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Rhenium 2-Oxoalkyl (Enolate) Complexes: Synthesis and Carbon–Carbon Bond-Forming Reactions with Nitriles

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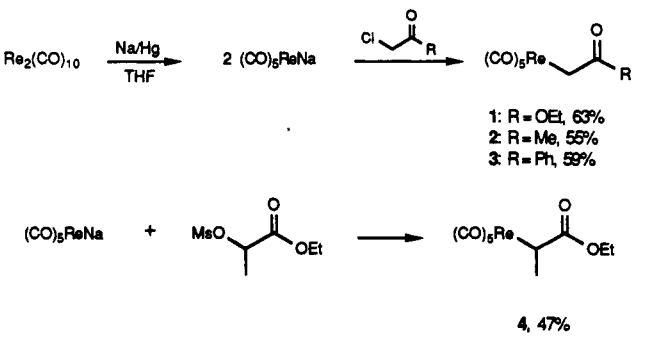
The (2-oxoalkyl)rhenium complexes (rhenium enolates) $(CO)_5ReCH_2COR^1$ (R^1 = OEt, Me, Ph, **1–3**) can be prepared on a multigram scale by alkylation of $(CO)_5ReNa$ with $ClCH_2COR^1$. The secondary enolate $(CO)_5ReCH(Me)CO_2Et$ (**4**) can also be prepared in a similar fashion with use of $MsOCH(Me)CO_2Et$ (Ms = CH_3SO_2–). The mono(phosphine) enolates *cis*-$(Ph_3P)(CO)_4ReCH_2R^2$ (R^2 = CO_2Et, CO_2Bu^t, $CONEt_2$, COMe, COPh, CN, **8–13**) are prepared in high yield via alkylation of $(Ph_3P)(CO)_4ReNa$ with $ClCH_2R^2$. Synthesis of the secondary enolate *cis*-$(Ph_3P)(CO)_4ReCH(Me)CO_2Et$ (**14**) is accomplished in 75% yield by alkylation with $TfOCH(Me)CO_2Et$ (Tf = CF_3SO_2–). Acidolysis of **9** with CF_3CO_2H gives the carboxylic acid *cis*-$(Ph_3P)(CO)_4ReCH_2CO_2H$ (**17**). Heating **1** and 1,2-bis(diphenylphosphino)ethane (dppe) at 130 °C gives *fac*-$(dppe)(CO)_3ReCH_2CO_2Et$ (**18**) in 86% yield. The chelating phosphine complex is substitutionally inert under forcing thermal and photochemical conditions. Reaction of **1** and **4** with excess Ph_3P in R^4CN at 120 °C produces the nitrile insertion complexes *trans*-$(Ph_3P)_2(CO)_2ReNHC(R^4)C(R^3)CO(OEt)$ (R^3 = H, R^4 = Me, Et, Pr^i, Ph, **19–22**; R^3 = Me, R^4 = Et, **23**). The insertion is proposed to occur via the coordinated nitrile complexes *fac*-$(R^4CN)(Ph_3P)(CO)_3ReCH(R^3)CO_2Et$ (**27**). Nitrile complex **27** (R^3 = H, R^4 = Me) can be prepared independently by reaction of **8** with trimethylamine *N*-oxide in CH_3CN; heating **27** in benzene at 80 °C yields *fac*-$(Ph_3P)(CO)_3ReNHC(Me)CHCO(OEt)$ (**28**), which is converted to **19** with Ph_3P at 80 °C. Kinetic studies of the nitrile insertion reaction revealed a weak linear dependence of the rate constant of the reaction on the concentration of added CH_3CN in benzene; we believe this to be a medium effect. Other nitrile complexes *fac*-$(MeCN)(Ph_3P)(CO)_3ReCH(R^2)(R^3)$ (R^2 = CN, R^3 = H, **35**; R^2 = CO_2Et, R^3 = H, **36**) were also prepared in high yield by the reaction of **13** and **14** with Me_3NO in CH_3CN. When treated under identical conditions, the amide enolate **10** does not afford a nitrile complex; the amide oxygen intramolecularly coordinates to rhenium to give *fac*-$(Ph_3P)(CO)_3ReCH_2CO(NEt_2)$ (**41**).

