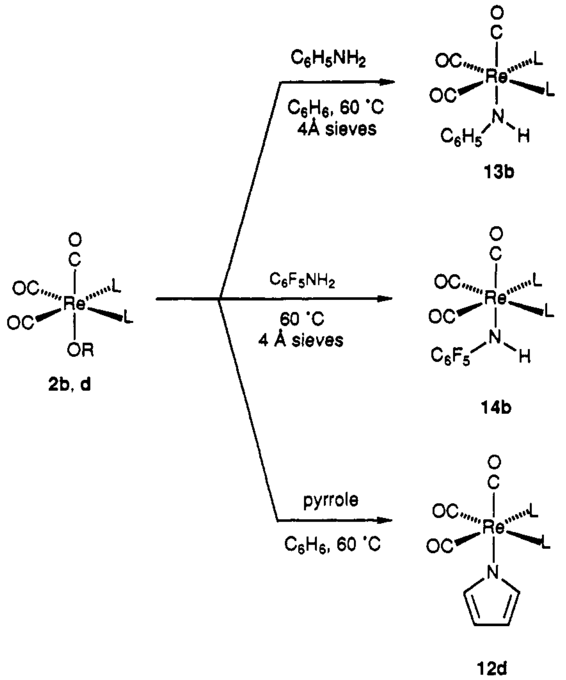


Figure 5. Carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum of **9c**, taken at −56 °C in THF-d_8.

The phosphido complexes are fluxional in solution. The temperature dependence of the $^{31}P\{^1H\}$ NMR spectrum of **9c** is shown in Figure 3. At room temperature, the $^{31}P\{^1H\}$ spectrum of $(CO)_3(PMe_3)_2RePH(C_6H_{11})$ consists of two broad peaks at δ −44.6 and −106 ppm. As the temperature is raised, the resonance of the phosphido ligand sharpens, becoming a 1:2:1 triplet at 94 °C. Interestingly, the same coupling to the PMe_3 ligands is not resolved. Broadening of the coordinated phosphine ligand in many of these complexes has been observed (see experimental section). At −55.5 °C, the two PMe_3 ligands are inequivalent and give rise to an ABX spectrum (A = P_AMe_3, B = P_BMe_3, X = $P_XHC_6H_{11}$). The PMe_3 resonances display a large coupling to each other (J_{AB} = 31.4 Hz), but they have very different couplings to the phosphido ligand; J_{AX} = 5.9 Hz, while J_{BX} = 57.0 Hz. This asymmetry is also seen in the low temperature $^{13}C\{^1H\}$ NMR spectrum. The six resonances for the cyclohexylphosphido ligand are all well resolved (Figure 4). Two different $P(CH_3)_3$ resonances are observed in both the ^1H and $^{13}C\{^1H\}$ NMR spectra. The carbonyl region of the spectrum shows three sets of resonances (Figure 5). The low-field resonances assigned to the carbonyls trans to the PMe_3 ligands differ little in chemical shift and each displays a large trans coupling as well as smaller cis couplings to the chemically inequivalent PMe_3 ligand and the phosphido ligand. The very small difference in chemical shift results in several overlapping lines. The high-field resonance belongs to the carbonyl trans to the phosphido ligand. Coupling to the two PMe_3 ligands are approximately equal, J_{PC} = 8.0 Hz; however, the coupling to the trans ligand is small (J_{PC} = 17 Hz).[41]

Scheme VI



Similar dynamic behavior is displayed by the other phosphido complexes. In the low temperature ^{1}H NMR spectrum of **8b**, the resonance of the P–H proton is a doublet of doublet of doublets due to coupling to two inequivalent Et_2P ligands, $^3J_{PAH}$ = 8.2 and $^3J_{PBC}$ = 7.7 Hz. Only one-half of the resonance was observed; the other set of resonances is buried underneath the depe resonances. As the temperature is raised, the signal simplifies to a doublet of triplets with $^3J_{PH}$ = 8.1 Hz. Further heating causes the signals to broaden and at +50 °C no three-bond coupling is resolved. The temperature dependence of the $^{31}P\{^1H\}$ NMR spectrum is similar to that observed in **9c**. Using the coalescence temperature of the phosphine ligands in the $^{31}P\{^1H\}$ NMR spectra,[42] the activation barriers for the fluxional process in **8b** and **9c** were estimated to be 13.8 ± 0.5 kcal/mol for **8b** and 12.1 ± 0.6 kcal/mol for **9c**.[43] We assume that this corresponds to the barrier for inversion at phosphorus, but as a referee has pointed out, both phosphorus inversion and Re–PRR′ bond rotation must occur to carry out the observed averaging, and rotation may not be rapid compared to inversion.[25,44]

Pyrrole reacts with **2d** to form the η^1-pyrrole complex **12d** (61% yield) and ethanol (Scheme VI). In the complex bearing the chiral phosphine ligand, only two sets of pyrrole α and β protons are observed in the ^{1}H NMR spectrum at temperatures as low as −100 °C. This demonstrates that the η^1-pyrrole ligand is still freely rotating at these temperatures. In the $^{13}C\{^1H\}$ NMR spectrum of **14d**, the pyrrole carbons are observed as two singlets at δ 129.0 and 108.5 ppm.

Reversible Exchange Reactions. The coordinated ethoxide ligand may be exchanged with aniline (Scheme VI).[10] Addition of aniline to a C_6D_6 solution of **2b** results in the development of a pale yellow color and the formation of ethanol and a new depe-containing product in the ^{1}H NMR spectrum which has been shown to be the arylamido complex $(CO)_3(depe)ReNHC_6H_5$ (**13b**). Under these conditions, the reaction proceeds to only a slight extent; heating the solution has little effect on the ratio of **2b** to the new product. On a preparative scale, complete exchange can be effected by addition of activated 4-Å molecular sieves and heating the reaction mixture to 60 °C for 18 h. The reaction is reversible (Scheme VII), and the sieves serve to sequester the liberated ethanol. The anilide $(CO)_3(depe)ReNH(C_6H_5)$ (**13b**) can be prepared in 80% yield using this method. The complex is a bright yellow crystalline solid (λ = 402 nm, ϵ = 327 M^{-1} cm^{-1}). The NH proton was not observed in the ^{1}H NMR spectrum, presumably because it is buried beneath the depe resonances. The presence of an N–H bond was confirmed by the IR spectrum. A weak stretch at 3359 cm^{-1} was assigned to the N–H stretch, which shifts to 2375 cm^{-1} in the isotopomer $(CO)_3(depe)ReND(C_6H_5)$, as predicted by Hooke's law (ν_{NH}/ν_{ND} = 1.39). The ^{15}N spectrum of **13b**-^{15}N, recorded a using a DEPT90 pulse sequence, showed a broad resonance at δ −387 ppm relative to aniline-^{15}N at δ −322 ppm.[45,46] The signal was too broad to resolve the ^{15}N–^{31}P coupling.

Scheme VII

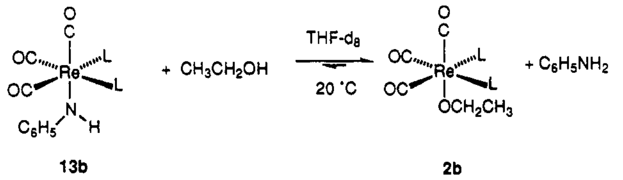


Table II. Crystal and Data Collection Parameters for 13b

empirical formula $C_{19}H_{30}NO_3P_2Re$
(A) cryst params at T = 25 °C^{a,b}
a = 14.936 (3) Å
b = 14.623 (2) Å
c = 19.927 (3) Å
V = 4352.4 (21) Å^3
size of cryst 0.16 × 0.30 × 0.40 mm
space group *Pbca*
formula wt = 568.6 amu
Z = 8
(B) data measurement parameters
radiation: Mo Kα (λ = 0.71073 Å)
monochromator: highly oriented graphite (2θ = 12.2)
detector: crystal scintillation counter, with PHA
diffractometer: Enraf-Nonius CAD-4
reflns measd: +H, +K, +L
2θ range: 3–54°
scan type: θ–2θ
scan width: $\Delta\theta$ = 0.80 + 0.35 tan θ
scan speed: 5.49 (θ, deg/min)
background: measd over 0.25($\Delta\theta$) added to each end of the scan
vert aperture = 3.0 mm
horiz aperture = 2.0 + 1.0 tan θ mm
no. of reflns collected: 5267
intensity standards: (945), (395), (2,4,13); measured every 1 h of X-ray exposure time. Orientation: Three reflections were checked after every 200 measurements. Crystal orientation was redetermined if any of the reflections were offset by more than 0.10° from their predicted positions. Reorientation was performed once during the data collection

[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 of the 24 reflections with 2θ between 26° and 30°. [b] In this table the esd's of all parameters are given parentheses, right justified to the least significant digit(s) of the reported value.

A single-crystal X-ray diffraction study of **13b** was undertaken. Diffusion of pentane vapor into a toluene so-

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(41) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data For Organometallic Compounds*; Academic Press: London, 1981; pp 151–182.

(42) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; pp 79–80.

(43) The uncertainty in the inversion barrier was estimated by assuming a 10 °C error in the determination of the coalescence temperature.

(44) Buhro, W. E.; Zwick, B. D.; Georgiou, S.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 2427.

(45) Lichter, R. L. In *The Multinuclear Approach to NMR Spectroscopy*; Lambert, J. B., Riddell, F. G., Eds.; D. Reidel: Dordrecht, Holland, 1983; pp 207–244.

(46) von Philipsborn, W.; Muller, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 383–413.

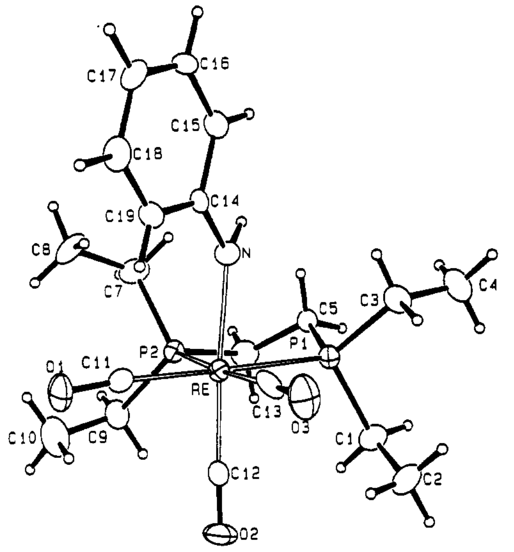


Figure 6. ORTEP diagram of the complex $(CO)_3$(depe)ReNH-(C_6H_5) (**13b**). The disorder of one of the ethyl groups of the depe ligand is not displayed (see Experimental Section).

