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Comparison of the Reactivity of $(CO)_3L_2ReOR$, $(CO)_3L_2ReOAr$, and $(CO)_3L_2ReNHAr$ with CO_2 and Other Electrophiles

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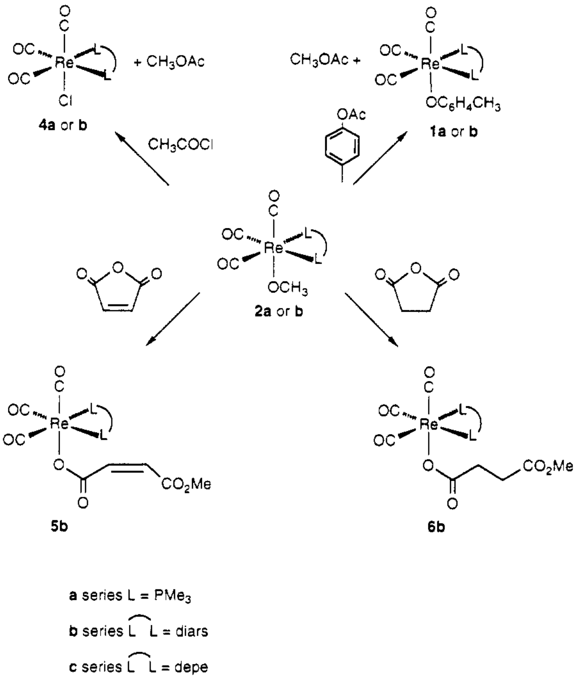
The reactivity of a series of low-valent Re alkoxides, aryloxides, and arylamides with CO_2, CS_2, and other electrophiles has been investigated. The methoxide complexes *fac*-$(CO)_3(L_2)ReOCH_3$ (**2a**, L = PMe_3; **2b**, L_2 = 1,2-$(AsMe_2)_2C_6H_4$ (diars)) react with activated organic carbonyl compounds such as acid chlorides, anhydrides, and activated esters to give products resulting from cleavage of the Re–OCH_3 bond. The methoxide complexes react rapidly with CO_2 and CS_2 to give the expected insertion products *fac*-$(CO)_3(L_2)ReX(CX)OCH_3$ (**8**, X = O; **9**, X = S). The analogous aryloxides **1** do not react with CO_2 and only the PMe_3-substituted system reacts with CS_2. In the latter transformation *fac,cis*-$(CO)_3(PMe_3)_2ReOC_6H_4CH_3$ leads to the isomerized product *mer,trans*-$(CO)_3(PMe_3)_2ReS(CS)OC_6H_4CH_3$. The arylamide *fac*-$(CO)_3$(depe)$ReNHC_6H_5$ (**3c**) reacts with CO_2 to give the metallaurethane **10c**. The metallacarbonates **8** were found to be quite reactive. They readily deinsert CO_2 to reform the methoxide complexes. Hydrolysis of **8b** leads to a bridging carbonate complex $(CO)_3$(diars)Re–(μ-CO_3)–Re(diars)$(CO)_3$, whose structure has been determined by an X-ray diffraction study. Kinetic studies on the formation of **9b** suggest that the reaction of **2b** with CX_2 is a simple bimolecular process.

Introduction

The insertion of small molecules into metal–carbon bonds is a fundamental step in many catalytic and stoichiometric reactions mediated by transition-metal complexes. The importance of these processes has led to many mechanistic studies focusing on the determination of the detailed mechanisms of CO, CO_2, CH_2O, C_2H_2, C_2H_4, and other insertion reactions into M–H and M–C bonds. However insertions of these small molecules into metal–heteroatom bonds (e.g., M–OR, M–NR_2, M–SR, etc.) have received much less attention. Such insertions are believed to be important steps in the water-gas shift reaction,[1] the carboalkoxidation of olefins,[2] reductions of ketones and aldehydes to alcohols,[3] and enzymatic transformations such as the action of carbonic anhydrase.[4] As part of our investigations of the reactivity of metal–heteroatom bonds, we have studied the reaction of low-valent Re(I) alkoxides, aryloxides, and arylamides with CO_2, CS_2, and other electrophiles, focusing on the effect of varying the different substituent coordinated to the rhenium center.

Although several examples of the insertion of CO_2 into metal hydrides,[5,6] metal–carbon bonds,[7] and metal–heteroatom bonds[8–14] are known, the mechanisms of these transformations vary greatly with both the metal and ligand systems. In this paper, we report our observations of substantial differences in the reactivity of Re(I)–alkoxide, aryloxide and arylamide complexes with CO_2 and other substrates.[15]

Scheme I



Results

Reactions with Electrophilic Organic Carbonyl Compounds. To systematically investigate the chemistry of different heteroatom–metal bonds, we have prepared

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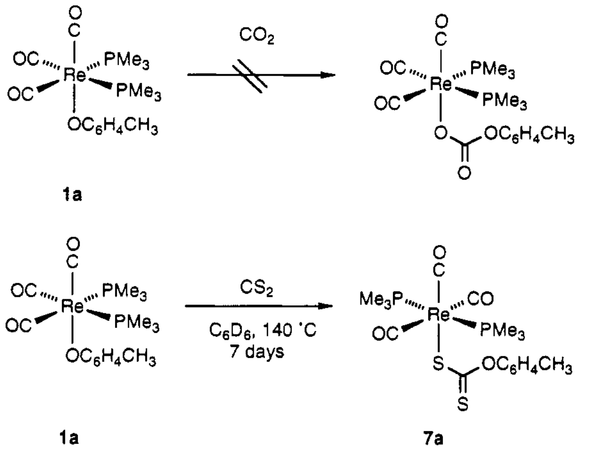
the following series of compounds: aryloxides $(CO)_3(L_2)ReOC_6H_4CH_3$ (**1a**,**b**), alkoxides $(CO)_3(L_2)ReOCH_3$ (**2a**,**b**), and arylamides $(CO)_3(L_2)ReNHC_6H_5$ (**3c**) (**a** series, L = PMe_3; **b** series, L = 1,2-$(AsMe_2)_2C_6H_4$ = diars; **c** series L = $Et_2PCH_2CH_2PEt_2$ = depe). As observed with other metal–alkoxide and aryloxide complexes, the metal–oxygen bond in these Re(I) compounds may be cleaved by a variety of electrophiles. These reactions are summarized for the methoxide complexes **2a** and **2b** in Scheme I. Treatment of the complexes $(CO)_3(PMe_3)_2ReOC_6H_4CH_3$ (**1a**) or $(CO)_3(diars)ReOCH_3$ (**2b**) with acetyl chloride in C_6D_6 at room temperature leads to rapid formation of the corresponding metal chlorides $(CO)_3(PMe_3)_2ReCl$ or $(CO)_3(diars)ReCl$ (**4**) and tolyl acetate $(CH_3CO_2C_6H_4CH_3)$ or methyl acetate, respectively.

The methoxide complexes can be used to carry out trans-esterification reactions.[16] Addition of tolyl acetate to a C_6D_6 solution of **2b** leads to formation of $(CO)_3(diars)ReOC_6H_4CH_3$ and methyl acetate. The rate of this reaction is highly dependent upon the nature of the esters. In a qualitative rate study, **2b** reacts almost instantaneously with $CH_3CO_2C_6H_4NO_2$ to form the phenolate $(CO)_3(diars)ReOC_6H_4NO_2$, while formation of **1b** from **2b** and tolyl acetate requires 12 h at room temperature. This reaction occurs only with esters of phenols; no formation of the ethoxide complex $(CO)_3(diars)ReOC_2H_5$ is observed when **2b** is treated with ethyl acetate. Analogous reactions do not occur with the aryloxide complexes; treatment of compounds **1a**,**b** with $CH_3CO_2C_6H_4CF_3$ shows no formation of the *p*-CF_3 cresolate complexes. However, they do react with $CH_3CO_2C_6H_4NO_2$ to form the *p*-nitrophenolate complex.

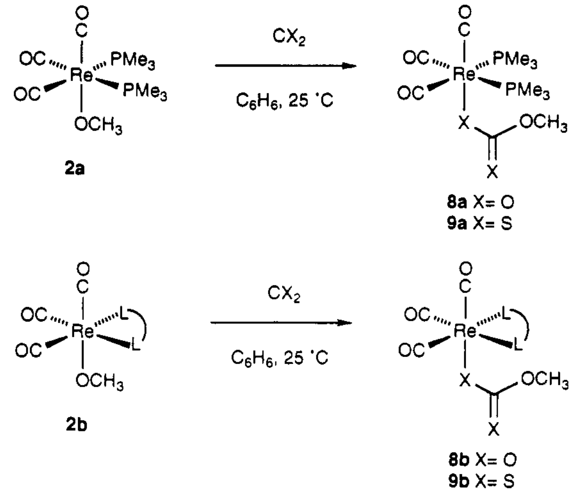
The methoxide complexes also react with cyclic anhydrides. Reaction of **2b** with 1 equiv of maleic anhydride in CH_2Cl_2 leads to the metalla ester **5b**.[10] The product is readily identified by its spectral properties. The infrared spectrum shows two absorptions at 1734 and 1624 cm^{-1} which can be assigned to the two organic carbonyl stretches. The carbonyl resonances appear in the $^{13}C\{^1H\}$ NMR spectrum at δ 171.3 and 166.1 ppm, respectively. The cis stereochemistry of the olefin is preserved in the ring-opened product. The olefinic hydrogens appear in the ^1H NMR spectrum as an AB quartet with $\delta_A = 6.13$ ppm and $\delta_B = 5.69$ ppm and a coupling constant of 12 Hz, a value typical for cis olefin geometry.[17] A double bond is not required for the insertion to occur since succinic anhydride also reacts rapidly with **2b** to yield the related metalla ester **6b**. Its spectral properties are quite similar to those of the unsaturated analogue.