Main-group-metal enolates are well-known for their utility as nucleophiles in carbon–carbon bond-forming reactions. Some of the most important of these reactions include alkylation with organic halides, aldol additions with carbonyl compounds, and Michael addition reactions with α,β-unsaturated carbonyl compounds.[1] The chemical transformations of transition-metal complexes, which are generally quite different from organic reactions, include migratory-insertion, oxidative-addition, and reductive-elimination reactions.[2] A complementary combination of a nucleophilic enolate with the reactivity of transition metals might produce interesting new carbon–carbon bond-forming reactions.

Carbon-bound transition-metal enolates are known for virtually every triad of transition elements, including molybdenum,[3] tungsten,[3b,4] manganese,[3b,5] rhenium,[3b,6] iron,[3b-d,7] cobalt,[8] rhodium,[9] iridium,[9b,10] nickel,[11] palladium,[12] platinum,[13] copper,[14] zinc,[15] and mercury.[16] Although some of these complexes were synthesized 20 years ago, their chemical reactivity has received little attention. We report here the synthesis and characterization of sev-

Scheme I



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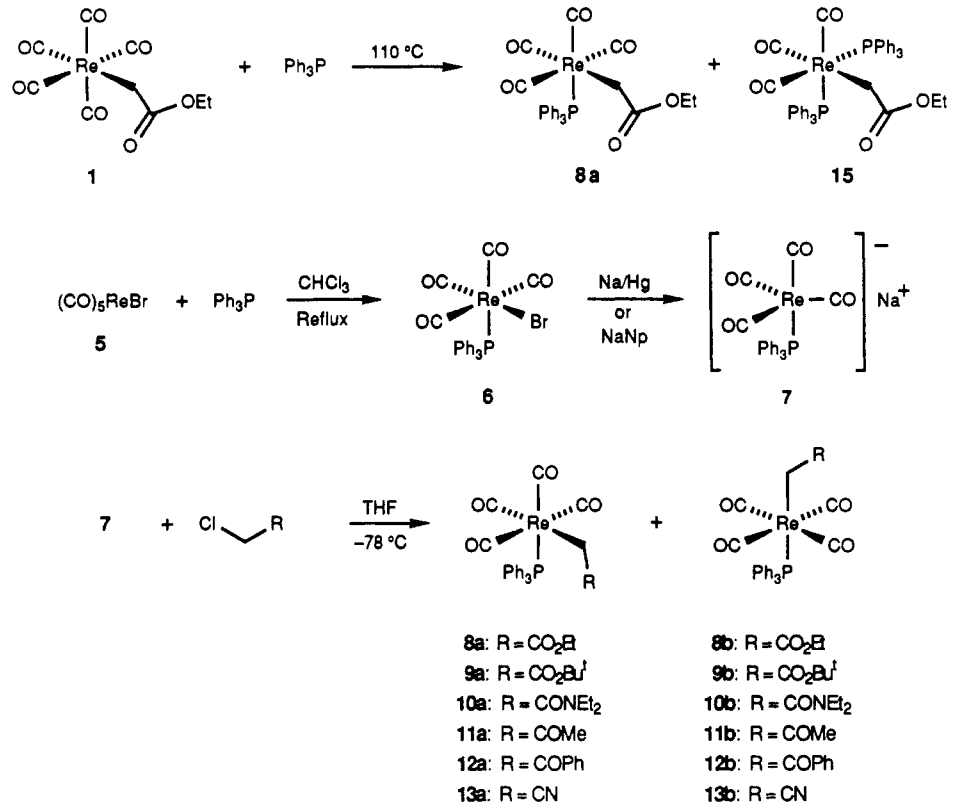
Scheme II



eral rhenium(I) carbon-bound enolates and the insertion of nitriles into the rhenium–carbon bond to give rhenium heterometallacycles. Mechanistic details of the nitrile insertion reaction will also be presented. Some of these results have been communicated in a preliminary form.[17]

Results and Discussion

Synthesis. A wide variety of transition-metal enolates have been prepared; these include complexes having both oxygen-bound and carbon-bound structures. A discussion of these types of enolates is reported elsewhere.[4a] In group 7 metals, there are two reports of carbon-bound enolates of the type $(CO)_5Mn$ for manganese;[3b,5] for rhenium, carbon-bound enolates have been described in the $(CO)_5Re$[3b] and $Cp(NO)(Ph_3P)Re$[6] systems. An oxygen-bound enolate of Re(I) has also been reported.[18] The previous syntheses of $(CO)_5M$ (M = Mn, Re) enolates were accomplished by the alkylation of $(CO)_5MNa$ (M = Mn, Re) with α-halo carbonyl compounds.