Table III. Intramolecular Distances for $(CO)_3$(depe)ReNH(C_6H_5)

atom 1	atom 2	dist (Å)	atom 1	atom 2	dist (Å)
Re	P_2	2.452 (2)	C_5	C_6	1.535 (13)
Re	P2	2.459 (2)	C_7	C_8	1.566 (23)
Re	N	2.170 (7)	C_7	$C_{8'}$	1.498 (22)
Re	C_{11}	1.953 (10)	C_9	C_{10}	1.496 (15)
Re	C_{12}	1.911 (10)	C_{11}	O_1	1.152 (10)
Re	C_{13}	1.935 (10)	C_{12}	O_2	1.149 (11)
P_1	C_1	1.818 (9)	C_{13}	O_3	1.156 (11)
P_1	C_3	1.813 (10)	N	C_{14}	1.375 (11)
P_1	C_5	1.809 (10)	N	H(N)	1.047 (7)
P_2	C_6	1.829 (10)	C_{14}	C_{15}	1.431 (12)
P_2	C_7	1.813 (10)	C_{15}	C_{16}	1.370 (13)
P_2	C_9	1.829 (10)	C_{16}	C_{17}	1.371 (13)
C_1	C_2	1.535 (14)	C_{17}	C_{18}	1.385 (13)
			C_{18}	C_{19}	1.391 (13)

Table IV. Intramolecular Angles for $(CO)_3$(depe)ReNH(C_6H_5)

atom 1	atom 2	atom 3	angle (deg)	atom 1	atom 2	atom 3	angle (deg)
P_1	Re	P_2	80.97 (8)	C_6	P_2	C_9	103.0 (5)
P1	Re	N	83.0 (2)	C_7	P_2	C_9	104.7 (5)
P_1	Re	C_{11}	174.5 (3)	P_1	C_1	C_2	112.9 (7)
P_1	Re	C_{12}	91.1 (3)	P_1	C_3	C_4	117.0 (7)
P_1	Re	C_{13}	92.6 (3)	P_1	C_5	C_6	109.8 (6)
P_2	Re	N	86.9 (2)	P_2	C_6	C_5	111.4 (6)
P_2	Re	C_{11}	9.35 (3)	P_2	C_7	C_8	115.9 (10)
P_2	Re	C_{12}	89.6 (3)	P_2	C_7	$C_{8'}$	117.4 (10)
P_2	Re	C_{13}	174.5 (3)	P_2	C_9	C_{10}	116.4 (7)
N	Re	C_{11}	96.6 (3)	Re	C_{11}	O_1	174.6 (8)
N	Re	C_{12}	173.6 (3)	Re	C_{12}	O_2	178.0 (8)
N	Re	C_{13}	91.4 (4)	Re	C_{13}	O_3	176.6 (9)
C_{11}	Re	C_{12}	89.0 (4)	Re	N	C_{14}	132.5 (6)
C_{11}	Re	C_{13}	91.6 (4)	Re	N	H(N)	125.0 (6)
Re	P_1	C_1	116.2 (3)	C_{14}	N	H(N)	100.8 (7)
Re	P_1	C_3	117.2 (4)	N	C_{14}	C_{15}	119.5 (8)
Re	P_1	C_5	108.4 (3)	N	C_{14}	C_{19}	124.9 (8)
C_1	P_1	C_3	104.5 (5)	C_{15}	C_{14}	C_{19}	115.5 (8)
C_1	P_1	C_5	105.2 (4)	C_{14}	C_{15}	C_{16}	121.7 (9)
C_3	P_1	C_5	105.2 (4)	C_{15}	C_{16}	C_{17}	121.9 (9)
Re	P_2	C_6	107.8 (3)	C_{16}	C_{17}	C_{18}	117.9 (9)
Re	P_2	C_7	117.5 (2)	C_{17}	C_{18}	C_{19}	121.7 (9)
Re	P_2	C_9	118.2 (3)	C_{14}	C_{19}	C_{18}	121.5 (8)
C_6	P_2	C_7	103.8 (5)				

Table V. Positional Parameters and Their Estimated Standard Deviations for $(CO)_3$(depe)ReNH$(C_6H_5)^a$

atom	*x*	*y*	*z*	*B* (Å^2)
Re	0.02179 (1)	0.18038 (1)	0.18232 (1)	1.257 (5)
P_1	−0.0202 (2)	0.1178 (2)	0.2920 (1)	1.44 (4)
P_2	−0.1169 (2)	0.1011 (2)	0.1499 (1)	1.44 (4)
O_1	0.0554 (5)	0.2565 (5)	0.3092 (3)	2.7 (1)
O_2	−0.0870 (5)	0.3533 (5)	0.2190 (4)	3.5 (2)
O_3	0.1912 (5)	0.2717 (5)	0.2407 (4)	3.3 (2)
N	0.886 (5)	0.0495 (5)	0.1713 (4)	1.9 (2)
C_1	−0.0726 (7)	0.1971 (6)	0.3503 (5)	2.2 (2)
C_2	−0.0086 (7)	0.2723 (7)	0.3745 (5)	3.0 (2)
C_3	0.0672 (7)	0.0630 (6)	0.3406 (5)	2.1 (2)
C_4	0.0390 (7)	0.0139 (7)	0.4037 (5)	3.0 (2)
C_5	−0.1041 (6)	0.0303 (6)	0.2792 (4)	1.6 (2)
C_6	−0.1723 (6)	0.0626 (6)	0.2267 (5)	2.1 (2)
C_7	−0.1062 (6)	−0.0023 (7)	0.1003 (5)	2.2 (2)
C_8	−0.052 (2)	0.007 (2)	0.033 (1)	3.2 (5)**
$C_{8'}$	−0.176 (2)	−0.074 (1)	0.109 (1)	3.3 (5)**
C_9	−0.2042 (6)	0.1672 (7)	0.1077 (5)	2.2 (2)
C_{10}	−0.1752 (8)	0.2237 (8)	0.0489 (6)	3.5 (3)
C_{11}	0.0451 (6)	0.2243 (6)	0.0915 (5)	1.7 (2)
C_{12}	−0.0457 (6)	0.2890 (6)	0.1990 (4)	1.9 (2)
C_{13}	0.1295 (6)	0.2358 (6)	0.2176 (5)	2.0 (2)
C_{14}	0.1611 (6)	0.0219 (6)	0.1339 (4)	1.3 (2)
C_{15}	0.1912 (6)	−0.0708 (6)	0.1382 (5)	1.7 (2)
C_{16}	0.2589 (6)	−0.1032 (6)	0.0983 (5)	1.8 (2)
C_{17}	0.3026 (6)	−0.0482 (7)	0.0532 (5)	2.0 (2)
C_{18}	0.2768 (6)	0.0427 (7)	0.0496 (5)	2.1 (2)
C_{19}	0.2082 (6)	0.0774 (6)	0.0892 (5)	1.6 (2)
H(N)	0.06097 (1)	−0.01382 (1)	0.18443 (1)	4.0*

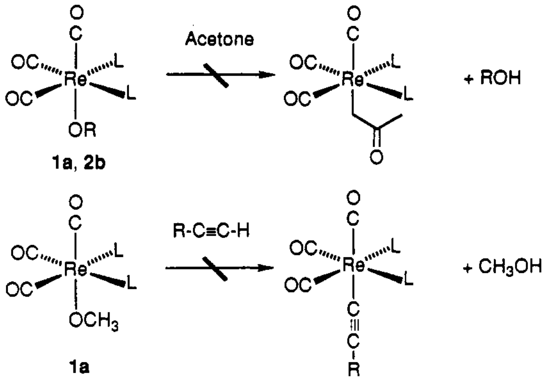
[a] Starred atoms were included with isotropic thermal parameters. Double-starred atoms are disordered at half occupancy. The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$, where *a*, *b*, *c* are real cell parameters and $\beta(i,j)$ are anisotropic β's.

lution at −40 °C resulted in formation of both rodlike and polyhedral clear yellow crystals, which gave identical ^1H NMR spectra. Data collection parameters are given in Table II and in the Experimental Section. An ORTEP diagram and labeling scheme are presented in Figure 6; bond lengths and angles are given in Tables III and IV. The structure consists of individual molecules of the compound packed in the unit cell with no abnormally close contacts between molecules. The Re atom is coordinated in an octahedral geometry that is only slightly distorted. There is a slight indication of a trans effect on the Re–CO distances, but it is on the edge of statistical significance. The amine hydrogen was located on a difference Fourier map and was included, but not refined. The Re–N distance is 2.170 (7) Å. The Re–N–C_{14} angle is 132.5 (6)°, while the Re–N–H(N) angle is 125.0 (6)°. The arylamido ligand is planar at nitrogen, as evidenced by the sum of all of the angles about the anilido nitrogen being almost exactly 360°. One of the arms of the depe ligands is disordered; this is described in the Experimental Section.

This reaction can be applied to the synthesis of certain other rhenium amido complexes. Reaction of **2b** with pentafluoroaniline 60 °C in the presence of sieves results in a 68% yield of the pentafluoroanilide complex **14b**. When the reaction is performed without added sieves, a ~4:1 mixture of **14b**:**2b** is formed. The ^{19}F NMR spectrum displays three multiplets at −165, 169, and −186 ppm for the coordinated pentafluoroarylamido ligand. None of the resonances of this ligand were observed in the $^{13}C\{^1H\}$ NMR spectrum of **14b**, due to long-range C–F coupling in the aromatic ring. The IR spectrum again consists of three strong carbonyl stretches at 2015, 1930, and 1894 cm^{-1}, as well as a weak band at 3374 cm^{-1} assigned to the N–H stretch. Unlike the perprotiophenylamido complex, **14b** is an off white solid.

Treatment of the alkoxide complexes with alkylamines does not result in the formation of the desired alkylamido complexes. Addition of benzylamine to solutions of **1a** or **1b** in the presence of sieves shows no reaction at room

Scheme VIII



temperature. Upon heating the reaction mixture at 60 °C for 1 week, the major component of the reaction mixture is still the starting alkoxide complex, although several other sets of diars-methyl resonances are observed. The only identifiable product of this reaction is the hydride $(CO)_3(diars)ReH$ (**15g**).

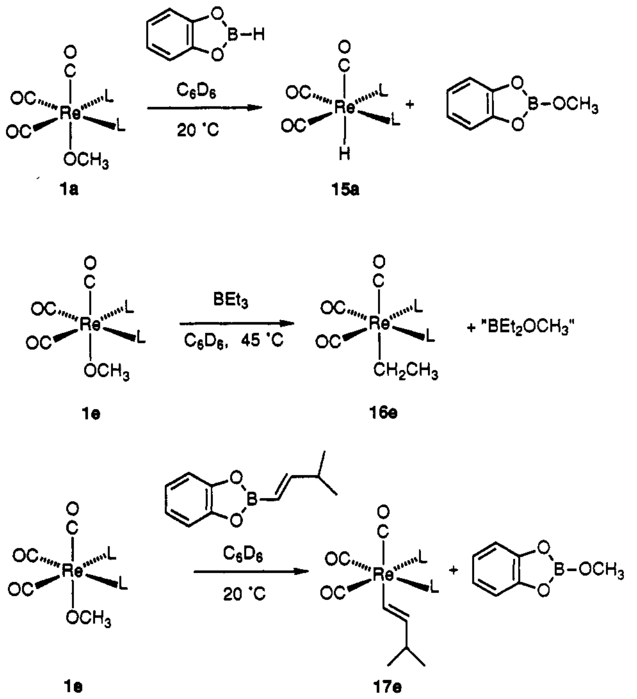
Reactions of Alkoxide Complexes with Carbon Acids. While the previously mentioned reactions occur quite easily to the give the exchanged organometallic products and the alcohol, there are several examples of compounds with acidic hydrogens that cannot be exchanged. Carbon acids such as terminal alkynes, ketones, esters and nitriles do not react with **1** or **2** to give the acetylides or enolates (Scheme VIII). These potential products have been prepared independently and do not exchange with added alcohols to form the alkoxide complexes.[47] More highly activated carbon acids such as acetylacetone and Meldrum's acid react with alkoxides **1** and **2** to form methanol or ethanol, but the organometallic product of these reactions could not be isolated. No reaction was observed when **1a** was treated with freshly distilled cyclopentadiene.

Estimation of the Equilibrium Constant for the Exchange of 2b with Aniline. The equilibrium constant for the previously mentioned exchange reaction of **2b** and aniline is related to the Re–N, Re–O, N–H, and O–H bond dissociation energies (BDE). Assuming that entropy effects are negligible ($\Delta S \cong 0$ e.u.), then $\Delta G \cong \Delta H$, and $\Delta G \cong [\mathrm{BDE(H{-}OCH_2CH_3)} + \mathrm{BDE(Re{-}NHC_6H_5)}] - [\mathrm{BDE(H{-}NH(C_6H_5))} + \mathrm{BDE(Re{-}OCH_2CH_3)}]$. At 24 °C in THF-$d_8$ this equilibrium constant was measured to be 0.14 (Scheme VII). Using values for the N–H BDE of aniline of 88 kcal/mol and the O–H BDE of ethanol of 106 kcal/mol,[48] the Re–OR bond was estimated to be ~17 kcal/mol stronger than the Re–NAr bond.