Reaction of Rhenium Aryloxides with CO_2 and CS_2. Heterocumulenes such as CO_2 and CS_2 are known to insert into the metal–oxygen bond of alkoxide complexes to form new complexes containing O or S bonds to the metal. The rhenium alkoxide, aryloxide, and arylamide complexes also react with CO_2 and CS_2. However the rates and reactivity for these insertion reactions are vastly different. None of the cresolate complexes exhibited any reactivity toward CO_2 under a variety of conditions, but the accompanying ligands on the rhenium center had a marked effect on the reactivity with CS_2.

Scheme II



Scheme III



Treatment of the cresolate complexes bearing chelating ligands (e.g., **1b**) with excess CS_2 produced none of the expected product of insertion of CS_2 into the Re–O bond. No reaction was observed even after extended reaction times. However, the PMe_3-substituted complex does react slowly with CS_2. Addition of 20 equiv of CS_2 to **1a** gave after 7 days at 140 °C a 52% yield of the deep orange xanthate complex **7a** (Scheme II). The xanthate ipso carbon appears as a 1:2:1 triplet at δ 228.3 with a P–C coupling constant of 6.9 Hz. The ipso carbon of the cresolate group is a singlet at δ 150.5, demonstrating that it is located farther than three bonds from the PMe_3 ligands. The carbons of the PMe_3 ligands are no longer a multiplet as seen in **1b** but appear as a sharp virtual triplet at δ 17.34 due to coupling to the magnetically inequivalent ^{31}P nuclei. These deceptively simple spectra have been observed earlier for a trans arrangement of PMe_3 ligands.[18] The infrared spectrum shows only two inorganic carbonyl stretches at 1919 and 1844 cm^{-1}. The carbonyl region of the IR spectrum was similar to that of *trans,mer*-$(PPh_3)_2(CO)_3ReCl$,[19] further supporting the proposed structure. A C=S stretch of the xanthate ligand is observed at 1504 cm^{-1}.

Reactions of Rhenium Methoxides with CO_2 and CS_2. The rhenium methoxides exhibit a much greater reactivity toward CO_2 than the corresponding aryloxide complexes. Treatment of $(CO)_3(PMe_3)_2ReOCH_3$ (**2a**) with CO_2 at temperatures as low as −40 °C results in rapid formation of the CO_2 insertion product $(CO)_3(PMe_3)_2ReO(CO)OCH_3$ (**8a**) in 95% isolated yield (Scheme

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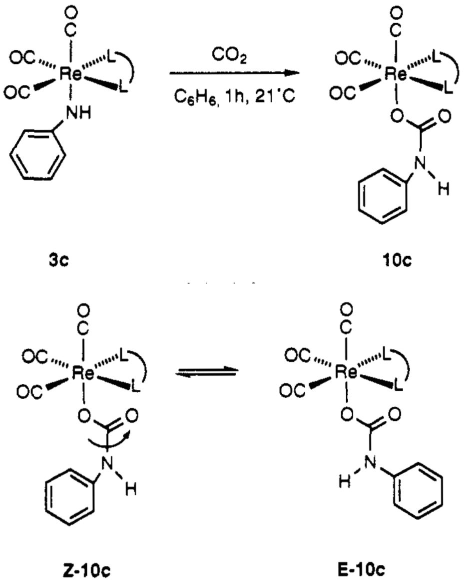
Scheme IV



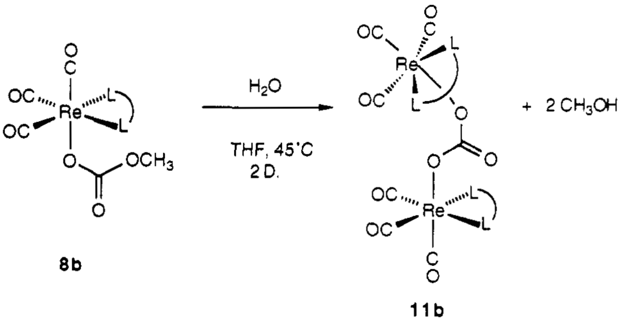
III). A resonance at δ 159.8 with a P–C coupling of 2.7 Hz can be assigned to the carbonate ligand derived from insertion of CO_2 into the Re–O bond. The C═O stretch of the coordinated carbonate ester is observed at 1670 cm^{-1} in the infrared spectrum. This insertion reaction also occurs when the rhenium center bears a chelating ligand. The diars-substituted complex $(CO)_3(diars)ReOCH_3$ (**2b**) also undergoes rapid insertion of CO_2; the reaction is complete almost instantaneously at room temperature. The carbonate carbon of **8b** is observed at δ 159.4 in the $^{13}C\{^1H\}$ NMR spectrum, and the C═O stretch appears at 1665 cm^{-1} in the IR spectrum.

Analogous reactions occur with CS_2 (Scheme III). Reaction of **2a** with CS_2 at room temperature in C_6D_6 affords the bis-PMe_3-substituted xanthate $(CO)_3(PMe_3)_2ReS(CS)OCH_3$ (**9a**) in 89% isolated yield. The spectral properties of this complex differ markedly from those of the xanthate complex derived from CS_2 insertion into the Re–O bond of $(CO)_3(PMe_3)_2ReOC_6H_4CH_3$. The xanthate carbon signal occurs at δ 223.2 as a triplet with a P–C coupling constant of 6.0 Hz, while the PMe_3 resonances appear as a five-line AXX′ pattern at δ 17.2 ppm. Three CO stretching bands are seen in the IR spectrum at 2019, 1950, and 1894 cm^{-1}, characteristic of a facial arrangement of carbonyls about the rhenium center. Again the insertion reaction occurs rapidly for the diars-substituted system. Reaction of **2b** with CS_2 results in an immediate color change from pale yellow to a brighter yellow. Examination of the product obtained from this reaction shows a resonance at δ 223.3 and an IR absorption 1559 cm^{-1} for the xanthate carbon and C═S stretch, respectively.

Reaction of Rhenium Amides with CO_2. In contrast to the aryloxide complexes 1, which showed no reactivity with CO_2, arylamide complexes were found to undergo insertion of CO_2 into the Re–N bond. Addition of 5 equiv of CO_2 to a benzene solution of **3c** resulted in the disappearance of the bright yellow color of the anilide complex and conversion to the CO_2 insertion product $(CO)_3(depe)ReO(CO)NHC_6H_5$ (Scheme IV). This transformation requires reaction times longer than that of the methoxide complexes **2**; complete conversion of **3c** to **10c** required 2 h at 20 °C.

The metallaurethane **10c** was characterized by multinuclear NMR, IR, and combustion analysis. The IR spectrum shows absorptions at 1594 and 1370 cm^{-1} which were assigned to the C═O stretches of the urethane ligand.

Scheme V



The N–H stretch is a weak band at 3323 cm^{-1}. A shift to 2352 cm^{-1} was observed when the deuterated analogue $(CO)_3(depe)ReO(CO)NDC_6H_5$ was prepared (ν_{NH}/ν_{ND} = 1.41). The facial arrangement of carbonyl ligands about rhenium is confirmed by the presence of three strong carbonyls stretches; ν_{CO} = 2021, 1939, and 1884 cm^{-1}. In the parent anilide **3c**, the CO stretches are observed at 1996, 1904, and 1869 cm^{-1}. This shift to higher CO stretching frequencies demonstrates that the metal center is less electron rich in the CO_2 insertion product.

The N–H resonance of **10c** undergoes a large downfield shift in the ^1H NMR spectrum. It appears as a broad singlet at δ 7.16 in THF-d_8. The carbon derived from CO_2 displays a broad resonance at δ 159.4 in the $^{13}C\{^1H\}$ NMR spectrum of **10c**. No coupling to the ^{31}P nuclei could be resolved, but when the sample is warmed to 35 °C, a 2.3-Hz coupling is observed. In contrast to **3c**, the resonances of the CO ligands are sharp even at ambient temperature, and the couplings to the depe ligand are observed. The CO trans to the $O(CO)NHC_6H_5$ ligand appears as a 1:2:1 triplet (J_{PC} = 6.8 Hz) due to coupling to the two equivalent ^{31}P nuclei while the cis carbonyls gives rise to a doublet of doublets (J_{PcisC} = 9.5 Hz, $J_{PtransC}$ = 51.7).

Recent studies have shown that insertion of CO_2 into the N–H bond of metal amides can precede insertion into the M–N bond.[18,20] However, when a mixture of **3c** and CO_2 is carefully monitored by ^1H and $^{31}P\{^1H\}$ NMR, one observes no intermediates during the reaction. ^1H NMR analysis of mixtures of **3c** and CO_2 showed no downfield resonances which could be assigned to an O*H* proton of a carbamic acid.

When THF-d_8 solutions of **10c** are cooled, rotation about the amide bond becomes slow on the NMR time scale and two rotamers are observed (Scheme IV). At −100 °C, two peaks at δ 40.41 and 39.81 are observed in the $^{31}P\{^1H\}$ NMR spectrum. The ratio of the two rotamers at −100 °C is ~9:1, favoring the one whose resonance appears upfield. As the temperature is raised, the two peaks coalesce, and only a single peak at δ 39.53 is seen at −27 °C.

Hydrolysis of Metallacarbonate Ester 8b. The metallacarbonate ester complexes are prone to hydrolysis. Treatment of **8b** with 2 equiv of water in THF at 45 °C results in formation of the bridging carbonate complex $(CO)_3(diars)Re(\mu\text{-}CO_3)Re(diars)(CO)_3$ (**11b**, Scheme V). The bridging carbonate ligand exhibits an IR absorption at 1533 cm^{-1}, a value in the range typically observed for symmetrical bridging carbonates.[21] The resonance for the carbonate carbon is observed at δ 166.6 in the $^{13}C\{^1H\}$ NMR spectrum. This value is very similar to that observed in the metallacarbonate esters obtained from CO_2 insertion into the Re–OCH_3 bond.