We have found this method to be effective as long as a proper choice of leaving group is made. As has been observed in the preparation of group 6 enolates,[4a] the use of α-chloro carbonyl compounds is essential for the successful isolation of primary enolates; α-bromo compounds result in metal–halogen exchange. Thus, multigram quantities of $(CO)_5ReCH_2COR$ (R = OEt, Me, Ph, 1–3) can be prepared as depicted in Scheme I by the reductive cleavage of $Re_2(CO)_{10}$ with sodium amalgam (Na/Hg) followed by addition of $ClCH_2COR$ (R = OEt, Me, Ph). Unfortunately, metal–halogen exchange again becomes a complicating factor in the synthesis of a secondary enolate, as ethyl 2-chloropropanoate fails to give any of the desired product. However, ethyl 2-[(methylsulfonyl)oxy]propanoate reacts smoothly to give $(CO)_5ReCH(Me)CO_2Et$ (4) in 47% yield (Scheme I).

The reactivity of the rhenium enolates is quite different from that of analogous tungsten enolates, which react in a photochemically efficient manner to yield an η^3-oxaallyl species.[4a] In contrast, no η^3-oxallyl species have been detected in the rhenium system; irradiation of the rhenium enolates primarily leads to decomposition of the carbonyl compound through metal–carbon bond cleavage. The tungsten enolates are substitutionally inert under thermal conditions, but the rhenium enolates undergo substitutions with dative ligands, aldol reactions,[17] and nitrile insertion reactions (vide infra) at 100–110 °C. Although the thermal reactions of the esters generally proceed without a large amount of decomposition, the ketone enolates are much less stable and result in formation of the free ketones. The high temperature required for the substitutions limits the utility of these reactions.

One additional comparison of the stability of rhenium and tungsten enolates is noteworthy. The secondary ester enolate 4 is no less stable than its primary analogue 1 with respect to metal–carbon bond cleavage. This is in contrast to the case for the tungsten derivative $Cp(CO)_3WCH(Me)CO_2Et$, which under thermal or photochemical conditions gives ethyl acrylate and $Cp(CO)_3WH$ by β-hydride elimination.[4a] In reactions of 4, no ethyl acrylate is observed and only a trace amount of ethyl propionate is observed as a byproduct.

The instability of the $(CO)_5Re$ enolates 1–4 suggests a mono(phosphine) derivative might possess the desired reactivity and stability. Additionally, *cis*-$(Ph_3P)(CO)_4ReCH_2CO_2Et$ (8a) has been proposed as an intermediate in the reaction of 1 and acetonitrile in the presence of excess Ph_3P.[17] Thus, a general synthesis of *cis*-$(Ph_3P)(CO)_4Re$ enolates was desired. As shown in Scheme

(17) (a) Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1985**, *107*, 3724–6. (b) Burkhardt, E. R.; Doney, J. J.; Slough, G. A.; Stack, J. G.; Bergman, R. G.; Heathcock, C. H. *Pure Appl. Chem.* **1988**, *60*, 1–6. (c) Burkhardt, E. R.; Doney, J. J.; Stack, J. G.; Bergman, R. G.; Heathcock, C. H. *J. Mol. Catal.* **1987**, *41*, 41–57. (d) Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *Pure Appl. Chem.* **1985**, *57*, 1789–98.

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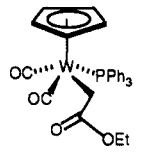
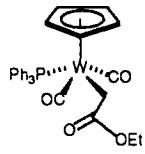
Table I. Selected Spectroscopic Data for Ph_3P-Substituted Rhenium and Tungsten Complexes

compd	δ_{MCH_2}	J_{PH}, Hz
8a	1.81	6.9
8b	2.50	2.7
	1.59, 1.94	9.5
	2.56	3.5

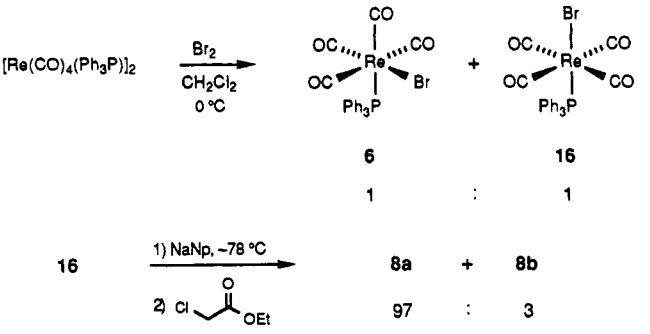
II, direct substitution of **1** with Ph_3P at 110 °C does give **8a** as the major product; however, formation of the bis-substituted product *fac*-$(Ph_3P)_2(CO)_3ReCH_2CO_2Et$ (**15**) was also observed even at low conversion or with less than 1 equiv of Ph_3P. It was not possible to obtain pure **8a** by this route. Similar bis-substitution has been observed in the thermal substitution of $(CO)_5ReMe$ with Ph_3P.[19] Additionally, the greater instability of the rhenium ketone enolates toward metal–carbon bond cleavage prevented the use of elevated temperatures necessary for the substitution.