Cleavage of Re–Alkoxide Bonds Using Boranes. As previously discussed, carbon acids do not react cleanly with the alkoxide complexes **1** and **2** or the arylamido complex **13b**. However, the Re–O bond may be cleaved by the addition of boron hydrides or alkyl boranes, resulting in the formation of rhenium alkyl or hydride complexes and the boron ether (Scheme IX). Addition of catechol borane to a C_6D_6 solution of $(CO)_3(diars)ReOCH_3$ results in the rapid formation of the hydride $(CO)_3(diars)ReH$ and $C_6H_4(O)_2BOCH_3$. The ^1H NMR chemical shifts of **15a** prepared by this method are identical to those of a sample of this compound prepared by the addition of $LiHBEt_3$ to $(CO)_3(diars)ReBr$.[40]

Both alkyl groups and vinyl groups may be transferred to the rhenium center using this reaction. Treatment of

Scheme IX



1e with BEt_3 in C_6H_6 at 45 °C leads to a 62% yield of the alkyl complex $(CO)_3(dppe)ReCH_2CH_3$ (**16e**). In this reaction the boron-containing product was not observed; presumably a complex of the stoichiometry $(EtO)_n(Et)_{3-n}B$ (n = 1 or 2) is formed in analogy to the catechol borane reaction. An upfield triplet at δ −8.29 ppm (J_{PC} = 7.7 Hz) in the $^{13}C\{^1H\}$ NMR spectrum confirms the formation of a Re–C bond. Treatment of **1e** with the vinyl borane prepared by the hydroboration of isopropylacetylene with catechol borane, shown in Scheme IX, leads to a 60% yield of the vinylrhenium complex **17e**. The trans stereochemistry of the double bond is preserved in **17e**. A large vicinal coupling constant of 17.5 Hz is observed between the α- and β-hydrogens of the coordinated vinyl group, characteristic of a trans stereochemistry about the double bond.[49] In the $^{13}C\{^1H\}$ NMR spectrum the resonances for the vinyl carbons appear as 1:2:1 triplets. The α-carbon resonance at δ 127.3 ppm has J_{PC} = 11.6 Hz, while that of the β carbon appears at δ 155.7 ppm with a P–C coupling constant of 5.7 Hz.

A strong electron donor attached to the rhenium center appears to be a requirement for this reaction to proceed. The reaction does not occur when either $(CO)_3(dppe)ReCl$ or $(CO)_3(dppe)ReOC_6H_4CH_3$ is treated with vinyl- or alkylboranes.

The ease of synthesis of a wide variety of alkyl- and vinylboranes makes this reaction an attractive route for the synthesis of a wide range of alkyl- and vinylrhenium complexes which would be difficult to synthesize using existing methodology. Unfortunately, this reaction is limited by the steric requirements of the group being transferred. Treatment of **1e** with secondary alkyl- and α-substituted vinylboranes leads to low yields of the desired rhenium complexes.

Discussion

Thermodynamic Preferences in Exchange Reactions. The alkoxide ligands of $(CO)_3(L_2)ReOR$ undergo exchange with a number of of acidic compounds (X–H)

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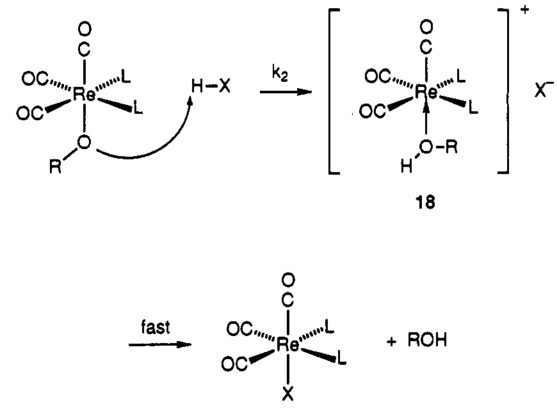
[47] Stack, J. G. Thesis, University of California, Berkeley, 1989.

[48] Values are taken from: McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

[49] Becker, E. D. *High Resolution NMR Theory and Chemical Applications*; Academic Press: Orlando, FL, 1980; pp 96–97.

Scheme X



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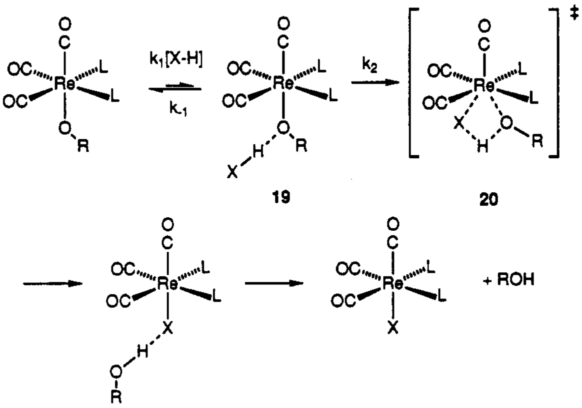
Scheme XI



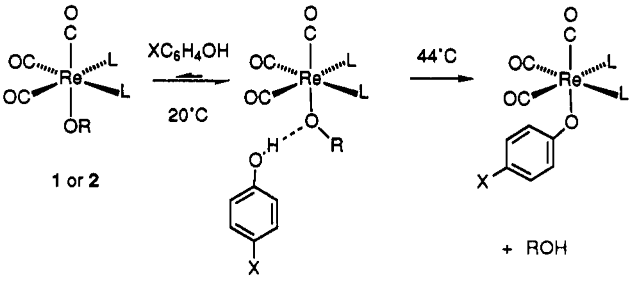
19 20

to afford ROH and the substituted complex $(CO)_3(L_2)ReX$. As in the $Cp^*(PMe_3)_2Ru–X$ and $(dppe)(CH_3)Pt–X$ systems studied by Bryndza, Bercaw, and co-workers, exchange reactions with second-row X–H substrates (H–Cl, RS–H, $R_2P–H$, and the group VI hydrides) are irreversible, while exchanges with first row substrates (RO–H, $R_2N–H$) are reversible.[2,3] This trend has been rationalized as arising from the greater bond strengths between the metal (Ru or Pt) and the second-row elements. The same trend appears to apply to the rhenium system.

The most striking difference between the rhenium alkoxides and the Ru and Pt systems is the lack of reactivity with carbon acids $RC\equiv CH$ and $RC(O)CH_3$. The Re(I) acetylides and enolates may be prepared by alternate routes, and these compounds have been shown to be quite inert toward weak acids such as methanol and ethanol, but they are protonated by strong acids such as HBF_4.[47] The lack of reactivity of $(CO)_3(L_2)ReOR$ with carbon acids (or conversely $(CO)_3(L_2)ReCH_2C(O)R$ and $(CO)_3(L_2)Re—C\equiv C—R$ with alcohols) demonstrates that the reaction is inhibited by a kinetic rather than a thermodynamic barrier.

Mechanisms of Alkoxide Exchange. Two possible mechanisms for alkoxide exchange are shown in Schemes X and XI. They are quite similar, but differ in the timing of proton transfer and Re–X bond formation. In Scheme X, direct protonation of the coordinated alkoxide oxygen occurs prior to transfer of the X group to the metal center. This results in the transient formation of an ion pair **18** in which the alcohol is coordinated to the metal cation. It is then quickly displaced by the newly formed anion to form the observed products. This type of mechanism seems most likely to occur for the addition of strong acids such HCl and CF_3SO_3H to the alkoxide or phosphido complexes (e.g., formation of **11c** by the addition of triflic acid to **9c**).

Scheme XII



1 or 2 19

The second mechanism is a more complex stepwise process analogous to that proposed in 1987.[50] The first step involves reversible attachment of the substrate X–H to the alkoxide ligand via the formation of a hydrogen bond. When the acid X–H is a phenol, the hydrogen bond is very strong and the complex **19** may be isolated (Scheme XI).[40] In a second slower step, the hydrogen-bonded group is then transferred to the rhenium center.

The linear dependence on the rate of formation of the dimer **4a** on the $CpW(CO)_3H$ concentration is consistent with either mechanism. The thermodynamic acidities of the tungsten hydride and phenol are quite similar; the pK_a of $CpW(CO)_3H$ in acetonitrile was measured to be 16.1,[51] while the pK_a of phenol is 18.0 in DMSO.[52,53] The first-order rate constants for conversion of the hydrogen-bonded complexes **19** to the corresponding rhenium aryloxides[40] are on the order of 10^{-4} s^{-1} at 44 °C. The observed second-order kinetics for the formation of **4a** demonstrates that if the tungsten hydride does associate with the alkoxide via a hydrogen bond, this interaction is much weaker than that of **1a** with phenols.[54] This accounts for the faster exchange rate with the tungsten hydride.

The kinetic acidities of both M–H[55,56] and C–H bonds[57,58] are low compared to alcohols and amines having comparable pK_a's because of the large structural and electronic changes that accompany deprotonation. Therefore the lack of reactivity of **1** and **2** with $CpW(CO)_2(PMe_3)H$ and carbon acids may be mechanistically related. The thermodynamic acidity of $CpW(CO)_2(PMe_3)H$ is lower than that of several acids which readily exchange. However, the kinetic acidity of the substituted tungsten hydride is 5 orders of magnitude lower than that of the parent tricarbonyl.[56] The extremely slow rate of proton transfer seems clearly due to this high pK_a value.

Mechanism of Alkyl Transfer from Boranes. The transfer of alkyl groups from boron to a transition metal is believed to be a key step in the palladium-catalyzed cross coupling of alkyl halides with alkyl boranes.[59,60] Abel has

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[53] pK_a's in CH_3CN tend to be much higher than in DMSO. Thus $CpW(CO)_3H$ is much more acidic than C_6H_5OH. We are grateful to Professor A. Streitwieser for bringing this point to our attention.

[54] In the neutron structure of $[IrH(OH)(PMe_3)_4]PF_6$, the hydride ligand appears to be functioning as a base in an intramolecular hydrogen bond with the hydroxy group. Stevens, R. C.; Bau, R.; Milstein, D.; Blum, O.; Koetzle, T. F. *J. Chem. Soc., Dalton. Trans.* **1990**, 1429–1432.

[55] Walker, H. W.; Kresge, C. T.; Ford, P. C.; Pearson, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 7428.

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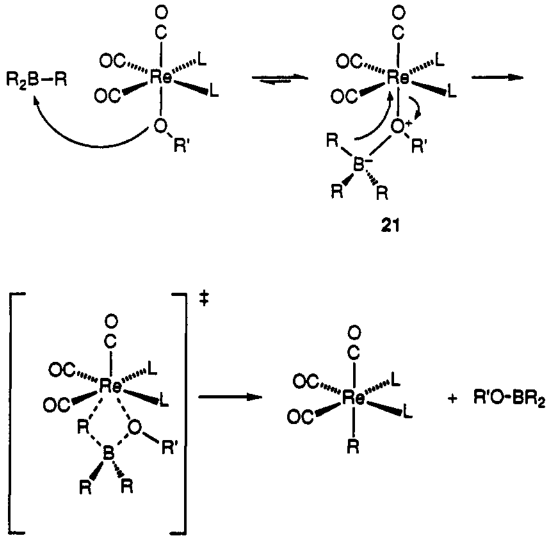
Scheme XIII



also reported the formation of bridging halides from alkoxides by the addition of boron trihalides.[61]

The proposed mechanism for the transfer of alkyl groups from boranes is shown in Scheme XIII. The first step is the formation of a Lewis acid–base adduct between the borane and the rhenium. The formation of this "ate" complex **21** increases the nucleophilicity of the group bonded to the boron and weakens the Re–O bond. This synergistic interaction then provides a pathway for the alkoxide-for-alkyl exchange. Coordination of the boron to the methoxide oxygen appears to be a requirement for the reaction to proceed, since no reaction is observed when the corresponding aryloxide or chloride is treated with a borane. These observations suggest that a very basic group attached to the rhenium is required in order to facilitate the coordination of the boron compound to the alkoxide complex. In the case of the chloride and aryl oxide complexes, the oxygen or halogen is not a good enough donor for this coordination to occur.