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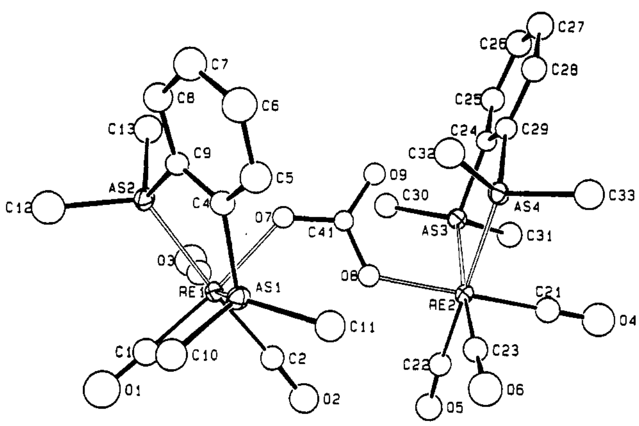


Figure 1. ORTEP diagram of $(CO)_3(diars)Re(\mu\text{-}CO_3)Re(diars)(CO)_3$.

Table I. Crystal and Data Collection Parameters for 11b

Empirical Formula $C_{41}H_{48}As_4O_9Re_2$

(A) Crystal Parameters at $T = -103$ °C[a,b]

$a = 12.522$ (3) Å	space group: $P\bar{1}$
$b = 12.804$ (4) Å	formula wt = 1356.9 amu
$c = 15.248$ (3) Å	$Z = 2$
$\alpha = 99.54$ (2)°	d(calc) = 1.95 g cm^{-1}
$\beta = 95.21$ (2)°	μ(calc) = 82.1 cm^{-1}
$\gamma = 105.00$ (2)°	
$V = 2305.8$ (22) Å^3	
size of cryst: 0.14 × 0.20 × 0.40 mm	

(B) Data Measurement Parameters

radiation: Mo Kα (λ = 0.071073 Å)
monochromator: highly oriented graphite (2θ = 12.2°)
diffractometer: Enraf-Nonius CAD-4
reflns measd: $\pm H$, $\pm K$, $+L$
2θ range: 3–45°
scan type: θ–2θ
scan width = $\Delta\theta = 0.75 + 0.35 \tan\theta$
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: 6021

[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 22 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.

Table II. Selected Intramolecular Distances for 11b

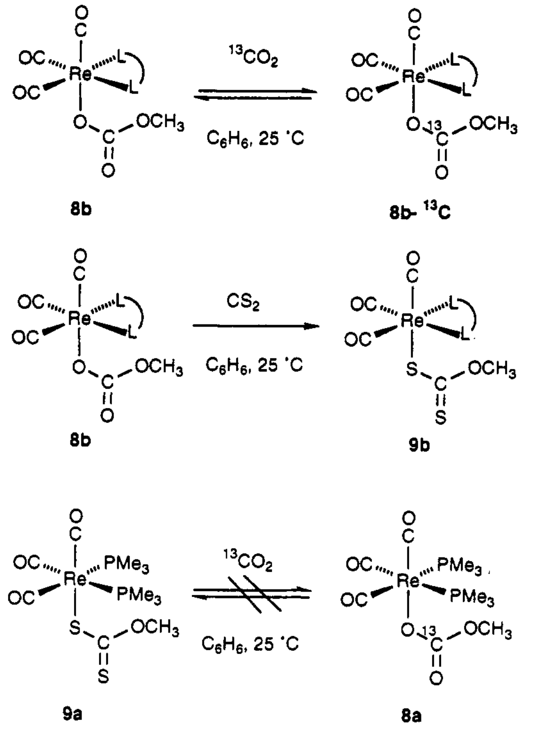
atom 1	atom 2	dist (Å)	atom 1	atom 2	dist (Å)
Re1	As2	2.527 (1)	Re2	O8	2.138 (6)
Re1	O7	2.143 (6)	Re2	C21	1.885 (10)
Re1	C1	1.876 (10)	Re2	C22	1.932 (9)
Re1	C2	1.927 (10)	Re2	C23	1.902 (9)
Re1	C3	1.898 (10)	C41	O7	1.296 (10)
Re2	As3	2.558 (1)	C41	O8	1.308 (10)
Re2	As4	2.542 (1)	C41	O9	1.245 (10)

The structure of compound **11b** has been determined by a single crystal X-ray diffraction study performed by Dr. Frederick J. Hollander at the U.C. Berkeley CHEXRAY facility (Figure 1). The dimer crystallized in space group $P(\bar{1})$ from a toluene–pentane mixture with two molecules of toluene in the unit cell. Data collection parameters are listed in Table I and the Experimental Section. The structure was solved by Patterson methods and refined by standard least-squares and Fourier techniques. An ORTEP diagram and labeling scheme are included in Figure 1, while selected intramolecular distances and angles are listed in Tables II and III.

Table III. Selected Intramolecular Angles for 11b

atom 1	atom 2	atom 3	angle (deg)
As_1	Re_1	As_2	79.96 (3)
As_1	Re_1	O_7	82.87 (15)
As_2	Re_1	O_7	78.6 (2)
O_7	Re_1	C_1	172.43 (3)
O_7	Re_1	C_2	96.7 (3)
O_7	Re_1	C_3	89.3 (3)
C_1	Re_1	C_2	90.6 (4)
C_1	Re_1	C_3	92.6 (4)
C_2	Re_1	C_3	92.6 (4)
As_3	Re_2	As_4	80.63 (3)
O_8	Re_2	C_{21}	179.7 (9)
O_8	Re_2	C_{22}	90.2 (3)
O_8	Re_2	C_{23}	91.7 (3)
Re_1	O_7	C_{41}	128.9 (5)
Re_2	O_8	C_{41}	123.9 (5)
O_7	C_{41}	O_8	116.7 (8)
O_7	C_{41}	O_9	121.4 (8)
O_8	C_{41}	O_9	121.9 (8)

Scheme VI



The two rhenium centers in the dimer are not related by any rotation or reflection operations. All of the carbonyl distances and rhenium–oxygen distances are similar to those seen in the alkoxide and aryloxide complexes. The C=O distance is 1.245 (10) Å, a value which is typical for other transition-metal monodentate binuclear carbonate complexes.[21] The O_7–C_{41}–O_8 bond angle of 116.7° in the carbonate ligand is slightly more acute than previously reported values.[21]

Reversibility of CO_2 Insertions. The Re–OCH_3 CO_2 insertion reaction is reversible as shown in Scheme VI. Similar equilibria between metallacarbonates and alkoxide/CO_2 have been observed in several systems.[9,11,22,23] However, the CS_2 insertion reactions do not exhibit this easy reversibility. Thus, during treatment of the carbonate complex **8b** with an excess of $^{13}CO_2$ in C_6D_6, one observes rapid incorporation of labeled CO_2 into the carbonate resonance as evidenced by a singlet at 160.4 ppm in the

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Table IV. Rate Constants[a] for the Reaction of $(CO)_3(diars)ReOCH_3$ with CS_2[b]

$[CS_2]$ ($\times 10^3$ M)	equiv of CS_2	solvt	temp (K)	k_{obs} ($\times 10^4$ s)	k_2 ($\times 10^2$ M^{-1} s^{-1})
2.31	10.1	THF	273	0.857	3.71
4.65	20.2	THF	273	1.91	4.10
4.65	20.2	THF	273	1.96	4.21
6.98	30.3	THF	273	3.17	4.54
9.30	39.3	THF	273	5.88	6.30
14.0	60.9	THF	273	9.89	7.06
4.65	20.2	THF	265	1.09	2.34
4.65	20.2	THF	283	3.38	7.27
4.65	20.2	THF	293	6.50	14.0
1.59	9.10	C_7H_8	273	0.318	2.00
1.59	9.10	C_7H_8	273	0.337	2.12
3.18	18.2	C_7H_8	273	0.632	1.98
4.02	23.2	C_7H_8	273	0.905	2.25
6.03	34.7	C_7H_8	273	1.42	2.35
9.54	54.8	C_7H_8	273	3.12	3.27
2.44	10.2	CH_3CN	273	1.53	6.27
4.88	20.3	CH_3CN	273	2.99	6.13
7.32	30.5	CH_3CN	273	5.00	6.83
9.76	40.7	CH_3CN	273	6.11	6.26

[a] The error in each rate constant k_{obs} estimated from the reproducibility of randomly chosen runs (typically ± 0.1 s^{-1}). [b] The [**2a**] for the experiments in the different solvent is as follows: THF, [**2a**] = 2.30×10^{-4} M; C_7H_8, [**2a**] = 1.74×10^{-4} M; CH_3CN, [**2a**] = 2.40×10^{-4} M.

$^{13}C\{^1H\}$ NMR spectrum (Scheme VI). When the NMR experiment is performed without ^1H decoupling, the signal now appears as a quartet with $^3J_{CH} = 4.2$ Hz. Consistent with this observation, the ^1H spectrum shows a methoxide resonance at δ 3.54 with $^3J_{CH} = 4.2$ Hz. When the carbonate complex **8b** is treated with a slight excess of CS_2, conversion to the xanthate **9b** is observed. The rate of this exchange is qualitatively dependent upon the amount of added CS_2. Addition of 15 equiv of CS_2 to **8b** leads to more rapid conversion to **9a** than when only 5 equiv is added.

In contrast to the behavior of the CO_2 insertion product **8b**, when xanthate **9a** is treated with $^{13}CO_2$, one observes no formation of the carbonate. When **8b** and **9a** are allowed to stand together in C_6D_6 at room temperature, no crossover is observed; the complexes **8a** and **9b** are not detected by ^1H or $^{31}P\{^1H\}$ NMR. These results confirm that the CS_2 insertion reaction is effectively irreversible.

The added CO_2 or CS_2 is not required for the deinsertion to occur. Bubbling N_2 gas through a toluene solution of **8b** results in reformation of the methoxide **2b** in 70% isolated yield.