One possible solution to this problem would be to make use of the alkylation reactions used in the synthesis of **1–4**. However, the appropriate dimer, $[(Ph_3P)(CO)_4Re]_2$, reportedly cannot be cleaved by Na/Hg to the desired anion, $[(Ph_3P)(CO)_4Re]Na$ (**7**).[20] The literature contains only a single report of **7**, derived from the Na/Hg reduction of *cis*-$(Ph_3P)(CO)_4ReBr$ (**6**); no mention was made of its use in the formation of metal–carbon bonds.[21] The synthesis of **6** can be accomplished in a straightforward manner and is outlined in Scheme II. Thermal substitution of $(CO)_5ReBr$[22] (**5**) with Ph_3P in boiling $CHCl_3$ by the literature method[23] does produce **6**, but a substantially longer reaction time (18 h instead of 8 h) was required to obtain **6** in 99% yield.

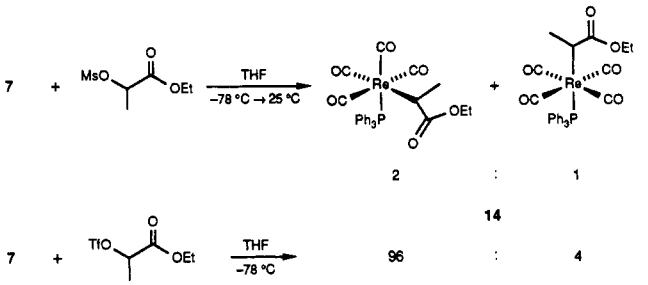
Reduction of **6** in THF with Na/Hg produces an orange solution of **7**, which exhibits an infrared spectrum (1951, 1858, 1826, 1777 cm^{-1}) similar to that displayed by the well-characterized manganese analogue $[(Ph_3P)(CO)_4Mn]Na$.[24] Addition of excess ethyl chloroacetate results in the immediate consumption of the anion; the desired product is obtained in 48% yield as an 87:13 mixture of cis and trans isomers **8a** and **8b** (Scheme II). The major isomer is assigned as the cis isomer on the basis of NMR spectroscopic data (Table I). Though not isolated in pure form, **8b** was identified by comparison with the tungsten enolate *trans*-$Cp(Ph_3P)(CO)_2WCH_2CO_2Et$[4a] (Table I).

Performing the alkylation at −78 °C resulted in an improvement in the cis:trans ratio to 97:3. One possible explanation of the effect of temperature on the cis:trans ratio is that the intermediate anion itself has stereoisomeric forms, that the "cis" anion is formed kinetically, and that the low temperature inhibits conversion to the "trans" anion. If this hypothesis were correct, then generation of the rhenium anion from *trans*-$(Ph_3P)(CO)_4ReBr$[23] (**16**) might be expected to give a predominance of trans-substituted product. Reduction of **16** at −78 °C with sodium naphthalenide (NaNp),[25] followed by addition of the chloro ester, resulted in the identical 97:3 ratio of cis and trans isomers (Scheme III). Apparently, the anion is not configurationally stable, even at −78 °C, and the transition state leading to the cis product **8a** has a free energy significantly lower than that leading to trans product **8b**.

Scheme III



Scheme IV



The need to carry out alkylations at low temperature led to exclusive use of NaNp to generate the rhenium anion. Besides being more convenient, the use of NaNp results in higher yields of isolated enolates. With use of this improved method, **8** was obtained in 86% yield; other primary enolates **9–13** were also prepared in high yield in a similar manner with $ClCH_2R$ (Scheme II; R = CO_2Bu^t, $CONEt_2$, COMe, COPh, CN). Yields and cis:trans ratios are presented in the Experimental Section. The synthesis of a secondary enolate again presented a problem: alkylation with ethyl 2-[(methylsulfonyl)oxy]propanoate is very sluggish at −78 °C and gives an inseparable 2:1 mixture of cis and trans isomers. Fortunately, the analogous triflate reacts rapidly at −78 °C with **7** and gives **14** in 75% yield as a 96:4 mixture of cis and trans isomers (Scheme IV).