The stereospecificity of the reaction strongly suggests that the transfer of a vinyl group from boron to rhenium occurs with retention of the double bond's stereochemistry. However, we were not able to prepare the corresponding cis compound to test this hypothesis. Therefore, the stereochemical result may simply reflect a thermodynamic preference for the trans geometry about the double bond.

Comparison of $(CO)_3(depe)ReNH(C_6H_5)$ with Other Rhenium Arylamides. La Monica and co-workers synthesized rhenium η^2-amides of the type *trans*-$(PPh_3)_2(CO)_2Re(\eta^2\text{-}NH(CO)C_6H_5)$.[18] Interestingly, these compounds do not react with H_2O to form the expected hydroxo complex *trans*-$(PPh_3)_2(CO)_2ReOH$, but the amido proton does exchange with added D_2O to yield *trans*-$(PPh_3)_2(CO)_2Re(\eta^2\text{-}ND(CO)C_6H_5)$.

Other arylamido complexes of rhenium have been synthesized in a number of oxidation states, allowing for a comparison of the effect of the metal's oxidation state and other ancillary ligands on the geometry of the $Re–NH(C_6H_5)$ linkage. Gladysz has prepared cyclopentadienyl(nitrosyl)rhenium amido complexes,[25] and in 1981 Wilkinson and co-workers reported the synthesis of a series of rhenium arylamido complexes by the reduction of the arylimido complex $Re(NC_6H_5)Cl_3(PPh_3)_2$ with sodium amalgam in the presence of excess PMe_3 and other ligands.[29] The structure of the butadiene complex *mer*-$(PMe_3)_3Re(\eta^4\text{-}C_4H_6)(NHC_6H_5)$ is not well defined due to disorder and/or symmetry correlation effects, so the following discussion will be limited to *cis*-$Re(N_2)(NHC_6H_5)(PMe_3)_4$. Substitution of a carbonyl ligand trans to the arylamido ligand results in a decrease of 0.03 Å in the Re–N bond distance. This decrease in bond distance may be ascribed to an increase in π-donation of the arylamido ligand to the rhenium upon substitution of a trans ligand with greater π-acceptor properties. A similar decrease in Ru–O bond distances has been observed in the complexes *cis*-$(PMe_3)_3Ru(OC_6H_4CH_3)(H)$ and *mer*-$(PMe_3)_4Ru(CO)(H)(OC_6H_4CH_3)$.[14] Upon substitution of a CO for PMe_3 trans to the aryloxide ligand, the Ru–O bond distance decreases 0.04 Å. The arylamido nitrogen in *cis*-$Re(N_2)(NHC_6H_5)(PMe_3)_4$ is slightly pyramidal, while it is planar in *fac*-$(CO)_3(depe)ReNHC_6H_5$. As would be expected for these coordinatively saturated metal centers, this effect is small.

Rhenium–Phosphido Complexes. The fluxionality of the phenylphosphido complex **8b** compared to the analogous arylamido complex is caused by the higher barrier to inversion of phosphorus compared to that of the nitrogen. Inversion at the coordinated phosphido phosphorus is slow on the NMR time scale, thus creating a chiral center adjacent to the rhenium center. This causes the other ligands on the metal to be inequivalent. This is clearly seen in a Newman projection viewed down the P–Re–C axis. As the temperature is raised, inversion of the phosphido phosphorus becomes faster on the NMR time scale and the resonances broaden. In the high-temperature limit, inversion is fast and the $^{31}P\{^1H\}$ NMR spectrum simplifies to a A_2X spin system. This is consistent with the pyramidal phosphido group undergoing inversion through a planar intermediate. Since the phosphido ligand does undergo inversion at close to room temperature, the activation energy for this process is much lower than that of the uncomplexed phosphines, which are typically on the order of >30 kcal/mol.[62–64] This decrease in the barrier of inversion has been observed in other metal phosphido complexes.[65–67] Measured barriers for inversion of coordinated phosphido ligands have ranged from 11–14 kcal/mol, so the estimated phosphido inversion barriers of 12.1 and 13.8 kcal/mol are consistent with the observed fluxionality in complexes **7**–**9**.

The lowering of this barrier has been attributed to the π-donation of the phosphido lone pair to an electropositive substituent.[44,65] The extremely low carbonyl stretching frequencies in the cyclohexylphosphido complex **9c**, especially in comparison with those of the protonated complex **11c**, suggest that there is substantial $p\pi$–$d\pi$ donation from the phosphido ligand to the metal center.[68,69]

Summary. Cleavage of the Re–O bond bond in the alkoxide complexes **1** and **2** with Lewis and Brønsted acids

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[69] An example of phosphido inversion by π-donation from the phosphido to the metal is seen in: Baker, R. T.; Whitney, J. F.; Wreford, S. S. *Organometallics* **1983**, *2*, 1049.

provides routes to a wide range of new compounds. In the case of the Brønsted acids, the reaction is affected by not only the pK_a of the acid but also by its ability to associate to the coordinated oxygen atom via a hydrogen bond. Unlike previous work on the exchange of alkoxides with phenols,[40] exchange with $CpW(CO)_3H$ follows simple bimolecular kinetics. Carbon acids such as alkynes and carbonyl compounds and the substituted hydride $CpW(CO)_2(PMe_3)H$ do not exchange cleanly. Comparison of the kinetic acidities of the "nonreactive" acids shows that they are very low compared to those of the acids which exchange readily. Therefore, we propose that cleavage of the Re–O bond by Brønsted acids is governed by not only the pK_a of the acid but also by the ability of the acid to associate to the coordinated alkoxide's oxygen. This can result in the formation of a very stable hydrogen-bonded complex as in the case of the phenols, or only transiently as in the case of the acids discussed in this paper.

The Re–O bonds may be cleaved with alkyl- or vinylboranes to form rhenium alkyl or vinyl complexes. We believe that this reaction is mechanistically similar to the reaction with Brønsted acids, because a good donor atom adjacent to the rhenium center is required. Coordination of the borane to the electron-rich atom forms an "ate" complex which mimics a hydrogen bond, thus allowing for the cleavage of the Re–O bond. This then leads to transfer of the alkyl or hydride group to the rhenium.

Experimental Section

General Techniques. Unless otherwise stated, all reactions and manipulations were accomplished in dry glassware under nitrogen or argon atmospheres in a Vacuum Atmospheres HE-553-2 drilab with an attached MO-40 dri-train.

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. ^{15}N spectra were obtained at 50.67 MHz using a Bruker AM500 spectrometer. $^{13}C\{^1H\}$ NMR assignments were made using standard DEPT pulse sequences. A DEPT 90 pulse sequence was used to obtain the ^{15}N spectrum of **13b**. ^{15}N chemical shifts are referenced relative to aniline-^{15}N in C_6D_6 at δ −322 ppm used as an external standard. ^{19}F NMR chemical shifts are reported relative to $CFCl_3$ (0.0 ppm), which was used as an external standard. $^{31}P\{^1H\}$ NMR chemical shifts are reported relative to 85% H_3PO_4 which was used as an external standard. For second-order spin systems (AXX′, ABX), the value listed is the sum of the one-bond and three-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 a method for identification and is not meant to represent the actual coupling constant. Infrared spectra were recorded on a Nicolet 510 FT-IR interfaced to a 620 data processor. UV–vis spectra were recorded on a Hewlett-Packard 8450a UV–vis spectrophotometer in 1.0-cm quartz cells fused to Kontes vacuum stopcocks. 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 synthesis of compounds **1–2** and **10c** will be reported separately.[40] $CpW(CO)_3H$ was prepared by the procedure of Piper and Wilkinson,[70] $CpW(CO)_2(PMe_3)H$ by the procedure of Poilbanc.[71] Isopropylthiol was obtained from Aldrich and dried over $CaSO_4$. Ethanol was distilled from magnesium turnings. Phenyl-, diphenyl-, and cyclohexylphosphine were purchased from Strem and used as received. Aniline was distilled from Na and stored at −40 °C under N_2 in an amber bottle. Aniline-^{15}N and aniline-d_2 were purchased from Cambridge Isotopes laboratories and purified as described for the nonlabeled compound. Pentafluoroaniline was used as received from Aldrich. Pyrrole was distilled from zinc dust. Catechol borane and triethylboron were used as received from Aldrich. The vinyl borane used to prepare **18e** was synthesized using the procedure of Brown and Gupta.[72] Unless otherwise mentioned, all materials were obtained from commercial sources and used as received.

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 a MKS Baratron gauge. Sealed NMR tubes were prepared using Wilmad 505-PP tubes attached to a vacuum line via a Cajon adapters fitted with Kontes vacuum stopcocks.[73]

$(CO)_3(depe)ReCl$ (3b). In the drybox, an NMR tube was charged with 15 mg (0.029 mmol) of **2b** and 0.5 mL of $CDCl_3$, fitted with a gum rubber septum, and removed from the box. An initial ^1H NMR spectrum was taken in order to determine the relative intensities of the coordinated depe and ethoxide resonances versus those of the residual chloroform. Gaseous HCl (0.04 mmol, 2 equiv) was added using a gastight syringe. Examination of the reaction mixture by ^1H NMR spectroscopy showed complete formation of CH_3OH (100%) and $(CO)_3(depe)ReCl$ (**3b**; 90%). ^1H NMR ($CDCl_3$) δ 2.15–1.66 (m, depe-CH_2), 1.17 (m, depe-CH_3) ppm. Accurate integrals for the depe-CH_3 resonances could not be obtained because they overlap with the liberated ethanol. Lit.:[40] ^1H NMR ($CDCl_3$) δ 2.15–1.66 (m, 12 H, depe-CH_2), 1.17 (m, 12 H, depe-CH_3) ppm.

$(CO)_3(diars)ReW(CO)_3(\eta^5\text{-}C_5H_5)$ (4a). In the drybox an NMR tube was charged with 20 mg (0.034 mmol) of **1a**, and 11 mg (0.034 mmol, 1 equiv) of $CpW(CO)_3H$. C_6D_6 (0.6 mL) was added via pipet to produce an intense yellow solution. The tube was stoppered and removed from the drybox. The reaction mixture was heated to 44 °C for 3 h. Examination of the reaction mixture by ^1H NMR showed a sharp Cp resonance at δ 5.34 ppm, along with a small amount of unreacted $CpW(CO)_3H$. The tube was taken into the drybox, and the solvent removed to yield a yellow solid. This was washed with pentane to remove unreacted $CpW(CO)_3H$. The yellow solid was recrystallized from toluene/Et_2O to yield 23 mg (76%, 0.26 mmol) of analytically pure **4a**. ^1H NMR ($CDCl_3$) δ 7.71 (m, 2 H, diars-CH), 7.53 (m, 2 H, diars-CH), 5.34 (s, 5 H, (η^5-C_5H_5)), 1.80 (s, 6 H, diars-CH_3), 1.79 (s, 6 H, diars-CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 196.5 (CO), 190.9 (CO), 188.4 (CO), 186.5 (CO), 140.2 (s, diars-ipso), 130.8 (s, diars-CH), 129.3 (s, diars-CH), 88.4 (s, (η^5-C_5H_5)), 16.3 (s, diars-CH_3), 13.8 (s, diars-CH_3) ppm. IR (KBr) ν_{CO} 2038 (sh), 2011 (s), 1940 (s), 1933 (s), 1891.3 (s), 1850 (s), 1809 (sh). UV–vis (THF) λ_{max} = 410 nm (ϵ = 3340 cm^{-1} M^{-1}). Anal. Calcd for $C_{21}H_{21}As_2O_6ReW$: C, 28.36; H, 2.38. Found: C, 28.23; H, 2.12.