The metallaurethane **10c** is more robust than the metallacarbonates **6**. No deinsertion of CO_2 is observed when N_2 gas is bubbled through solutions of **10c**. Also treatment of **10c** with $^{13}CO_2$ shows no incorporation of the label into the product.

Kinetics and Mechanism of CS_2 Insertion with 2b. Millimolar solutions of methoxide complexes **2a** and **2b** react with excess CO_2 and CS_2 in toluene at temperatures as low as −40 °C. Dilute solutions of diars substituted complex **2b** react with CS_2 slowly enough at 0 °C to conveniently monitor the rate by UV–vis spectrophotometry, leading to a large increase in absorbance at 410 nm. Under pseudo-first-order conditions (excess CS_2), excellent first-order plots were obtained. The observed rate constants are listed in Table IV. They were found to be linearly dependent upon the added CS_2 concentration. From plots of k_{obs} versus $[CS_2]$ (Figure 2) the second-order rate constants (k_2) for the insertion reactions were obtained. These were found to be $(8.0 \pm 0.6) \times 10^{-2}$ M^{-1} s^{-1} in THF, $(6.3 \pm 0.4) \times 10^{-2}$ M^{-1} s^{-1} in acetonitrile, and $(2.4 \pm 0.3) \times 10^{-2}$ M^{-1} s^{-1} in toluene. Activation parameters were obtained by varying the temperature of the reaction in THF. An Eyring plot (Figure 3) yields an enthalpy of activation ($\Delta H^{\ddagger}$) of 8.9 ± 0.4 kcal M^{-1} and an entropy of activation ($\Delta S^{\ddagger}$) of −31 ± 6 eu.

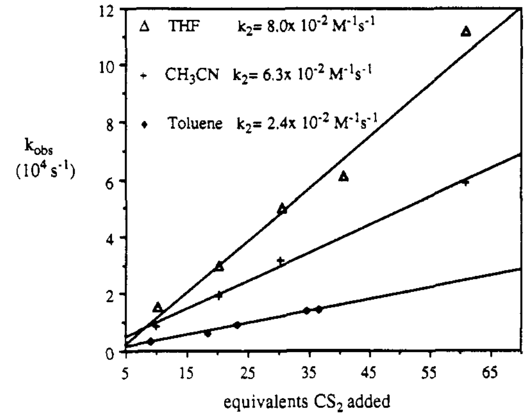

Figure 2. Dependence of k_{obs} on $[CS_2]$ and solvent for the formation of **9b**.

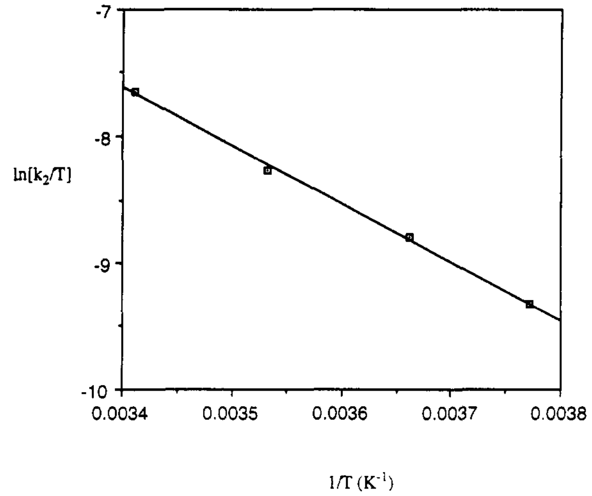

Figure 3. Eyring plot for reaction of CS_2 with **2b**.

Discussion

The coordinated oxygen atom of an alkoxide or aryloxide ligand coordinated to a transition-metal center can act as a nucleophile toward certain electrophiles. The Re–O bonds of both **1** and **2** are cleaved by strong electrophiles such as acetyl chloride to yield the rhenium chlorides and the corresponding organic acetates in nearly quantitative yield. This nucleophilic behavior is also displayed in the reaction of the methoxides with cyclic anhydrides, leading to ring-opened products in 90–100% yield. The methoxide complexes will also mediate the transesterification of activated esters.[16,24] These reactions require a rather electrophilic carbon for the transfer of the substituted phenol to proceed. Consistent with the coordinated alkoxide ligand acting as a nucleophile and attacking the carbonyl carbon of the ester, the reaction occurs more readily with the more electrophilic aryl esters while no reaction occurs with alkyl esters.

This propensity to attack electrophilic carbon atoms has been extended in at least certain cases to the activation of heterocumulenes such as CO_2 and CS_2. The related alkoxide and aryloxide complexes show drastically different reactivity toward CO_2 and CS_2. The methoxide complexes

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react with CO_2 at temperatures as low as −40 °C to yield the metallacarbonate complexes **8a** and **8b**, respectively. The insertion is reversible as evidenced by the incorporation of $^{13}CO_2$ into the carbonate ligand of **8b** and by the reconversion to the methoxide complex by bubbling N_2 through a solution of **8b**. Despite the reversibility of this reaction, no re-formation of the methoxide complexes was observed when the CO_2 or CS_2 were removed from the reaction mixtures and the products are crystallized. These results suggest that the insertion of CO_2 into the Re–O bond is reversible but the equilibrium lies far in favor the metallacarbonates **8**. The increased stability of these complexes is in marked contrast to their anionic tungsten relatives prepared by Darensbourg.[8,9] The complex $W(CO)_5OC_6H_5^-$ also inserts CO_2 into the tungsten–oxygen bond, but the phenoxide complex is reformed when the CO_2 is removed.

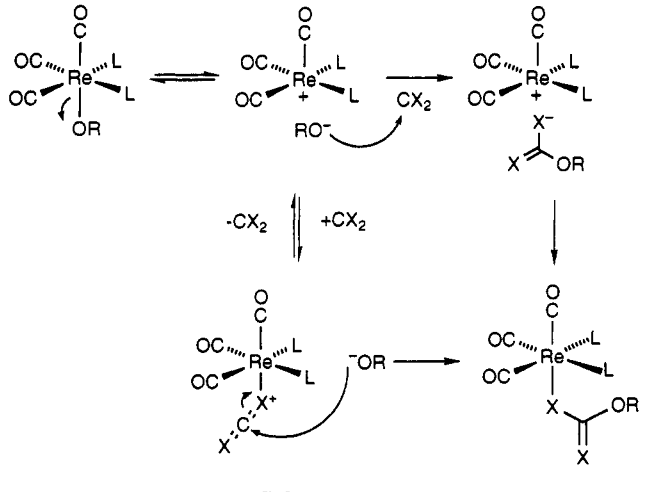
We do not know whether lack of reactivity of CO_2 with the aryloxides **1a–c** is due to a kinetic or thermodynamic effect. The aryloxide's oxygen may not be nucleophilic enough[25] to react with CO_2, thus providing an high kinetic barrier. Alternatively, if the equilibrium for the insertion reaction greatly favors the aryloxide complex and free carbon dioxide, then no reaction would be observed under the conditions employed. Attempts to independently synthesize the expected product of CO_2 insertion into the Re–OAr bond by reaction of $(CO)_3(diars)ReOSO_2CF_3$ with $KO(CO)OC_6H_4CH_3$ resulted in the formation of the aryloxide complex **1b**. This product could arise by formation of a rhenium carbonate followed by rapid CO_2 deinsertion or by decarboxylation of the added potassium salt before reaction with the rhenium center. Therefore, this result is not informative regarding the thermodynamic stability of the aryloxide carbonate complexes.

The coordinated nitrogen of the arylamide complexes **3** is nucleophilic enough to react with CO_2, leading to metallaurethane **10**. The enhanced reactivity of metal–arylamides versus metal–aryloxides has been observed in other d_6 systems. No insertion of CO_2 into the Ru–O bond of $(PMe_3)_4Ru(\eta^2\text{-}OC_6H_4)$ is observed, while CO_2 insertion in the Ru–N bond of $(PMe_3)_4Ru(\eta^2\text{-}NHC_6H_4)$ occurs at room temperature.[18] Interestingly, the only other reported Re(I)–amide complex does not undergo CO_2 insertion into the Re–N bond. Wilkinson and co-workers reported that the reaction of *trans*-$Re(NHC_6H_5)(N_2)(PMe_3)_4$ with CO_2 gives only the η^2-CO_2 complex *mer*-$(PMe_3)_3Re(NHC_6H_5)(\eta^2\text{-}CO_2)$.[26]

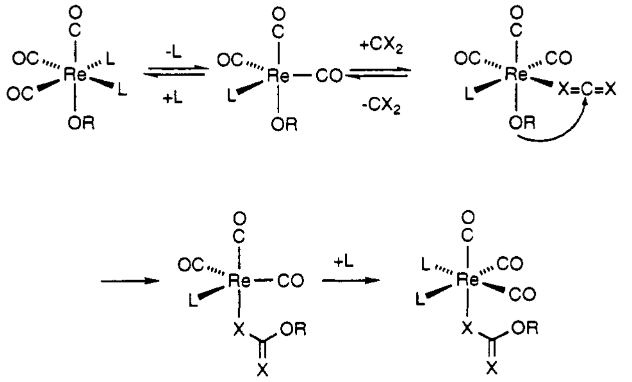
Hydrolysis of the CO_2 insertion product **8b** yields the bridging carbonate complex $(CO)_3(diars)Re(\mu\text{-}CO_3)Re(diars)(CO)_3$. Similar symmetrical bridged carbonates have been formed by the interactions of unsaturated metal hydrides with CO_2.[1,21] Darensbourg and co-workers have shown that $W(CO)_5O(CO)OC_6H_5^-$ undergoes hydrolysis to form the dianionic mononuclear complex $W(CO)_4(CO_3)^{2-}$. The increased susceptibility toward hydrolysis has been observed in several other carbonate and urethanes coordinated to metal centers.[9,27,28]