Direct synthesis of the carboxylic acid **17** from an α-chloro carboxylic acid derivative proved to be unsuccessful. Alkylation of **7** with $ClCH_2CO_2SiMe_3$ produced low yields of **17**, accompanied by *cis*-$(Ph_3P)(CO)_4ReH$[26] (Scheme V); the mechanism for the production of the rhenium hydride is unknown, and the reaction was not pursued further. Attempted hydrolysis of **8** to the carboxylic acid under conditions[4a] (aqueous HCl) successful for the tungsten ester $Cp(CO)_3WCH_2CO_2Et$ resulted in recovery of **8** unchanged.

(19) McKinney, R. J.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3066–72.
(20) Jolly, P. W.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc.* **1965**, 5830–7. We have subsequently found that NaNp will cleave $[(Ph_3P)(CO)_4Re]_2$, but the overall yield of **7** from $Re_2(CO)_{10}$ is higher than the yield of $[(Ph_3P)(CO)_4Re]_2$ from the phosphine-substituted dimer.
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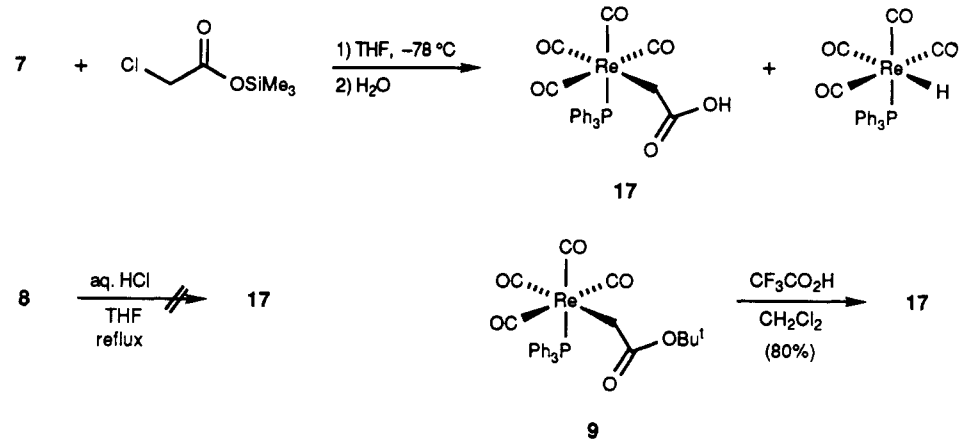
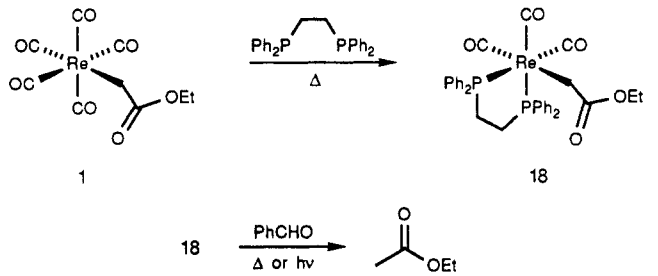
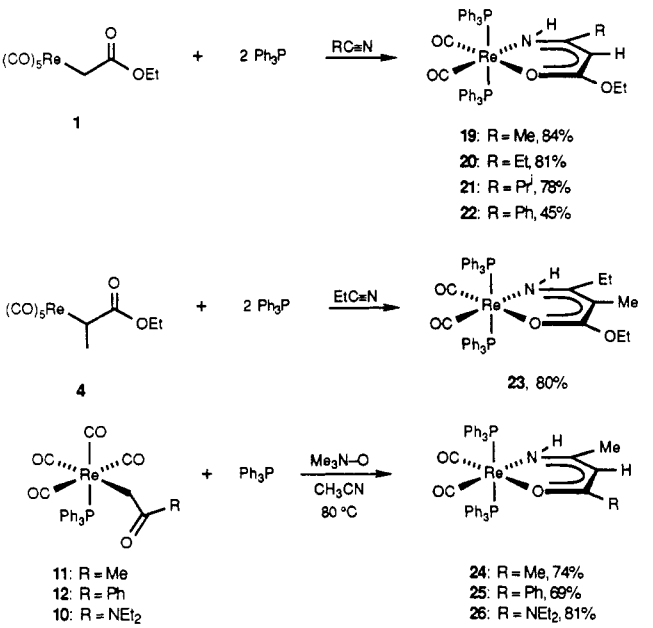
Scheme V



Scheme VI



Scheme VII



However, the *tert*-butyl ester proved to be more labile: treatment of **9** with CF_3CO_2H in CH_2Cl_2 gives **17** in 80% yield (Scheme V).