$(CO)_3(diars)ReSH$ (5a). In the drybox a bomb was charged with 59 mg (0.10 mmole) of **1a** and 5 mL of C_6H_6. The bomb was removed from the box and attached to a vacuum line equipped with an MKS baratron gauge. It was evacuated and H_2S (0.5 mmol, 5 equiv) condensed into the bomb at −196 °C. The bomb was thawed and heated at 45 °C overnight. The pale yellow solution had turned colorless after this time. The volatile compounds were removed from the bomb using a vacuum line, leaving a white powder. The bomb was taken into the drybox and the white powder collected on a frit and washed with hexanes and residual solvent removed in vacuo to yield 45 mg (74%, 0.074 mmol) of **5a**. ^1H NMR (C_6D_6) 7.05 (b, 4 H, diars-CH), 1.44 (s,

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6 H, diars-CH_3), 1.15 (s, 6 H, diars-CH_3), −2.64 (s, 1 H, SH) ppm. ^{13}C{^{1}H} NMR (C_6D_6) δ 191.5 (bs, CO), 140.2 (s, diars-ipso), 130.9 (s, diars-CH), 130.1 (s, diars-CH), 14.4 (s, diars-CH$_3$), 7.5 (s, diars-CH$_3$). IR (KBr) ν_{CO} 2015 (s), 1934 (s), 1887 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{17}As_2O_3ReS$: C, 26.49; H, 2.91. Found: C, 26.69; H, 2.70.

$(CO)_3(PMe_3)_2$ReSH (5c). In the drybox a bomb was charged with 110 mg (0.225 mmol) of **1c** and 2 mL of Et_2O and 2 mL of toluene. The bomb was removed from the box and attached to a vacuum line equipped with an MKS baratron gauge. It was evacuated and H_2S (1.13 mmol, 5 equiv) condensed into the bomb at −196 °C. Upon thawing, the pale yellow solution bleached and a small amount of a white precipitate formed. The solution was allowed to stand at room temperature for 4 h, and then the volatile materials were removed on a vacuum line to yield a white powder. The bomb was returned to the drybox and the residue extracted with Et_2O (4 × 2 mL). The solution was concentrated to 1 mL, layered with ~4 mL of pentane, and cooled to −40 °C. After standing overnight, 85 mg (0.186 mmol, 83%) of white crystals had formed. ^{1}H NMR ($CDCl_3$) δ 1.59 ($A_9A_9'XX'$, 18 H, "J_{PH}" = 8.0, P(CH_3)$_3$), −2.64 (t, J_{PH} = 9.3, ReSH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 191.1 (b, CO), 17.5 (AXX′, $^1J_{PC} + {}^3J_{PC}$ = 66.3, P(CH$_3$)$_3$) ppm. ^{31}P{^{1}H} δ −45.0 ppm. IR (KBr) ν_{CO} 2012 (s), 19406 (s), 1885 (s), 1876 (s) cm^{-1}. Anal. Calcd for $C_9H_{19}O_3P_2ReS$: C, 23.73; H, 4.20. Found: C, 23.90; H, 3.98.

$(CO)_3((S,S)$-bdpp)ReSCH$(CH_3)_2$ (6d). In the drybox, a bomb was charged with 54 mg (0.071 mmol) of $(CO)_3((S,S)$-bdpp)ReOCH$_2$CH$_3$ and 3 mL of C_6H_6. The bomb was removed from the box and attached to a vacuum line. Isopropylthiol (100 μL, 1.1 mmol, 15.1 equiv) was added via syringe. The bomb was stoppered and heated to 46 °C for 8 h. The colorless solution turned yellow over this period. The bomb was removed from the bath and attached to a vacuum line, and the volatile materials were removed. The remainder of the procedures were conducted on the benchtop because the product is air and moisture stable. The yellow residue was extracted into 5 mL of Et_2O and filtered through a plug of Celite. The solvent was then removed using a rotary evaporator and the residue dissolved in a minimum volume of Et_2O (~0.5 mL). Pentane vapor was allowed to diffuse into the solution at room temperature. After 15 h, yellow crystals had formed. The residual solvent was removed by exposing the crystals to high vacuum for 8 h. The yield of **6d** was 33 mg, 57%. ^{1}H NMR (C_6D_6) δ 8.29 (bm, 2 H, (S,S)-bdpp-ortho CH)), 7.61–7.51 (m, 4 H, two sets of (S,S)-bdpp-ortho CH), 7.31–6.90 (m, 14 H, (S,S)-bdpp-aromatic), 3.69 (bm, 1 H, (S,S)-bdpp-CH), 2.70 (bm, 1 H, (S,S)-bdpp-CH), 2.20 (septet, 1 H, J = 6.54, ReSCH(CH$_3$)$_2$), 2.01 (bm, 1 H, (S,S)-bdpp-CH_2), 1.69 (d, 3 H, J = 6.03, ReSCH(CH_3)$_2$), 1.49 (d, 3 H, J = 6.61, ReSCH(CH_3)$_2$), 1.28 (bm, 1 H, (S,S)-bdpp-CH_2), 1.16 (d of d, 3 H, J_{HH} = 7.39, J_{PH} = 14.48, (S,S)-bdpp-CH_3), 0.67 (d of d, 3 H, J_{HH} = 7.03, J_{PH} = 10.67, (S,S)-bdpp-CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 137.52 (d, J_{PC} = 44.40, (S,S)-bdpp-ipso), 136.25 (d, J_{PC} = 10.42, (S,S)-bdpp-ortho or meta), 135.28 (d, J_{PC} = 10.21, (S,S)-bdpp-ortho or meta), 134.66 (d, J_{PC} = 46.15, (S,S)-bdpp-ipso), 133.07 (d, J_{PC} = 7.84, (S,S)-bdpp-ortho or meta), 132.46 (d, the other wing of the doublet is buried underneath the neighboring resonance, (S,S)-bdpp-ipso), 132.15 (d, J_{PC} = 9.16, (S,S)-bdpp-ortho or meta), 130.47 (d, J_{PC} = 2.02, (S,S)-bdpp-para), 130.14 (d, J_{PC} = 1.91, (S,S)-bdpp-para), 129.90 (d, J_{PC} = 2.00, (S,S)-bdpp-para), 129.21 (d, J_{PC} = 2.01, (S,S)-bdpp-para), 128.90 (d, J_{PC} = 35.89, (S,S)-bdpp-ipso), 128.24 (d, J_{PC} = 8.87, (S,S)-bdpp-ortho or meta), 127.99 (d, J_{PC} = 9.98, (S,S)-bdpp-ortho or meta), 127.30 (d, J_{PC} = 9.21 (S,S)-bdpp-ortho or meta), 127.15 (d, J_{PC} = 8.92, (S,S)-bdpp-ortho or para), 37.89 (d, J_{PC} = 5.99, (S,S)-bdpp-CH), 37.24 (d of d, J_{PC} = 4.20, $J_{P'C}$ = 8.14, ReSCH(CH$_3$)$_2$), 33.00 (d, J_{PC} = 23.14, (S,S)-bdpp-CH), 29.39 (ReSCH(CH$_3$)$_2$), 28.49 (ReSCH(CH$_3$)$_2$), 18.30 (d, J_{PC} = 6.49, (S,S)-bdpp-CH$_3$), 17.12 (d, J_{PC} = 3.10, (S,S)-bdpp-CH$_3$), 16.16 (d of d, J_{PC} = 3.04, $J_{P'C}$ = 27.40, (S,S)-bdpp-CH$_2$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$) δ −4.26 (b), −10.90 (b) ppm. IR (KBr) ν_{CO} = 2015 (s), 1934 (s), 1896 (s) cm^{-1}. UV–vis (THF) λ = 363 nm (ϵ = 596 M^{-1} cm^{-1}). Anal. Calcd for $C_{35}H_{37}O_3P_2ReS$: C, 53.49; H, 4.75. Found: C, 53.16; H, 4.72.

$(CO)_3$(depe)ReP$(C_6H_5)_2$ (7b). In the drybox a bomb was charged with 63 mg (0.121 mmol) of $(CO)_3$(depe)ReOCH$_2$CH$_3$ and 3 mL of C_6H_6. It was stoppered and attached to a Schlenk line. Diphenylphosphine (50 μL, 0.251 mmol, 2.07 equiv) was added via syringe. The bomb was stoppered and heated at 60 °C for 3 days. Over this period, the solution turned bright yellow. The bomb was removed from the bath and allowed to cool to room temperature. It was attached to a vacuum line and the volatile materials removed, leaving an oily yellow residue. The bomb was taken into the drybox, and the residue washed with pentane to remove the excess HP$(C_6H_5)_2$. The residue was dissolved in toluene (2 mL) and filtered through a plug of Celite. The Celite was washed with an additional 2 mL of toluene. The combined toluene extracts were concentrated to a volume of ~1 mL in a 1-dram vial. This vial was placed in a larger vial filled with ~7 mL of pentane. The larger vial was stoppered and the pentane vapor was allowed to diffuse into the toluene solution at −40 °C. After 1 day, yellow crystals had formed. They were washed with pentane and residual solvent was removed by exposing the crystals to vacuum for 12 h, yielding 26 mg (31% yield, 0.034 mmol) of $(CO)_3$(depe)ReP$(C_6H_5)_2$. Note: This compound decomposes in chloroform. ^{1}H NMR (THF-d_8) δ 7.62 ("t", 4 H, "J" = 6.8, P(C_6H_5)$_2$ ortho), 7.05 ("t", 4 H, "J" = 7.2, P(C_6H_5)$_2$ meta), 6.95 ("t", 2 H, "J" = 7.4, P(C_6H_5)$_2$ para), 2.09–1.77 (m, 12 H, depe-CH_2), 1.12 (d of t, 6 H, J_{HH} = 7.6, J_{PH} = 15.6, depe-CH_3), 0.86 (d of t, 6 H, J_{HH} = 7.6, J_{PH} = 15.3, depe-CH_3). ^{13}C{^{1}H} NMR (THF-d_8) δ 149.7 (d of t), J_{PC} = 28.38, 3.70, P(C_6H_5)$_2$-ipso), 137.1 (d, J_{PC} = 15.1, P(C_6H_5)$_2$-ortho), 127.6 (d, J_{PC} = 13.8, P(C_6H_5)$_2$-meta), 124.6 (P(C_6H_5)$_2$-para), 24.18 (AXX′, $^1J_{PC} + {}^2J_{PC}$ = 41.6, depe-CH$_2$), 22.01 (AXX′, $^1J_{PC} + {}^4J_{PC}$ = 31.0, depe-CH$_2$CH$_3$), 13.86 (AXX′, $^1J_{PC} + {}^4J_{PC}$ = 27.8, depe-CH$_2$CH$_3$), 8.53 (depe-CH$_3$), 7.65 (depe-CH$_3$) ppm. ^{31}P{^{1}H} NMR (THF-d_8) δ 20.64 (b, depe), −47.37 (t, J_{PP} = 27.64, P(C_6H_5)$_2$). IR (KBr) ν_{CO} = 2013 (s), 1996 (s), 1917 (s). UV–vis (THF) λ_{max} = 361 nm (ϵ = 1300 cm^{-1} M^{-1}). Anal. Calcd for $C_{25}H_{34}O_3P_3Re$: C, 45.38; H, 5.18. Found: C, 45.26; H, 5.03.