Certain aryloxide complexes do react with the more electrophilic reagent CS_2. No reactivity was observed for the aryloxide complex bearing the chelating arsine ligand,

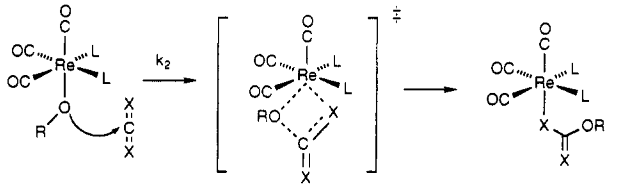
Scheme VII



Scheme VIII



Scheme IX



while isomerization accompanies CS_2 insertion in the bis-PMe_3-substituted system. The kinetic evidence obtained for the reaction of the methoxides with CS_2 strongly suggests that the insertions involve a simple bimolecular reaction, although the linear plots may reflect a failure to reach a saturation rate limit in a stepwise process. One potential stepwise mechanism involves preequilibrium ionization to a form a metal cation/methoxide anion ion pair, followed by nucleophilic attack of the free methoxide on CS_2 or CO_2, and then recoordination of the resulting xanthate or carbonate to the rhenium cation (Scheme VII). A similar ionic mechanism has been postulated for the insertion of CO into the Ir–O bond of an iridium alkoxide derived from Vaska's complex.[29] If this ion pair mechanism were operative, one might expect to see a large solvent effect upon the rate of the reaction.[30] However, only a small solvent effect is observed; k_2 was found to vary only by a factor of 2.6 on going from toluene (ϵ^{31} = 2.44) to acetonitrile (ϵ = 37.5), while the reaction was fastest in THF (ϵ = 7.58). The small effect on the observed rate constant k_2 makes an ionization mechanism seem unlikely.

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Another more complicated mechanism for CS_2 insertion involves initial dative ligand dissociation, or a change in the hapticity of the chelated arsine (Scheme VIII). This would again provide an open site for the CX_2 to coordinate to the rhenium and facilitate insertion into the Re–O bond. However, the PMe_3-substituted complex does not incorporate PMe_3-d_9 or ^{13}CO under conditions in which CO_2 insertion occurs rapidly. These observations are not consistent with a reaction that proceeds via initial ligand dissociation.

We conclude that the CX_2 insertion reactions—and probably the reactions with others electrophiles as well—occur by nucleophilic attack of the coordinated methoxide oxygen directly upon the sp- or sp^2-hybridized carbon of the heterocumulenes (Scheme IX). The small solvent effect suggests that there is little charge separation in the transition state,[32] and so we also propose that the CO_2 oxygen coordinates to Re as the OCH_3 or NHC_6H_5 group is being transferred to the electrophile. For CO_2 insertion to occur, a very nucleophilic atom adjacent to the metal is required. Anionic W(0) alkyl complexes insert CO_2 into the W–R bond, while the corresponding Re(I) alkyls $(CO)_5Re$–R show no reactivity toward CO_2. The neutral rhenium alkyls react with neat CS_2 at 80–90 °C to give the complexes $(CO)_4Re(\eta^2\text{-}S_2CR)$.[33-37] However, little information is available on the mechanisms of these reactions. Similarly, the coordinated aryloxide **1a** or **1b** does not attack CO_2, while the arylamide or methoxide ligands in **2a** or **2b** and **3c** are nucleophilic enough to undergo this reaction. Again the need for a very nucleophilic atom adjacent to the metal center to effect the insertion is shown by the differing reactivities of the related tungsten alkoxide and aryloxide complexes. As previously mentioned, the anionic W(0) system bearing only carbonyl ligands readily inserts CO_2 at low temperatures and pressures. However, if a neutral carbonyl ligand is replaced with a cationic nitrosyl ligand, 70 atm of CO_2 is required for the insertion to occur, even with the more basic methoxide ligand.[38] In both of these complexes the oxygen-bearing ligand is coordinated trans to either CO or NO^+, which are both strong π-acids. It is generally recognized that NO^+ is a better π-acid than the isoelectronic CO.[39] This enhanced trans π-acidity deactivates the nucleophilicity of the oxygen ligand just as changing from methoxide to aryloxide deactivates the neutral rhenium complexes toward CO_2 insertion. This effect can be overcome by replacement of coordinated oxygen by nitrogen.

Summary. Rhenium alkoxide, aryloxide, and arylamide complexes were found to react with activated organic carbonyl compounds such as acid halides, esters, and anhydrides. This results in cleavage of the Re–O bond with the acid halides and esters, or insertion of the anhydride into the Re–O bond. These complexes also react with CO_2 and CS_2, but the reaction is highly dependent upon the nature of the heteroatom substituent. The presence of a π-accepting phenyl group on the oxygen adjacent to the rhenium shuts down the reaction with CO_2 while insertion occurs quite rapidly with the methoxide complexes. In contrast, the arylamido complex does insert CO_2, though not as readily as the alkoxide complexes. These results suggest that complexes of the sort $(CO)_3(L)_2ReNHR$ should exhibit even greater reactivity with CO_2.

Experimental Section

General Methods. 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. 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, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ spectra were recorded on a Bruker AMX spectrometer at 400, 100, or 162 MHz, respectively. Assignments were made using standard DEPT pulse sequences. For second-order spin systems, the value listed is the sum of the 1-bond and n-bond (n = 2, 3, or 4) coupling constants in the spin system. For the PMe_3 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. Gas chromatographic analyses were performed using a Hewlett-Packard Model 3393A electronic integrator employing a J and W fused silica column with a DB-5 liquid phase. Elemental analyses were obtained from the UCB Microanalytical Laboratory.

Benzene, toluene, Et_2O, pentane, hexanes, and THF were distilled from sodium/benzophenone. Benzene-d_6, toluene-d_8, and THF-d_8 were vacuum transferred from sodium/benzophenone. Acetyl chloride was vacuum transferred from PCl_5. The esters $CH_3C_6H_4O_2CCH_3$ and $O_2NC_6H_4O_2CCH_3$ were prepared from the corresponding phenols and acetyl chloride in the presence of triethylamine. Maleic anhydride and succinic anhydride were obtained from Aldrich and recrystallized from chloroform and acetone respectively. CO_2 (Matheson, "bone-dry") and $^{13}CO_2$ (Cambridge Isotopes) were used as received. CS_2 was vacuum transferred from P_2O_5. The complexes **1a**,**b**, **2a**,**b**, and **3c** were prepared as described elsewhere.[40] Unless otherwise noted, all other reagents were 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 with 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.[41]

Kinetics. All kinetic experiments were performed on a Hewlett-Packard 8450A UV–vis spectrophotometer interfaced with a 82901M flexible disk drive and equipped with a 89100A temperature controller. Standard solutions of **2b** and CS_2 were prepared in the appropriate solvent in the drybox and stored in the drybox freezer and stored at −40 °C. For each run, 1 mL of the solution of **2b** was transferred to a 10-mL volumetric flask, and then an appropriate aliquot of the CS_2 solution was added using a volumetric pipet. The mixture was then diluted to 10 mL and shaken, and a UV–vis cell equipped with a Kontes vacuum stopcock charged with the reaction mixture and the stopcock sealed. The cells were removed from the drybox and placed into the temperature-controlled cells. Spectra were taken at regular intervals after the solutions had been allowed to reach the desired temperatures. The cuvette was equipped with a magnetic stir bar, and a flow of nitrogen was maintained over the cell during the experiment to avoid condensation on the cell windows.

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The reactions were monitored by observed the increase in absorbance at 410 nm due to formation of the product (CO)$_3$(diars)ReS(CS)OCH$_3$. In all cases reactions were observed for at least 3 half-lives. Plots of absorbance vs time were fit using the NEGINF program by Dr. Eric Wasserman of these laboratories to the increasing exponential function $y = A_1(1 - e(-A_2x)) + A_3$, 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 goodness of the data was then checked by plotting the ln ($A_\infty - A$) vs time.

***fac*-(CO)$_3$(diars)ReO(CO)CHCHCO$_2$CH$_3$ (5b).** In the drybox a 50-mL Schlenk tube was charged with 58 mg (0.10 mmol) of (CO)$_3$(diars)ReOCH$_3$ and 13 mg (0.13 mmol, 1.3 equiv) of maleic anhydride. The flask was stoppered and removed from the drybox, and then 5 mL of CH$_2$Cl$_2$ was added via syringe. The resulting mixture was allowed to stir for 12 h at room temperature. The mixture was then transferred to a round-bottom flask, and the solvent was removed on a rotary evaporator (the product is air and moisture stable). The resultant white solid was dissolved in a minimum amount of CH$_2$Cl$_2$, and the product was isolated as large clear crystals after the solution was allowed to slowly evaporate to a volume of ~1 mL at room temperature (49 mg, 71.5%). Concentration using a rotary evaporator and crystallization as described above yielded an additional 15 mg of **5b** (94% combined, 0.92 mmol). ^{1}H NMR (CDCl$_3$): δ 7.77 (m, 2 H, diars-CH), 7.57 (m, 2 H, diars-CH), 6.13 (AB quartet, J_{AB} = 12.0, 1 H, CH), 5.69 (AB quartet, J_{AB} = 12.0, 1 H, CH), 3.58 (s, 3 H, CO$_2$CH_3), 1.78 (s, 6 H, diars-CH_3), 1.66 (s, 6 H, diars-CH_3). ^{13}C{^{1}H} NMR (CDCl$_3$) δ 192.6 (CO cis to O$_2$CCHCHCO$_2$CH$_3$), 191.7 (CO trans to O$_2$CCHCHCO$_2$CH$_3$), 171.3 (CO$_2$R), 166.1 (CO$_2$R), 140.2 (diars-ipso), 136.1 (CH), 131.1 (diars-CH), 129.7 (diars-CH), 121.9 (CH), 51.4 (CO$_2$$CH_3$), 14.1 (diars-$CH_3$), 11.7 (diars-$CH_3$). IR (KBr) ν_{CO} = 2017 (s), 1933 (s), 1887 (s) cm^{-1}; $\nu_{\mathrm{C=O}}$ 1734 (m), 1624 (m) cm^{-1}. Anal. Calcd for C$_{18}$H$_{21}$As$_2$O$_7$Re: C, 31.50; H, 3.09. Found: C, 31.54; H, 2.70.