Bis(phosphine)-substituted rhenium enolate complexes were also investigated, with the aim of eventually developing systems capable of asymmetric induction in aldol or aldol-type reactions involving the rhenium–carbon bond. Toward this end the achiral chelating ligand 1,2-bis(diphenylphosphino)ethane (dppe) was chosen as a model for chiral phosphine ligands (Scheme VI). The desired chelating complex **18** could be prepared in 58% yield by heating a toluene solution of **1** and dppe at reflux for 45 h. However, a more convenient method proved to be heating the reactants in the absence of solvent at 130 °C for 12 h; this procedure provides **18** in 86% yield (Scheme VI). The substitution produces the facial isomer as the only detectable stereoisomer; the stereochemistry of the product was determined by ^{31}P and ^{13}C NMR spectroscopy.

Compound **18** is quite inert. Heating a benzene solution of **18** and benzaldehyde (1 equiv or a 5-fold excess) at 100 °C in a sealed tube for 4.5 days did not give any observable reaction by ^1H NMR spectroscopy. Irradiation of a similar reaction mixture through a uranium glass filter for 32 h resulted in the consumption of 34% (by ^1H NMR analysis vs an internal standard) of **18**, with ethyl acetate as the only observable organic product (Scheme VI). The ethyl acetate is presumably formed from cleavage of the rhenium–carbon bond; the source of the hydrogen atom has not been determined. An attempt to provide more photochemical energy to the system by using a Pyrex filter resulted only in more rapid decomposition to ethyl acetate.

Nitrile Insertion Reactions. Insertion of the C≡N bond into transition-metal–carbon single bonds is uncommon but has been found to occur with scandium(III),[27] titanium(IV),[28] chromium(III),[29] thorium(IV),[30] and uranium(IV).[30] These reactions have in common an electron-deficient metal center facilitating the insertion, possibly by inducing a polarization of the C≡N bond.[27] Insertion into transition-metal–carbon double bonds has been reported for uranium[31] and for group 6 carbene complexes.[32]

As reported in a preliminary communication,[17] heating a solution of **1** and excess Ph_3P in CH_3CN gives a crystalline product, **19**, formally derived from insertion of the C≡N bond into the rhenium–enolate bond. Other nitriles also react with **1** and **4** in the presence of excess Ph_3P to give the analogues **20**–**23** as shown in Scheme VII. The use of a nitrile solvent is not essential for insertion to occur. When a toluene solution of **1** and excess CH_3CN and Ph_3P

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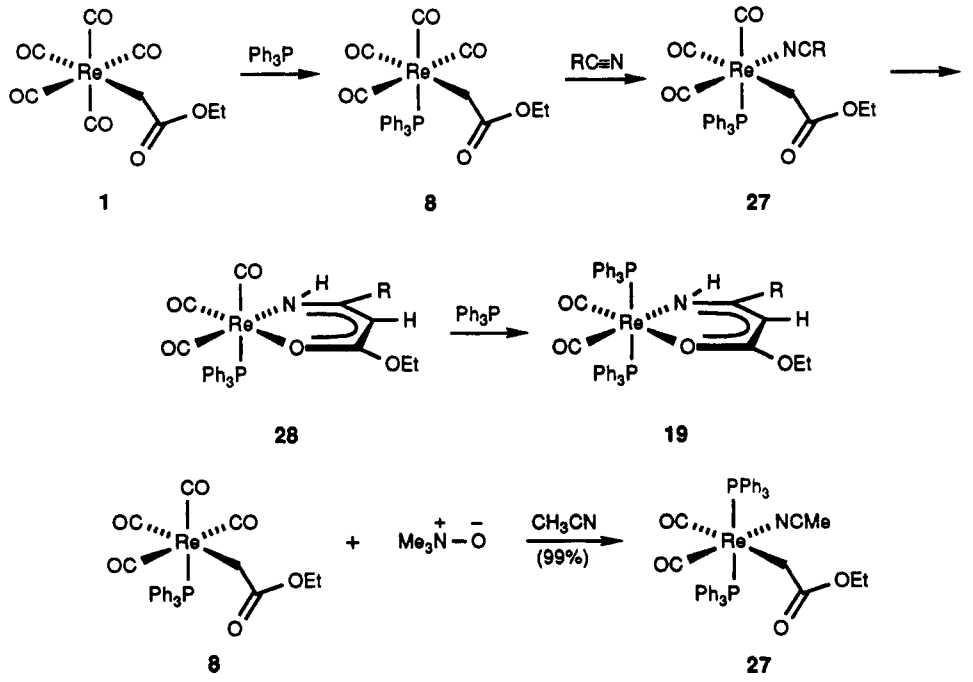
(32) (a) Yang, D. C.; Dragisich, V.; Wulff, W. D.; Huffman, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 307–9. (b) Fischer, H.; Zeuner, S. *J. Organomet. Chem.* **1987**, *327*, 63–75.