$(CO)_3$(depe)RePH(C_6H_5) (8b). The phenylphosphido complex **8b** was prepared using the same scale and procedure described for **7b**. The compound was recrystallized by diffusion of pentane vapor into a concentrated (~0.5 mL) toluene solution of **8b** at −40 °C. This procedure resulted in 32 mg (0.055 mmol, 45%), of **8b**. ^{1}H NMR (C_6D_6, 50 °C) δ 7.82 ("t", 2 H, J = 6.7, PH(C_6H_5)-ortho), 7.18, "t", 2 H, "J" = 7.0, PH(C_6H_5)-meta), 6.94 ("t", 1 H, "J" = 7.0, PH(C_6H_5)-para), 3.05 (bd, 1 H, J_{PH} = 273, PH(C_6H_5)), 1.92 (b, 2 H, depe-CH_2), 1.70 (b, 2 H, depe-CH_2), 1.52–1.23 (m, 6 H, depe-CH_2CH$_3$), 0.94 (m, 2 H, depe-CH_2CH$_3$), 0.77 (m, 12 H, depe-CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 50 °C) δ 147.25 (d of t, $^1J_{PC}$ = 27.5, $^3J_{PC}$ = 4.6, PH(C_6H$_5$)-ipso), 133.8 (d, J_{PC} = 14.9, PH(C_6H$_5$)-ortho), 127.8 (d, J_{PC} = 12.7, PH(C_6H$_5$)-meta), 124.9 (PH(C_6H$_5$)-para), 24.36 (AXX′, $^1J_{PC} + {}^2J_{PC}$ = 42.4, depe-CH$_2$), 21.78 (AXX′, $^1J_{PC} + {}^4J_{PC}$ = 29.8, depe-CH$_2$CH$_3$), 14.67 (AXX′, $^1J_{PC} + {}^4J_{PC}$ = 42.2, depe-CH$_2$CH$_3$), 8.23 (depe-CH$_3$), 7.71 (depe-CH$_3$) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 50 °C) δ 24.6 (d, J = 20.6, depe), −130.9 (t, J = 20.6, PH(C_6H_5)) ppm. IR (KBr) ν_{CO} = 2019 (sh), 1992 (s), 1915 (s), 1893 (s) cm^{-1}. ν_{PH} = 2284 (w). Repeated attempts at elemental analysis gave results which were consistently low in carbon. A typical result: Anal. Calcd for $C_{19}H_{30}O_3P_3Re$: C, 38.97; H, 5.16. Found: C, 37.76; H, 4.96.

$[(CO)_3(PMe_3)_2$RePH$_2(C_6H_{11})]CF_3SO_3$ (11c). A flame-dried Schlenk tube was charged with 300 mg (0.525 mmol) of $(CO)_3(PMe_3)_2$ReOSO$_2$CF$_3$. It was flushed with Ar and then evacuated. This procedure was repeated three times. THF (5 mL) was added via syringe, and the mixture was allowed to stir under Ar until **10c** had dissolved. Cyclohexylphosphine (100 mg, 0.861 mmol) was added via syringe. The tube was fitted with a reflux condenser and heated to 45 °C overnight. After this time, the condenser was removed, the flask was stoppered, and the volatile materials were removed under vacuum. The white residue was washed twice with 5 mL of pentane to remove excess cyclohexylphosphine. The residue was dissolved in 15 mL of THF, concentrated to a volume of ~5 mL, and then carefully layered with 5 mL of Et_2O, and cooled to −40 °C. After 2 days, white crystals had formed. The supernatant was removed with a cannula and crystals were washed with ~5 mL of pentane, which was removed with the aid of a cannula. Residual solvent was removed by exposing them to high vacuum for 12 h, yielding 332 mg (91%, 0.480 mmol) of the salt $[(CO)_3(PMe_3)$RePH$_2(C_6H_{11})]^+CF_3SO_3^-$. ^{1}H NMR (THF-$d_8$) δ 4.81 (d of q, ^3J = 5.78, ^1J = 357.40, PH_2(C_6H_{11}), 2.15–1.30 (m, PH$_2$(C$_6$$H_{11}$), 1.79 ($AA'X_9X'_9$, "$J$" = 8.66, P(C$H_3$)$_3$) ppm. Accurate integration of the P(CH$_3$)$_3$ and H$_2$P(C_6H_{11}) resonances was not possible because of overlapping signals. ^{13}C{^{1}H} NMR (THF-d_8)

δ 189.5 (b, *C*O), 122.3 (q, J_{FC} = 318.0, OSO_2CF_3), 33.51 (d, J_{PC} = 2.83, $H_2P(C_6H_{11})–CH_2$), 32.56 (d of t, $^3J_{PC}$ = 2.32, $^2J_{PC}$ = 33.52, $H_2P(C_6H_{11})–CH$), 27.52 (d, J_{PC} = 12.52, $H_2P(C_6H_{11})–CH_2$), 26.38 ($H_2PC_6H_{11}–CH_2$), 18.57 (d of AXX′, $^1J_{PC} + {}^3J_{PC}$ = 64.86, $^3J_{HPC}$ = 2.23, $P(CH_3)_3$ ppm. ^{19}F NMR (THF-d_8) δ −78.9 ppm. $^{31}P\{^1H\}$ NMR (THF-d_8) δ −47.4 (b, $P(CH_3)_3$), −71.7 (b, $H_2P(C_6H_{11})$ ppm. ^{31}P NMR (THF-d_8) δ −47.4 (b, $P(CH_3)_3$), −71.7 (bt, J_{HP} = 360, $H_2P(C_6H_{11})$ ppm. IR (KBr) ν_{CO} = 2034 (s), 1970 (s), 1944 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{31}F_3O_6P_3ReS$: C, 27.95; H, 4.54. Found: C, 27.95; H, 4.39.

$(CO)_3(PMe_3)_2RePH(C_6H_{11})$ (9c). Method A. In the drybox, $(CO)_3(PMe_3)_2ReOCH_3$ (15 mg, 0.033 mmol) was dissolved in 0.6 mL of C_6D_6 and added to an NMR tube. The tube was fitted with a gum rubber septum and removed from the box. Cyclohexylphosphine (19.2 mg, 0.17 mmol, 5 equiv) was added via syringe, and the septum tightly wrapped with parafilm. The tube was heated to 45 °C for 1 week. Examination of the reaction mixture by $^{31}P\{^1H\}$ NMR showed complete conversion to the phosphido complex **9c**. The characterization of this compound is described below.

$(CO)_3(PMe_3)_2RePH(C_6H_{11})$ (9c). Method B. A Schlenk flask was charged with 180 mg (0.218 mmol) of the salt $[(CO)_3(PMe_3)_2RePH_2(C_6H_{11})]^+CF_3SO_3^-$ and 5 mL of THF. A separate flask was charged with 48 mg (0.240 mmol, 1.1 equiv) of $KN(TMS)_2$ and 5 mL of THF. The flasks were stoppered, removed from the drybox, and attached to a Schlenk line. They were allowed to cool to −40 °C (dry ice/acetonitrile), and the solution of $KN(TMS)_2$ was transferred via cannula to the rapidly stirred solution of **10c**. No color change was observed. After stirring for 30 min at −40 °C, the flask was removed from the bath and allowed to warm to room temperature. The THF was removed using a vacuum line and the flask returned to the box. The resulting white residue was extracted with 3 × 5 mL of pentane and filtered through a bed of Celite on a medium frit.

The combined pentane extracts were concentrated to a volume of 2 mL and cooled to −40 °C for 3 days. The resulting white crystals were isolated by decanting off the supernatant followed by washing with 1 mL of cooled pentane. Residual solvent was removed by exposing the crystals to high vacuum for 6 h. The supernatant was concentrated to a volume of ~0.5 mL and the crystallization procedure repeated. The crystals obtained by this procedure exhibited ^1H and $^{31}P\{^1H\}$ NMR spectra identical those obtained from the first crop of crystals. The combined yield for the two crops of crystals was 52%. ^1H NMR (THF-d_8, −55.5 °C) δ 2.03–1.74 (m, C_6H_{11}), 1.73–1.65 (m, C_6H_{11}), 1.62 (d, "J" = 8.2, $P(CH_3)$), 1.54 (d, "J" = 8.3, $P(CH_3)_3$), 1.39–0.87 (m, C_6H_{11}) ppm. The resonance for the P–H was not observed, presumably because it was buried under the cyclohexyl resonances. Accurate integrals were not obtained because of overlapping resonances. $^{13}C\{^1H\}$ NMR (THF-d_8, −55.5 °C) δ 197.83 (d, J_{PC} = 8.0, *C*O cis to $PH(C_6H_{11})$), 197.3 (t, J_{PC} = 8.8, *C*O cis to $PH(C_6H_{11})$), 193.6 (q, J_{PC} = 8.1, *C*O trans to $PH(C_6H_{11})$), 40.72 ($PH(C_6H_{11})–CH_2$), 37.78 (d, J_{PC} = 22.51, $PH(C_6H_{11})–CH$), 34.71 (d of d, J_{PC} = 7.0, $PH(C_6H_{11})–CH_2$), 29.20 ($PH(C_6H_{11})–CH_2$), 28.78 (d, J_{PC} = 14.3, $PHC_6H_{11}–CH_2$), 27.26 ($PH(C_6H_{11})–CH_2$), 17.84 (d, J_{PC} = 30.5, $P(CH_3)_3$), 17.31 (d of d of d, $^3J_{PC}$ = 2.5, $^3J_{PC}$ = 9.5, $^1J_{PC}$ = 33.4, $P(CH_3)_3$ ppm. $^{31}P\{^1H\}$ NMR (THF-d_8, −55.5 °C) IR (KBr) ν_{CO} = 1996 (s), 1912 (s), 1897 (s) cm^{-1}; ν_{P-H} = 2245 cm^{-1} (m). Anal. Calcd for $C_{15}H_{30}O_3P_3Re$: C, 33.52; H, 5.63. Found: C, 33.28; H, 5.60.