***fac*-(CO)$_3$(diars)ReO(CO)CH$_2$CH$_2$CO$_2$CH$_3$ (6b).** In the drybox, a flask was charged with 60.0 mg (0.102 mmol) of (CO)$_3$(diars)ReOCH$_3$ and 3 mL of C$_6$H$_6$. To this solution was added via pipet a solution of 10.2 mg (0.102 mmol, 1.0 equiv) of succinic anhydride in 1 mL of C$_6$H$_6$. The resulting reaction mixture was allowed to stir for 5 h at room temperature. The flask was then removed from the drybox, and the colorless solution filtered through a bed of Celite on a sintered glass frit. The benzene was then removed using a rotary evaporator and the residue dissolved in Et$_2$O. Slow evaporation of this solution to a volume of ~1 mL at room temperature yielded 65 mg (93%) of colorless crystals. ^{1}H NMR (CDCl$_3$): δ 7.77 (m, 2 H, diars-CH), 7.57 (m, 2 H, diars-CH), 3.48 (s, 3 H, CO$_2$CH_3), 2.38 (m, 2 H, CH_2), 2.31 (m, 2 H, CH_2), 1.78 (s, 6 H, diars-CH_3), 1.62 (s, 6 H, diars-CH_3). ^{13}C{^{1}H} NMR (CDCl$_3$) δ 192.9 (CO cis to O$_2$CCH$_2$CH$_2$CO$_2$CH$_3$), 191.8 (CO trans to O$_2$CCH$_2$CH$_2$CO$_2$CH$_3$), 177.1 (CO$_2$R), 173.8 (CO$_2$R), 140.1 (diars-ipso), 131.2 (diars-CH), 129.9 (diars-CH), 51.2 (CO$_2$$CH_3$), 30.6 ($CH_2$) 30.3 ($CH_2$), 13.8 (diars-$CH_3$), 11.0 (diars-$CH_3$). IR (KBr) ν_{CO} 2026.5 (sh), 2017.6 (s), 1941.5 (s), 1886.6 (s), 1845.5 (sh) cm^{-1}; $\nu_{\mathrm{C=O}}$ 1737.5, 1617.0 cm^{-1}. Anal. Calcd for C$_{18}$H$_{23}$As$_2$O$_7$Re: C, 31.45; H, 3.37. Found: C, 31.12; H, 3.38.

***trans,mer*-(CO)$_3$(PMe$_3$)$_2$ReS(CS)OC$_6$H$_4$CH$_3$ (7a).** In the drybox, a bomb was charged with 52 mg (0.094 mmol) of (CO)$_3$(PMe$_3$)$_2$ReOC$_6$H$_4$CH$_3$ in 4 mL of C$_6$H$_6$. It was removed from the drybox, and 1.87 mmol (20 equiv) of CS$_2$ was condensed into the bomb. It was then stoppered and heated at 140 °C for 7 days, over which time the reaction mixture changed from colorless to deep yellow. The bomb was allowed to cool to room temperature and returned to the drybox. An aliquot removed and examined by ^{31}P{^{1}H} NMR showed no remaining starting cresolate. The C$_6$H$_6$ and CS$_2$ were then removed using a vacuum pump, leaving an orange powder. The powder was dissolved in toluene (0.5 mL), and pentane vapor was allowed to diffuse into the toluene solution at room temperature. After 4 days orange crystals had formed. They were washed with pentane and dried to yield 31 mg (0.049 mmol, 52%) of analytically pure **7a**. ^{1}H NMR (C$_6$D$_6$) δ 7.23 (d, J_{AB} = 7.01, 2 H, OC$_6$$H_4CH_3$), 6.99 (d, J_{AB} = 7.01, 2 H, OC$_6$$H_4CH_3$), 2.36 (s, 3 H, OC$_6H_4CH_3$), 1.59 (virtual t, "$J_{PH}$" = 8.42, 18 H, P(C$H_3$). ^{13}C{^{1}H} NMR (C$_6D_6$) δ 228.3 (t, J_{PC} = 6.92, S(C=S)), 198.4 (b, CO), 150.5 (s, OC$_6$H$_4$CH$_3$-ipso bonded to oxygen), 130.4 (s, OC$_6$H$_4$CH$_3$-ipso bonded to CH$_3$), 130.4 (s, OC$_6$H$_4$CH$_3$–CH), 121.8 (s, OC$_6$H$_4$CH$_3$–CH), 20.7 (s, OC$_6$H$_4$$CH_3$), 17.3 (virtual t, $^1J_{PC} + {}^3J_{PC}$ = 18.3, P(CH$_3$)$_3$). ^{31}P{^{1}H} (C$_6$D$_6$) δ −29.5. IR (CD$_2$Cl$_2$ difference) ν_{CO} 1918.8, 1884.4 cm^{-1}; $\nu_{\mathrm{C=S}}$ 1422.2 cm^{-1}. Anal. Calcd for C$_{17}$H$_{25}$O$_4$P$_2$ReS$_2$: C, 33.71; H, 4.16. Found: C, 33.67; H, 3.80.

***fac*-(CO)$_3$(PMe$_3$)$_2$ReO(CO)OCH$_3$ (8a).** In the drybox, a bomb was charged with 55.2 mg (0.122 mmol) of **2a** and 2 mL of C$_6$H$_6$. The bomb was stoppered, removed from the box and attached to a vacuum line equipped with a MKS baratron gauge. CO$_2$ (1.22 mmol, 10 equiv) was condensed into the reaction vessel at −196 °C. As the solution thawed, no visible color change occurred. After standing at room temperature for 0.5 h, the bomb was attached to a vacuum line, and the volatile materials were removed. The bomb was taken into the drybox, and the resulting white residue collected on a frit and washed with hexane to yield 57 mg (0.109 mmol, 89%). ^{1}H NMR (CDCl$_3$) δ 3.57 (s, 3 H, O(CO)OCH_3), 1.58 (A$_9$A$_9'$XX′, "J_{PH}" = 7.43, 18 H). ^{13}C{^{1}H} NMR (CDCl$_3$) δ 193.8 (t, J_{PC} = 7.1, CO trans to O(CO)OCH$_3$), 191.7 (AXX′, $^1J_{PC} + {}^3J_{PC}$ = 51.7, CO cis to O(CO)OCH$_3$), 159.8 (t, J_{PC} = 2.75, O(CO)OCH$_3$), 53.9 (s, O(CO)OCH$_3$), 17.11 (AXX′, $^1J_{PC} + {}^3J_{PC}$ = 33.0, P(CH$_3$)$_3$). IR (KBr) ν_{CO} 2026.6 (s), 1977.8 (s), 1922.8 (sh) 1904.6 (s) cm^{-1}; $\nu_{\mathrm{C=O}}$ 1670.0 cm^{-1}. Anal. Calcd for C$_{11}$H$_{21}$O$_6$P$_2$Re: C, 28.63, H, 3.26. Found: C, 28.66, H, 2.96.

***fac*-(CO)$_3$(diars)ReO(CO)OCH$_3$ (8b).** In the drybox, a bomb was charged with 315 mg (0.547 mmol) of (CO)$_3$(diars)ReOCH$_3$ and 40 mL of C$_6$H$_6$. It was taken out of the box and attached to a vacuum line equipped with a MKS Baratron gauge. CO$_2$ (2.68 mmol, 5 equiv) was condensed into the bomb at −196 °C. As the bomb was allowed to thaw, the pale yellow solution turned colorless and a white precipitate formed. The bomb was heated to 46 °C until the precipitate had dissolved. This step was taken to ensure that methoxide complex had all dissolved and reacted with the CO$_2$. The colorless solution was then refrozen in liquid nitrogen and attached to a vacuum line, and the benzene and CO$_2$ were removed to yield a white powder. The bomb was then taken into the drybox and the white residue slurried in hexanes and collected on a sintered glass frit to yield 328 mg of (CO)$_3$(diars)ReO(CO)OCH$_3$. An analytically pure sample was prepared by dissolving 50 mg of **8b** in 1 mL of toluene, layering it with 10 mL of pentane, and cooling to −40 °C for 7 days. The resulting white powder was collected and dried to yield 51 mg (95%) of analytically pure **8b**. ^{1}H NMR (CDCl$_3$) 7.77 (m, 2 H, diars-CH), 7.58 (m, 2 H, diars-CH), 3.47 (s, 3 H, O(CO)OCH_3), 1.81 (s, 6 H, diars-CH_3), 1.66 (s, 6 H, diars-CH_3). ^{13}C{^{1}H} NMR (CDCl$_3$) δ 192.7 (CO cis to O(CO)OCH$_3$), 191.4 (CO trans to O(CO)OCH$_3$), 159.6 (O(CO)OCH$_3$), 139.8 (diars-ipso), 131.4 (diars-CH), 130.0 (diars-CH), 53.9 (O(CO)OCH_3), 13.5 (diars-CH$_3$), 10.2 (diars-CH$_3$). IR (KBr) ν_{CO} 2002, 1950, 1905 cm^{-1}, $\nu_{\mathrm{C=O}}$ 1670 (m) cm^{-1}. Anal. Calcd for C$_{15}$H$_{19}$As$_2$O$_6$Re: C, 28.53; H, 3.03. Found: C, 28.32; H, 2.73.