Scheme VIII



is heated at reflux, **19** is obtained in 84% yield. These conditions are advantageous for low-boiling nitriles and for instances where use of the nitrile as the solvent would be impractical. The ketone enolates **2** and **3** are much more prone to decomposition at elevated temperatures than the ester enolates and give only trace amounts of the nitrile insertion products. However, the more stable Ph_3P-substituted enolates can be successfully utilized with modified reaction conditions to obtain the desired products (Scheme VII).

Elucidation of the structure of the nitrile insertion products was accomplished by single-crystal X-ray diffraction of **19**,[17a] carried out by Dr. F. J. Hollander of the University of California at Berkeley X-ray diffraction facility. An ORTEP diagram and selected bond lengths can be found in Figure 1 and Table II, respectively. Of particular interest are the nearly identical C4–C5 (1.396 (5) Å)/C5–C6 (1.372 (5) Å) and C4–N (1.312 (4) Å)/C6–O3 (1.262 (4) Å) bond lengths, indicating a delocalized system similar to that of acetylacetonate[33] (acac) and related Schiff base[34] ligands. Further evidence for delocalization is found in the ^{13}C chemical shifts of C4 and C5 at 167.8 and 168.3 ppm (specific assignments to C4 and C5 were not determined), consistent with a reduced bond order. The infrared spectrum also shows the reduced bond order and delocalization: a single band is observed at 1590 cm^{-1} for the C=X (X = N, O) bond.

Proposed Mechanism of Nitrile Insertion. Both the pentacarbonyl enolate **1** and the independently prepared phosphine-substituted enolate **8** react with Ph_3P in CH_3CN to give the condensation product **19**. No insertion is observed with **1** in CH_3CN in the absence of Ph_3P. Therefore, it is reasonable to assume that **8** is an intermediate in the sequence **1** → **19** (Scheme VIII). From **8**, substitution of a CO with RCN could be envisioned to give the coordinated nitrile complex **27**. Insertion of the C≡N bond into the rhenium–carbon bond could occur via direct migration of the metal–carbon bond or through rearrangement to an oxygen-bound enolate and addition of the nucleophilic enolate carbon to the coordinated nitrile. Replacement of the axial CO with Ph_3P would then give the observed bis-substituted product in the final step.

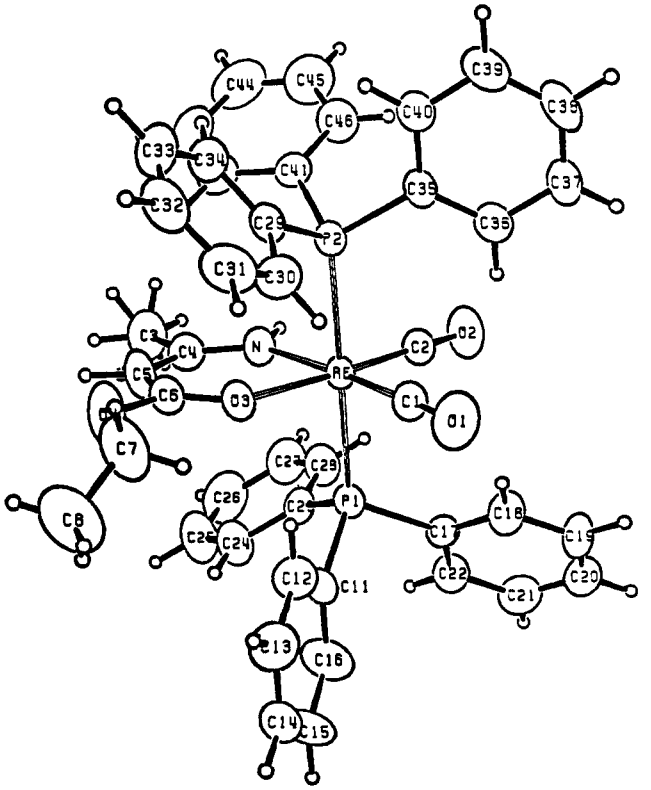


Figure 1. ORTEP diagram of nitrile insertion product **19** with 50% probability thermal ellipsoids. The diagram shows the numbering scheme used in the tables.