$(CO)_3((S,S)$-bdpp$)Re(NC_4H_4)$ (12d). In the drybox, a bomb was charged with 80 mg (0.106 mmol) of $(CO)_3((S,S)$-bdpp$)ReOCH_3CH_3$ and 3 mL of C_6H_6. It was removed from the box and attached to a Schlenk line. Pyrrole (100 μL, 1.54 mmol, 14.5 equiv) was added via syringe. The bomb was stoppered and heated to 60 °C for 2 days. After this time, an aliquot was removed and examined by $^{31}P\{^1H\}$ NMR. Complete conversion to the η^1-pyrrole complex was observed. The volatile materials were removed on the vacuum line and the tan residue was taken into the drybox. It was extracted with 3 × 2 mL of toluene, filtered through Celite, and then concentrated to 1 mL. It was layered with ~5 mL of pentane and cooled to −40 °C for 2 days. After this time, a tan powder had formed. The powder was collected on a frit and washed with 3 mL of pentane. Residual solvent was removed by exposing the sample to high vacuum for 12 h, yielding 48 mg (61%, 0.65 mmol) of the pyrrole complex **12d**. ^1H NMR (THF-d_8) d 7.56–7.10 (m, 20 H, ((S,S)-bdpp-C_6H_5), 6.52 (m, 2 H, pyrrole α-CH), 5.74 (m, 2 H, pyrrole β-CH), 3.49 (m, 1 H, bdpp-CH), 3.14 (m, 1 H, (S,S)-bdpp-CH), 2.76 (m, 1 H, (S,S)-bdpp-CH_2), 2.25 (m, 1 H, (S,S)-bdpp-CH_2), 1.22 (d of d, J_{HH} = 7.4, J_{PH} = 13.3, (S,S)-bdpp-CH_3), 1.07 (d of d, J_{HH} = 7.1, J_{PH} = 11.7, (S,S)-bdpp-CH_3). $^{13}C\{^1H\}$ NMR (THF-d_8) d 193.0 (b, *C*O), 141.70 (d, J_{PC} = 46.95, (S,S)-bdpp-ipso), 136.72 (d, J_{PC} = 10.69, (S,S)-bdpp-ortho or meta), 135.92 (d, J_{PC} = 7.5 (S,S)-bdpp-ipso), 135.38 (d, J_{PC} = 9.35, (S,S)-bdpp-ortho), 134.43 (d, J_{PC} = 9.18, (S,S)-bdpp-ortho or meta), 132.93 (d, J_{PC} = 42.42, (S,S)-bdpp-ipso), 132.83 (d, J_{PC} = 42.69, (S,S)-bdpp-ipso), 131.61 (d, J_{PC} = 8.75, (S,S)-bdpp-ortho or meta), 133.35 (d, J_{PC} = 2.18, (S,S)-bdpp-para), 131.18 (d, J_{PC} = 2.01, (S,S)-bdpp-para), 130.41 (d, J_{PC} = 1.88, (S,S)-bdpp-para), 130.15 (d, J_{PC} = 1.93, (S,S)-bdpp-para), 129.82 (d, J_{PC} = 9.01, (S,S)-bdpp-ortho or meta), 129.02 (pyrrole α-*C*H), 128.88 (d, J_{PC} = 5.64, (S,S)-bdpp-ortho or meta), 128.78 (d, J_{PC} = 6.16, (S,S)-bdpp-meta or para), 128.65 (d, J_{PC} = 9.18, (S,S)-bdpp-meta or para), 108.54 (pyrrole β-*C*H), 39.42 (t, J_{PC} = 6.40, (S,S)-bdpp-*C*H), 31.41 (d, J_{PC} = 21.49, (S,S)-bdpp-*C*H), 23.16 (d, J_{PC} = 20.93, (S,S)-bdpp-*C*H), 19.30 (d, J_{PC} = 5.53, (S,S)-bdpp-CH_3), 17.35 ((S,S)-bdpp-CH_3) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6) δ 4.01 (bd, J_{PP} = 28.46), −2.15 (bd, J_{PP} = 28.46) ppm. IR (KBr) ν_{CO} = 2021 (s), 19.34 (s), 1906 (s) cm^{-1}. Anal. Calcd for $C_{36}H_{34}NO_3P_2Re$: C, 55.66; H, 4.41. Found: C, 55.94, H, 4.57.

$(CO)_3(depe)ReNH(C_6H_5)$ (13b). In the drybox, a bomb was charged with 70 mg (0.134 mmol) of **2b**, 100 μL of aniline, ~100 mg of 4-Å molecular sieves, and 3 mL of benzene. The mixture was heated at 80 °C for 48 h. During this period, the colorless solution became bright yellow. After this time, an aliquot removed and examined by $^{31}P\{^1H]$ NMR spectrometry showed complete conversion of **2b** to the anilide. The bomb was attached to a vacuum line and the volatile materials removed. The oily yellow residue was returned to the drybox, washed with 2 × 2 mL of pentane, extracted with 3 × 2 mL of toluene, and filtered through a plug of glass wool. The yellow toluene solution was concentrated to a volume of ~1 mL, layered with pentane, and cooled for 15 h at −40 °C. After this time, bright yellow rodlike and polyhedral crystals of **13b** had formed. Residual solvent was removed by exposing them to high vacuum at room temperature for 12 h, yielding 61 mg (0.107 mmol, 80%) of **13b**. Both of the two forms of crystals formed had identical ^1H NMR spectra. ^1H (NMR (THF-d_8) δ 6.68 ("t", 2 H, "J" = 8.6, NHC_6H_5-meta, 6.33 ("d", 2 H, "J" = 7.8, NHC_6H_5-ortho), 5.92 ("t", 1 H, "J" = 6.9, NHC_6H_5-para), 2.07-1.72 (m, 12 H, depe-CH_2), 1.23–1.04 (m, 12 H, depe-CH_3) ppm. $^{13}C\{^1H\}$ NMR (THF-d_8) δ 162.6 (t, J_{PC} = 1.7, NHC_6H_5-ipso), 129.0 (NHC_6H_5-*C*H), 116.8 (s, NHC_6H_5-*C*H), 109.8 (NHC_6H_5-para *C*H), 24.09 (AXX′, $^1J_{PC} + {}^2J_{PC}$ = 40.9, depe-CH_2), 20.42 (AXX′, $^1J_{PC} + {}^4J_{PC}$ = 29.9, depe-CH_2CH_3), 14.55 (AXX′, $^1J_{PC} + {}^4J_{PC}$ = 26.2, depe-CH_2CH_3), 8.62 (CH_3), 8.17 (CH_3) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6) δ 28.3 (bs) ppm. IR (KBr) ν_{CO} = 1996 (s), 1905 (s), 1869 (s); ν_{NH} = 3359 (w) cm^{-1}. UV–vis (toluene) λ = 297 nm (ε = 3540 M^{-1} cm^{-1}), 301 (ε = 3330 M^{-1} cm^{-1}), 402 nm (327 M^{-1} cm^{-1}). MS (high res EI) calcd for $^{185}Re/^{187}Re$: 567.123900/569.126330. Found: 567.123073/569.125861.

$(CO)_3(depe)Re^{15}NH(C_6H_5)$ (13b-^{15}N). The labeled compound was prepared as described above, using 29 mg of $(CO)_3(depe)ReOCH_2CH_3$, 25 μL of $^{15}NH_2C_6H_5$, 50 mg of molecular sieves, and 2 mL of C_6H_6. The compound was crystallized as described above. The yield was 20 mg (63%, 0.035 mmol). ^{15}N NMR (C_6D_6) δ −358 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6) δ 28.3 (bs) ppm.

$(CO)_3(depe)ReND(C_6H_5)$ (13b-ND). The deuterated compound was prepared on the same scale as the ^{15}N analogue as described above, yielding 17 mg of **13b-ND** (55%). IR (KBr) ν_{CO} = 1996 (s), 1905 (s), 1869 (s); ν_{ND} = 2376 (w) cm^{-1}.

X-ray Crystal Structure Determination of 13b. Clear rodlike and polyhedral crystals were obtained by slow diffusion of pentane vapor into a toluene solution of **13b** at −40 °C. A crystal was chosen and mounted using Paratone N hydrocarbon oil. The crystal used for data collection was then transferred to an Enraf-Nonius CAD-4 diffractometer and centered in the beam. It was cooled to −104 °C by a nitrogen-flow low-temperature apparatus which had been previously calibrated by a thermocouple placed at the sample position. Automatic peak search and indexing procedures yielded an orthorhombic reduced primitive cell. The final cell parameters and specific data collection parameters are given in Table II.

The 5267 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the intensity standards revealed an increase of 7.3% of the original intensity over the data collection period. The data were corrected for this change. Inspection of the azimuthal scan data showed a variation $I_{min}/I_{max} = 0.84$ for the average curve. An empirical correction based on the observed variation was applied to the data. Inspection of the systematic absences indicated uniquely space group *Pbca*. Removal of the systematically absent data left 4673 unique data in the final data set.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. The disorder in one of the depe ligands was modeled very successfully with 50% occupancy at each of the two methyl carbon sites. In a difference Fourier map calculated following the refinement of all non-hydrogen atoms with all anisotropic thermal parameters, peaks were found corresponding to the positions of most of the hydrogen atoms. The amido hydrogen was assigned idealized locations and values of B_{iso} approximately 1.15 times of B_{eqv} of the atoms to which they were attached. They were included in the structure factor calculations but not refined.

The final residuals for the 244 variables refined against the 2875 data for which $F^2 > 3\sigma(F^2)$ were $R = 3.98\%$, $wR = 4.39\%$, and GOF = 1.284. The R value for all 4376 data was 8.4%.

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 intense reflections, was set to 0.04 in the last cycles of the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used, and all scattering factors corrected for both real and imaginary components of anomalous dispersion.

Inspection of the residuals ordered in the ranges of $\sin \theta/I$, $|F_o|$, 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 1.52 $e^-/Å^3$, and the lowest excursion −0.34 $e^-/Å^3$. The largest three peaks (all that were greater than 1.0 $e^-/Å^3$) were located near the rhenium atom. There was no indication of secondary extinction in the high-intensity low-angle data.

$(CO)_3(depe)ReNH(C_6F_5)$ (14b). In the drybox, a 100-mL Schlenk flask was charged with 31 mg (0.05 mmol) of **2b**, 46 mg (0.25 mmol, 5 equiv) of pentafluoroaniline, ~100 mg of activated 4-Å molecular sieves, and 20 mL of benzene. The flask was removed from the box and heated at 60 °C overnight. An aliquot was removed and examined by $^{31}P\{^1H\}$ NMR spectrometry, which showed complete conversion of **2b** to the desired product. The flask was attached to a vacuum line, and the volatile materials were removed and returned to the box. The residue was extracted with 10 mL of Et_2O, and filtered through a bed of Celite. The Et_2O extracts were concentrated to a volume of 0.5 mL and cooled at −30 °C for 2 days. The off white crystals which had formed were washed with cold pentane to yield 22 mg (68%, 0.034 mmol) of **14b**. ^1H NMR (C_6D_6) δ 1.41–1.32 (m, 8 H, depe-CH_2CH_3), 1.23–1.17 (m, 2 H, depe-CH_2), 0.86–0.77 (m, 2 H, depe-CH_2), 0.73–0.65 (m, 12 H, depe-CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6) δ 23.6 (AXX′, $^1J_{PC} + {}^2J_{PC} = 40.4$, depe-$CH_2$), 19.49 (AXX′, $^1J_{PC} + {}^4J_{PC} = 31.4$, depe-$CH_2CH_3$), 13.5 (AXX′, $^1J_{PC} + {}^4J_{PC} = 25.3$, depe-$CH_2CH_3$), 8.0 (depe-$CH_3$), 7.5 (depe-$CH_3$) ppm. The carbonyl and aromatic resonances were not observed. ^{19}F NMR (C_6D_6) δ −164.5 (vt, "J" = 15.7, C_6F_5-para), −168.6 (t, J = 22.3, C_6F_5-ortho), −186.0 (septet, "J" = 11.9, C_6F_5-meta) ppm. IR (KBr) ν_{CO} 2014 (s), 1930 (s), 1894 (s) cm^{-1}; ν_{NH} = 3374 cm^{-1}. MS (high res EI) calcd for $^{185}Re/^{187}Re$: 657.074200/659.078000. Found: 657.075964/659.078752.

Reaction of $(CO)_3(diars)ReOCH_3$ with Catechol Borane. In the drybox, a NMR tube was charged with 6.0 mg (0.01 mmol) of **1a**, ~1 μL of mesitylene, and 0.5 mL of C_6D_6. An NMR spectrum was taken to determine the ratio of **1a** and the internal standard. Catechol borane (2 μL, 0.015 mmol, 1.5 equiv) was added to the tube via syringe. An NMR spectrum taken 5 min after addition showed complete conversion of **1a** to **15a** (95% yield via integration against the internal standard). ^1H NMR (C_6D_6) δ 7.07–7.05 (m, 4 H, diars-CH), 1.40 (s, 6 H, diars-CH_3), 1.14 (s, 6 H, diars-CH_3), −5.71 (s, 1 H, Re-H). Lit.:[40] ^1H NMR (C_6D_6) δ 7.07–7.05 (m, 4 H, diars-CH), 1.40 (s, 6 H, diars-CH_3), 1.14 (s, 6 H, diars-CH_3), −5.71 (s, 1 H, Re-H).