***fac*-(CO)$_3$(PMe$_3$)$_2$ReS(CS)OCH$_3$ (9a).** In the drybox, a bomb was charged with 45 mg (0.100 mmole) of **2a** and 3 mL of C$_6$H$_6$. It was stoppered, removed from the box, attached to vacuum line equipped with a MKS baratron gauge, and frozen in liquid nitrogen. CS$_2$ (1.00 mmol, 10 equiv) was condensed into the reaction mixture. As the benzene thawed, the initially colorless solution turned a very pale yellow. After standing at room temperature for 1 h, the bomb was attached to a vacuum line, and the volatile materials removed. The bomb was then taken into the drybox, and the pale yellow solid was slurried in hexanes, collected on a frit, and washed with hexanes (2 mL) and cold Et$_2$O (2 mL). Residual solvent was then removed using a vacuum line to yield 47 mg (0.089 mmol, 89%) of **9a**. ^{1}H NMR (C$_6$D$_6$) δ 4.04 (s, 3 H, S(CS)OCH_3), 0.995 (m, 18 H, P(CH_3)$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$) 223.2 (t, J_{PC} = 6.0, S(CS)OCH$_3$), 192.4 (b, CO), 191.8 (b, CO), 59.6 (s, S(CS)OCH$_3$), 17.17 (AXX′, $^1J_{PC} + {}^3J_{PC}$ = 62.7, P(CH$_3$)$_3$. ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ −44.2. IR (KBr) ν_{CO} 2019.1 (s), 1949.7 (m), 1931.2 (s), 1894.0 (s), 1859.2 (sh); $\nu_{\mathrm{C=S}}$ 1425.3. Anal. Calcd for C$_{11}$H$_{21}$O$_4$P$_2$ReS$_2$: C, 24.95, H, 4.0. Found: C, 25.16, H, 3.53.

***fac*-(CO)$_3$(diars)ReS(CS)OCH$_3$ (9b).** In the drybox a bomb was charged with 59 mg (0.10 mmol) of (CO)$_3$(diars)ReOCH$_3$ and 10 mL of C$_6$H$_6$. It was removed from the drybox, attached to a vacuum line equipped with a MKS baratron gauge, and frozen in liquid nitrogen. CS$_2$ (2.0 mmol, 20 equiv) was condensed into the bomb. As the solution thawed, its color changed from pale yellow to a more intense shade of yellow. The reaction was allowed to stand at room temperature overnight. The bomb was then attached to a vacuum line, and the volatile materials were removed. The remaining yellow solid was taken into the drybox, slurried in hexanes, and collected on a sintered glass frit to yield 65 mg (98%) of analytically pure **9b**. ^{1}H NMR ($CDCl_3$) δ 7.73 (m, 2 H, diars-CH), 7.57 (m, 2 H, diars-CH), 4.02 (s, 3 H, S-(CS)OCH_3), 1.78 (s, 6 H, diars-CH_3), 1.75 (s, 6 H, diars-CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$) 223.3 (S(CS)OCH_3), 191.6 (br s, CO cis to S(CS)OCH_3), 189.7 (br s, CO trans to S(CS)OCH_3), 139.4 (diars-ipso), 131.5 (diars-CH), 129.9 (diars-CH), 59.6 (S(CS)OCH_3), 15.1 (diars-CH_3), 9.4 (diars-CH_3). IR (KBr) ν_{CO} 2023.8, 1936.6, 1911.5 cm^{-1}, $\nu_{C=S}$ 1419.0 cm^{-1}. Anal. Calcd for $C_{15}H_{19}As_2O_4ReS_2$: C, 27.15; H, 2.89. Found: C, 27.50; H, 2.70.

***fac*-(CO)$_3$(depe)ReO(CO)NHC$_6$H$_5$ (10c).** In the drybox, a bomb was charged with 37 mg (0.0604 mmol) of **3c** and 3 mL of C_6H_6. It was closed, removed from the box, and attached to a vacuum line equipped with a Baratron gauge. Carbon dioxide (0.302 mmol, 5 equiv) was condensed into the bomb at −196 °C. The contents were thawed, resulting in a yellow solution of the anilide **3c**. After 1 h at room temperature, the color of the solution was noticeably lighter. After 8 h, the solution was colorless. The bomb was attached to a vacuum line, and the volatile material removed in vacuo, leaving a white solid. This was returned to the drybox and washed with Et_2O. The compound was purified by slow diffusion of Et_2O vapor into a concentrated THF solution of **10c** at −40 °C. After 3 days, white crystals had formed. The residual solvent was removed by exposing the sample to high vacuum for 12 h, yielding 23 mg (0.038 mmol, 62 %) of **10c**. ^{1}H NMR (THF-d_8) δ 7.38 (d, 2 H, "J" = 7.94, O(CO)NHC$_6$H$_5$-ortho), 7.16 (br s, 1 H, O(CO)NHC$_6$H$_5$), 7.05 (t, 2 H, "J" = 7.45, O-(CO)NHC$_6$H$_5$-meta), 6.69 (t, 1 H, "J" = 7.31, O(CO)NHC$_6$H$_5$-para), 2.09–1.80 (m, 12 H, depe-CH_2's), 1.22–1.08 (m, 12 H, depe-CH_3's). ^{13}C{^{1}H} NMR (THF-d_8) δ 195.29 (d of d, J_{PcisC} = 9.5 Hz, $J_{PtransC}$ = 51.7, CO cis to O(CO)NHC$_6$H$_5$), 194.33 (t, J_{PC} = 8.82, CO trans to O(CO)NHC$_6$H$_5$), 159.45 (br s, O(CO)NHC$_6$H$_5$), 143.85 (br s, O(CO)NHC$_6$H$_5$-ipso), 129.03 (O(CO)NHC$_6$H$_5$-para), 120.2 (O(CO)NHC$_6$H$_5$-arom), 117.67 (O(CO)NHC$_6$H$_5$-arom), 24.15 (AXX′, $^1J_{PC} + {}^2J_{PC}$ = 41.14, depe-CH$_2$), 19.72 (AXX′, $^1J_{PC} + {}^4J_{PC}$ = 30.11, depe-CH$_2$CH$_3$), 15.40 (AXX′, $^1J_{PC} + {}^4J_{PC}$ = 25.74, depe-CH$_2$CH$_3$), 8.66 (depe-CH$_3$), 8.11 (depe-CH$_3$). ^{31}P{^{1}H} NMR (THF-d_8) δ 39.37. IR (KBr) ν_{CO} = 2021, 1939, 1884 cm^{-1}, $\nu_{C=O}$ 1594 cm^{-1}. Anal. Calcd for $C_{20}H_{30}NO_5P_2Re$: C, 39.21; H, 4.94; N, 2.29. Found: C, 39.02; H, 4.78; N, 2.02.

(CO)$_3$(diars)Re(μ-CO$_3$)Re(diars)(CO)$_3$ (11b). In the drybox, an NMR tube was charged with 25.6 mg (0.0405 mmol) of **8b** and 0.5 mL of THF-d_8. The tube was then fitted with a gum rubber septum and removed from the box. Distilled water (2 μL, 0.111 mmol, 2.75 equiv) was added via syringe and the top of the tube wrapped with parafilm. It was heated at 46 °C and periodically monitored by ^{1}H NMR spectrometry. After 48 h the ^{1}H NMR spectrum showed the disappearance of the methoxide resonance (δ 3.29 ppm) and formation of methanol (δ 3.25 ppm). The tube was then taken into the drybox, and the THF removed in vacuo. The white residue was dissolved in CH_2Cl_2 and filtered through a plug of glass wool. The CH_2Cl_2 was removed in vacuo and the clear glassy residue triturated with a 1:1 mixture of pentane/Et_2O to yield a white powder. Residual solvent was removed under vacuum to yield 15 mg of **11b** as a white powder (0.0127 mmol, 63%). ^{1}H NMR (THF-d_8) δ 7.83 (m, 2 H, diars-CH), 7.50 (m, 2 H, diars-CH), 1.65 (s, 6 H, diars-CH_3), 1.54 (s, 6 H, diars-CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 192.4 (b, CO), 166.6 (μ-CO$_3$), 140.9 (diars-ipso), 130.5 (diars-CH), 129.5 (diars-CH), 14.0 (diars-CH$_3$), 10.9 (diars-CH$_3$). The ^{13}C{^{1}H} NMR resonance of one carbonyl ligand was not observed. IR (KBr) ν_{CO} 2022, 1928, 1875 cm^{-1}, $\nu_{C=O}$ 1533 cm^{-1}. Anal. Calcd for $C_{27}H_{32}As_4O_9Re_2$: C, 27.66; H, 2.75. Found: C, 27.87; H, 2.91.

X-ray Crystal Structure Determination of 11b. Colorless crystals of compound **11b** were obtained from a toluene/pentane solution at −40 °C. A crystal was chosen and mounted on glass fibers using polycyanoacrylate cement. The crystal used for data collection was then transferred to an Enraf-Nonius CAD-4 diffractometer and centered in the beam. Automatic peak search and indexing procedures yielded the reduced triclinic primitive cell. The final cell parameters and specific data collection parameters are given in Table I.

The 6021 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. No correction for crystal decomposition was necessary. An empirical absorption correction based on the azimuthal scan data was applied: T_{max} = 1.000, T_{min} = 0.530. Inspection of the systematic absences indicated space group $P(\bar{1})$. The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques.

The final residuals for 255 variables refined against the 5163 data for which $F^2 > 3\sigma(F^2)$ were R = 3.4%, wR = 4.5%, and GOF = 2.12. The R value for all 6021 reflections was 4.2%. 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 0.03. The analytical forms of the of the scattering factor tables for the neutral atoms were used, and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion. The positional and thermal parameters of the refined atoms are available as supplementary material (see paragraph at end of paper).

Reactions with CH$_3$COCl. In the drybox, 10 mg (0.011 mmol) of (CO)$_3$(PMe$_3$)$_2$ReOC$_6$H$_4$CH$_3$ was dissolved in 0.5 mL of C_6D_6. Tetramethylsilane (~1 μL) was added an internal standard. An NMR spectrum was taken to determine the ratio of **1a** to the standard. The tube was taken into the drybox and fitted to a Cajon adapter attached to a Kontes vacuum stopcock. It was attached to a vacuum line, and acetyl chloride (0.011 mmol, 1.01 equiv) was condensed into the reaction mixture. An NMR spectrum was taken after 5 min at room temperature which showed complete conversion of **1a** to (CO)$_3$(PMe$_3$)$_2$ReCl (**4a**, 96%) and tolyl acetate (90%). The rhenium chloride was further identified by comparison of its ^{31}P{^{1}H} NMR chemical shift with that of an authentic sample. The tube was cracked open, and the C_6D_6 removed on a rotary evaporator without the use of a heating bath. The white residue was extracted into pentane and the solution examined by GC, which showed formation of tolyl acetate (75% yield by integration against decane which was added as an internal standard) by comparison of the retention time with that of an authentic sample.

Alkoxide Transesterification Reactions. In the drybox an NMR tube was charged with 7.5 mg (0.012 mmol) of **2b** and 0.5 mL of C_6D_6. Tolyl acetate (2.0 μL, 0.014 mmol, 1.1 equiv) was added via syringe. The tube was allowed to stand at room temperature for 12 h. Examination of the contents by ^{1}H NMR showed conversion to **1b** and methyl acetate. When **2b** was allowed to react with $O_2NC_6H_4O_2CCH_3$, an immediate color change from pale yellow to a bright orange-yellow was observed upon mixing. ^{1}H NMR analysis showed complete conversion to (CO)$_3$(diars)ReOC$_6$H$_4$NO$_2$ and methyl acetate.

Aryloxide Transesterification Reactions. In the drybox, an NMR tube was charged with 9.5 mg (0.014 mmol) of **1b**, ~1 μL of tetramethylsilane, and ~0.5 mL of $CDCl_3$. The tube was stoppered and a spectrum taken to determine the ratio of **1b** to the internal standard. It was returned to the box, and a solution of $O_2NC_6H_4O_2CCH_3$ (3 mg, 0.017 mmol) in ~0.1 mL of $CDCl_3$ was added via pipet. A bright yellow color develops on mixing. After 24 h, at room temperature, ^{1}H NMR analysis showed 100% conversion of **1b** to (CO)$_3$(diars)ReOC$_6$H$_4$NO$_2$. ^{1}H NMR ($CDCl_3$) δ 7.95 (d, 2 H, J = 9.3, OC$_6$H$_4$NO$_2$–CH), 7.87 (m, 2 H, diars-CH), 7.67 (m, 2 H, diars-CH), 6.34 (d, 2 H, J = 9.2, OC$_6$H$_4$NO$_2$), 1.84 (s, 6 H, diars-CH_3), 1.55 (s, 6 H, diars-CH_3). Lit.: ($CDCl_3$) δ 7.95 (d, 2 H, J = 9.3, OC$_6$H$_4$NO$_2$–CH), 7.87 (m, 2 H, diars-CH), 7.67 (m, 2 H, diars-CH), 6.34 (d, 2 H, J = 9.2, OC$_6$H$_4$NO$_2$), 1.84 (s, 6 H, diars-CH_3), 1.55 (s, 6 H, diars-CH_3).[15]

Exchange Reactions of 8b with ^{13}CO$_2$. In the drybox, an NMR tube was charged with 9.8 mg (0.0141 mmole) of **8b** in C_6D_6. The tube was fitted to a Cajon adaptor attached to a Kontes vacuum stopcock. This was in turn attached to a vacuum line equipped with an MKS Baratron gauge. ^{13}CO$_2$ (0.211 mmol, 15 equiv) was condensed into the tube at −196 °C, and the tube flame sealed under vacuum. When the tube was thawed, the carbonate had precipitated out of solution. The tube was heated briefly at 46 °C in order to dissolve the compound. After standing for 2 h at room temperature, ^{13}C{^{1}H} NMR analysis showed a resonance at 160.4 ppm, characteristic of the Re–O(CO)OCH$_3$ resonance, and free CO$_2$ (120.4 ppm). ^{1}H NMR analysis showed two methoxide resonances at δ 3.54 (s) and 3.53 (d, $^3J_{CH}$ = 4.2) in a

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~4:1 ratio. After standing overnight at room temperature, similar NMR analysis showed complete disappearance of the downfield resonance.

Exchange Reactions of 8b with CS_2. In the drybox, an NMR tube was charged with 9.8 mg (0.016 mmol) of **8b** in C_6D_6. After fitting the tube with a Cajon adaptor attached to a Kontes vacuum stopcock, it was attached to a vacuum line equipped with an MKS Baratron gauge. CS_2 (0.078 mmol, 5 equiv) was condensed in at −196 °C, and the tube flame sealed under vacuum. Upon thawing, the carbonate precipitated out of solution. Brief heating at 46 °C was necessary to dissolve the compound. After standing for 2 h at room temperature, ^{1}H NMR analysis showed two methoxide resonances at δ 4.56 (**9b**) and 3.54 (**8b**) in a ~1:7 ratio. After standing overnight at room temperature, similar NMR analysis showed growth of the downfield methoxide resonance, now in a ~1:3 ratio. Complete conversion to **9b** was observed after 5 days at room temperature. The yield of **9b** was 88% by integration against the C_6D_5H resonance.

Re-formation of 2b from 8b. In the drybox, a 100-mL Schlenk flask was charged with 30 mg (0.048 mmol) of $(CO)_3$(diars)ReO(CO)OCH_3 and 20 mL of toluene. The flask was removed from the box and attached to a Schlenk line. A suba seal was placed in the neck of the flask, and N_2 gas admitted through a 22-gauge needle. The flask was vented with a 24-gauge needle placed next to the N_2 inlet. N_2 gas was bubbled through the solution. After 2 days, 10 mL of toluene was added via syringe to compensate for evaporation. After 5 days, the toluene was removed in vacuo, and the flask taken into the drybox. The pale yellow residue dissolved in 4 mL of benzene and filtered through a plug of Celite. The benzene was removed to yield 19 mg (0.033 mmol, 70%) of the methoxide complex **2b**. ^{1}H NMR (C_6D_6) δ 7.01 (m, 4 H, diars-C*H*), 4.28 (s, 3 H, OCH_3), 1.29 (s, 6 H, diars-CH_3), 1.12 (s, 6 H, diars-CH_3). Lit.:[40] ^{1}H NMR (C_6D_6) δ 7.01 (m, 4 H, diars-C*H*), 4.29 (s, 3 H, OCH_3), 1.29 (s, 6 H, diars-CH_3), 1.12 (s, 6 H, diars-CH_3).

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Supplementary Material Available: Tables of positional parameters, anisotropic thermal parameters, and root-mean-amplitudes of **11b** (8 pages). Ordering information is given on any current masthead page.

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Hydrodimetalation of Alkynes and Diynes: Diiron Complexes of μ-η^1:η^2-Alkenyl Ligands with Pendant Alkynes: Crystal and Molecular Structure of $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu_2\text{-}\eta^1{:}\eta^2\text{-}CH{=}CH_2)$ and $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu_2\text{-}\eta^1{:}\eta^2\text{-}C(C{\equiv}CMe){=}CHMe)$

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The reactions of alkynes and diynes with $HFe_2(CO)_7(\mu\text{-}PPh_2)$ gives the bridging alkenyl complexes $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}R^2C{=}CHR^1)$. In the case of alkynes $R^1C{\equiv}CR^2$ (R^2 = TMS, H, Ph, OEt, CH_2Cl, and R^1 = H, or $R^2 = R^1$ = Ph) hydrodimetalation affords a single major isomer in which the stereochemistry of the substituents on the original unsaturated organic substrate is cis. There is also a high regiospecificity of reaction leading to gem dihydrides in the final products. The X-ray structure of the parent vinyl complex $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu_2\text{-}\eta^1{:}\eta^2\text{-}CH{=}CH_2)$ (**5**) has been determined. Crystals of **5** are monoclinic, space group $P2_1/c$, with a = 14.695 (4) Å, b = 11.410 (2) Å, c = 12.163 (3) Å, β = 92.90 (2) Å, V = 2037.5 (8) Å^3, and Z = 4. Refinement converged at R = 0.028 and R_w = 0.027 on the basis of 2902 observed reflections. A similar procedure was used to prepare the first diiron alkenyl complexes $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}R^2C{=}CHR^1)$ [R^1 = Ph, H, Me and R^2 = C≡CPh, $C_6H_4C{\equiv}CH$, C≡CMe] containing the pendant unsaturated functionalities, C≡CR. The structure of $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}C(C{\equiv}CMe){=}CHMe)$ has been determined by single-crystal X-ray diffraction studies. This compound crystallises in the monoclinic space group $P2_1/n$ with a = 10.966 (2) Å, b = 13.082 (3) Å, c = 16.180 (2) Å, β = 90.35 (1)°, V = 2320.6 (8) Å^3, and Z = 4. Refinement converged at R = 0.028 and R_w = 0.033 on the basis of 4397 observed reflections. The molecule $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}C(C{\equiv}CMe){=}CHMe)$ contains an yne–enyl ligand resulting from regiospecific hydrodimetalation at the diyne substrate (MeC≡CC≡CMe). In the major isomer the pendant unsaturated moiety is found on C_α. The variable temperature $^{13}C\{^1H\}$ NMR spectra of **5** revealed dynamic behavior involving three independent processes: two low-energy trigonal rotations of vastly disparate energies, and a much higher energy process involving equilibration of the two nonequivalent tricarbonyl iron sites.

Introduction

Numerous synthetic approaches exist for the preparation of σ- and σ–π alkenyl complexes including oxidative addition of a C–H bond of an alkene,[1] decarbonylation of an appropriate acyl cluster,[2] protonation of anionic acetylene derivatives,[3] reaction of μ-alkylidyne complexes with diazo compounds[4] or 1,2-disubstituted alkenes,[5] reaction of a

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