$(CO)_3(dppe)ReCH_2CH_3$ (16e). In the drybox, a bomb was charged with 50 mg (0.072 mmol) of **1e** and 1 mL of C_6H_6. Triethylboron (75 μL of a 1.0 M solution in hexane, 0.075 mmol, 1.05 equiv) was added via syringe. The bomb was stoppered and heated to 44 °C for 4 h. After removal from the bath, the contents were diluted with 10 mL of ether and added to a separatory funnel containing 20 mL of saturated $NaHCO_3$ solution. The funnel was vigorously shaken and the organic layer was separated and then dried over $MgSO_4$. The solvent was removed using a rotary evaporation. The off white residue was purified by flash chromatography[74] on SiO_2 (1 × 10 cm) eluting with 1:4 ethyl acetate:hexane. This resulted in a yield of 31 mg (62%) of $(CO)_3(dppe)ReCH_2CH_3$. ^1H NMR ($CDCl_3$) δ 7.65–7.58 (m, 4 H, dppe-ortho), 7.48–7.42 (m, 4 H, dppe-ortho), 7.30–7.40 (m, 12 H, dppe-meta and para), 2.83–2.73 (m, 2 H, dppe-CH_2), 2.38–2.25 (m, 2 H, dppe-CH_2), 1.03 (t, 3 H, J = 7.6, $ReCH_2CH_3$), −0.44 (virtual sextet, 2 H, "J" = 7.6, $ReCH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 198.0 (d of d, $J_{PtransC} = 56.4$, $J_{PcisC} = 9.9$, CO cis to CH_2CH_3), 193.3 (t, $J_{PC} = 4.8$, CO trans to CH_2CH_3), 135.4 (d, $J_{PC} = 44.1$, dppe-ipso), 132.6 (m, dppe-ortho of meta), 132.2 (d, $J_{PC} = 45.4$, dppe-ipso), 131.2 (m, dppe-ortho or meta), 130.4 (s, dppe-para), 129.7 (s, dppe-para), 128.7 (m, dppe-ortho or para), 128.4 (m, dppe-ortho or para), 26.9 (m, dppe-CH_2), 21.8 (t, $J_{PC} = 4.6$, $ReCH_2CH_3$), −8.3 (t, $J_{PC} = 7.7$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 35.2 ppm. IR (KBr) ν_{CO} 1997 (s), 1913 (s), 1883 (s). Anal. Calcd for $C_{31}H_{29}O_3P_2Re$: C, 53.57; H, 4.19. Found: 53.44; H, 4.58.

$(CO)_3(dppe)ReCH{=}CH$-*i*-Pr (17e). In the drybox, a bomb was charged with 167 mg (0.238 mmol) of $(CO)_3(dppe)ReOCH_3$, 62 mg (0.332 mmol, 1.4 equiv) of $C_6H_4O_2BHC{=}CH$-*i*-Pr, and 3 mL of C_6H_6. It was closed, removed from the box and placed into a 44 °C bath. The reaction vessel was kept at that temperature for 8 h and then removed. The reaction mixture was diluted with 20 mL of Et_2O and then washed with 20 mL of a saturated $NaHCO_3$ solution followed by 20 mL of water. The organic layer was then dried over $MgSO_4$ and filtered, and the solvents were removed using a rotary evaporator. The tan colored residue was purified by flash chromatography[74] (SiO_2, 1 × 16 cm) eluting with 4:1 hexane:EtOAc to yield 105 mg (0.142 mmol, 60%) of white needles of **17e**. An analytical sample was prepared by recrystallization from hot hexanes. ^1H NMR ($CDCl_3$) δ 7.61–7.51 (m, 8 H, dppe-ortho), 7.39–7.30 (m, 12 H, dppe-meta and para), 5.57–5.34 (*AB*MX, $\nu_A = 5.57$, $J_{AM} = 5.7$, $J_{AB} = 17.6$, $\nu_B = 5.42$, $J_{BX} = 6.7$, 2 H, $CH_A = CH_B$-*i*-Pr), 2.86–2.71 (m, 2 H, dppe-CH_2), 2.62–2.46, m, dppe-CH_2), 1.62 (m, 1 H, $CH(CH_3)_2$), 0.548 (d, J = 6.7, 6 H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 196.42 (d of d, $J_{PtransC} = 56.8$, $J_{PcisC} = 10.6$, CO cis to $CH{=}CH$-*i*-Pr), 194.0 (t, $J_{PC} = 6.5$, CO trans to $CH{=}CH$-*i*-Pr), 151.5 (t, $J_{PC} = 5.7$, $CH{=}CH$-*i*-Pr), 135.5 (d, $J_{PC} = 45.2$, dppe-ipso), 132.4 (m, dppe-ortho or -meta CH), 132.0 (m, dppe-ortho or -meta CH), 131.4 (d, $J_{PC} = 46.0$, dppe-ipso), 130.2 (dppe-para CH), 129.9 (dppe-para CH), 128.6 (m, dppe-ortho or -meta CH), 128.2 (m, dppe-ortho or -meta CH), 127.3 (t, $J_{PC} = 11.6$, $CH{=}CH$-*i*-Pr), 374 ($CH{=}CHCH(CH_3)_2$), 27.7 (m, dppe-CH_2), 22.2 ($CH{=}CHCH(CH_3)_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 32.9 ppm. IR (KBr) ν_{CO} 2005 (s), 1928 (s), 1894 (s). Anal. Calcd for $C_{34}H_{33}O_3P_2Re$: C, 55.35; H, 4.51. Found: C, 55.16; H, 4.57.

Reaction of $(CO)_3(depe)ReOCH_2CH_3$ with Aniline: Determination of K_{eq}. In the drybox, an NMR tube was charged with 7.4 mg (0.014 mmol) of **2b** and 0.5 mL of THF-d_8. Aniline (6.5 μL, 0.071 mmol, 5.0 equiv) was added via syringe and the tube was stoppered. When the aniline reached the solution, a pale yellow color developed. The tube was placed in an NMR probe at 21 °C and allowed to equilibrate for 1 h before a spectrum was taken using a single pulse to avoid potential problems with the observed protons having different relaxation times. The equilibrium constants were determined by dividing the product of integrated intensities of the resonances for the methylene group of released ethanol and the ortho proton resonances of **13b** by the product of the integrated intensities for the methylene of **2b** and the ortho proton resonances of the free aniline. This was repeated after a second hour to ensure the that the same value of K_{eq} was calculated.

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Protonation of 9c with Triflic Acid. In the drybox, an NMR tube was charged with the cyclohexylphosphido complex **9c** (5 mg, 0.009 mmol) and ~0.5 mL of toluene. It was fitted with a gum rubber septum and removed from the box. Triflic acid (1.0 μL, 0.01 mmol, 1.1 equiv) was added all at once using a microliter syringe. As soon as the acid was added, a white precipitate formed. The tube was vigorously shaken and the solid collected on a glass frit. The white solid was washed with distilled water (~1 mL), and then ether (~1 mL) and allowed to air dry for 3 h. IR analysis (KBr) of the solid showed that the salt **11c** was the only carbonyl-containing compound.

Kinetic Studies on the Reaction of 1a with $CpW(CO)_3H$. Standard solutions of **1a** and $CpW(CO)_3H$ were prepared in THF in the drybox and stored in the dry box freezer and stored at -40 °C. For each run, 1 mL of the solution of **1a**, measured using a 1.0-mL volumetric pipet, was transferred to a 10-mL volumetric flask, and then an appropriate aliquot of the $CpW(CO)_3H$ solution was added using a volumetric pipet. The mixture was then diluted to 10 mL and shaken, a UV-vis cell equipped with a Kontes vacuum stopcock charged with the reaction mixture, and the stopcock sealed. The cell was removed from the drybox and placed into the temperature controlled cells. Spectra were taken at regular intervals after the solutions had been allowed to equilibrate in the cell holder. The temperature of the cell holder was calibrated using a thermocouple which had been previously calibrated using ice and boiling water.

The reactions were monitored by observing the increase in absorbance at 410 nm due to formation of the product $(CO)_3$-(diars)$ReW(CO)_3Cp$. In all cases reactions were observed for at least 3 half-lives. Plots of absorbance vs time were fit to the increasing exponential function $y = A_1(1 - e(-A_2x)) + A_3$ using the IGOR Wavemetrics curve fitting program,[75] where y is the absorbance and x = time in seconds. The least-squares fit of the data gives the observed rate constant (k_{obs}) and the infinity point as $A_1 + A_3$. The linearity of the data was then checked by plotting $\ln(A_\infty - A_t)$ vs time.

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Supplementary Material Available: ORTEP diagrams of **13b** and tables of positional parameters, anisotropic thermal parameters, and root-mean-amplitudes for **13b** (7 pages). Ordering information is given on any current masthead page.

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(75) The Igor graphing and data analysis software is distributed by Wavemetrics, Lake Oswego, OR.

Reactions of Di- or Trialkynylphosphine and Di- or Trialkynylarsine Oxides with a Cationic Platinum-Hydride Complex: Mechanistic Features

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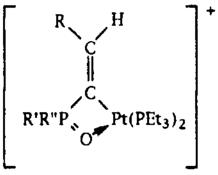
The reaction between a cationic Pt-H complex and $O{=}P(C{\equiv}CCMe_3)_3$ was followed by ^{31}P NMR at three temperatures. Addition of the Pt-H bond to an alkynyl substituent to give a Pt,P-μ-alkenylidene complex is observed with subsequent formation of the expected 1,2-dihydrophosphete product. A similar reaction with $O{=}AsPh(C{\equiv}CCMe_3)_2$ occurs with unexpected overall transfer of both alkynyl substituents from the As atom to the Pt ion, giving eventually a cationic $Pt^{II}(\eta^1\text{-alkynyl})(\eta^1\text{-alkenyl})$ product. The X-ray structure of this latter complex has been determined: $P\bar{1}$; $Z = 2$; $a = 11.391$ (4) Å, $b = 16.040$ (4) Å, $c = 10.801$ (1) Å; $\alpha = 100.13$ (1)°, $\beta = 100.71$ (2)°, $\gamma = 80.23$ (2)°. A mechanism of formation of 1,2-dihydrophosphete or -arsete complexes involving Pt-H addition and subsequent alkynyl transmetalation is postulated.

Introduction

We have reported previously that cationic platinum-hydride reagents of the type $[trans\text{-}PtH(PEt_3)_2(solvent)]^+$ (**1**) react with alkynylphosphine or -arsine oxides by one of two routes, depending on the nature of the substituents within the *P*- or *As*-oxides. Monoalkynylphosphine oxides react with **1** to give Pt,P-μ-alkenylidene products **2** by regio- and stereoselective cis addition of the Pt-H bond across the alkynyl C-C triple bond.[1] Di- or trialkynylphosphine oxides containing propynyl- or phenylacetylide substituents also react with **1** to form addition products such as **2**.[2] However, di- or trialkynylphosphine oxides having *tert*-butylacetylide substituents react with **1** to afford complexes containing 2-alkylidene-1,2-dihydro-3-phosphete *P*-oxide ligands **3**.[1,2] The unexpected formation of the 1,2-dihydrophosphete ring system occurs presumably by an overall process of cis addition of the Pt-H bond



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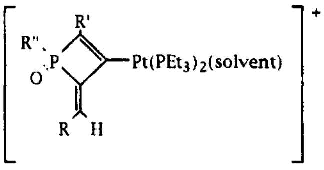

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