In order to test this hypothesis, an independent synthesis of **27** was required under conditions that would not induce insertion. Trimethylamine *N*-oxide (Me_3NO) is a mild oxidant that reacts irreversibly with coordinated carbonyl groups to give CO_2 and the unsaturated metal, which can be trapped by various ligands.[35] Indeed, when

(33) Fackler, J. P., Jr. *Prog. Inorg. Chem.* **1966**, *7*, 361–425.
(34) Holm, R. H.; Everett, G. W., Jr.; Chakravorty, A. *Prog. Inorg. Chem.* **1966**, *7*, 83–214.

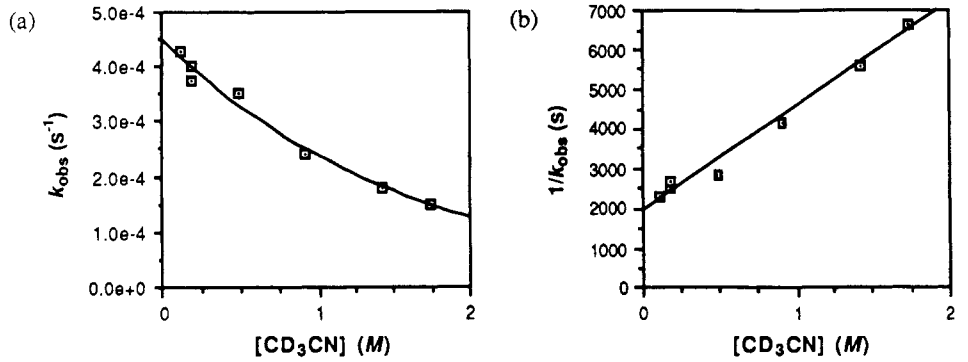


Figure 2. Plots of the observed rate constant for the disappearance of **27**: (a) k_{obs} vs CD_3CN concentration (curve fitted with the general form $y = a*10^{-bx}$); (b) $1/k_{obs}$ vs CD_3CN concentration.

Table II. Selected Intramolecular Distances (Å) and Angles (deg) for 19[a]

	Distances		
Re-P1	2.425 (1)	O3-C6	1.262 (4)
Re-P2	2.424 (1)	N-C4	1.312 (4)
Re-O3	2.172 (2)	C4-C3	1.512 (5)
Re-N	2.145 (3)	C4-C5	1.396 (5)
Re-C1	1.895 (4)	C5-C6	1.372 (5)
Re-C2	1.872 (4)	C6-O4	1.347 (4)
		O4-C7	1.435 (5)
C1-O1	1.162 (4)	C7-C8	1.430 (6)
C2-O2	1.174 (4)		
		P1-C11	1.838 (4)
		P1-C17	1.854 (3)
		P1-C23	1.827 (4)
		P2-C29	1.838 (4)
		P2-C35	1.841 (4)
		P2-C41	1.821 (4)
	Angles		
P1-Re-P2	179.27 (3)	Re-C1-O1	179.2 (3)
P1-Re-O3	92.50 (6)	Re-C2-O2	178.2 (3)
P1-Re-N	88.69 (7)		
P1-Re-C1	90.74 (10)	Re-O3-C6	128.51 (22)
P1-Re-C2	88.07 (11)	Re-N-C4	130.78 (23)
P2-Re-O3	87.77 (6)	N-C4-C3	119.0 (3)
P2-Re-N	90.68 (7)	N-C4-C5	123.9 (3)
P2-Re-C1	89.92 (10)	C3-C4-C5	117.1 (3)
P2-Re-C2	91.62 (11)	C4-C5-C6	125.4 (3)
O3-Re-N	82.83 (9)	C5-C6-O3	128.4 (3)
O3-Re-C1	92.47 (12)	C5-C6-O4	113.8 (3)
O3-Re-C2	176.19 (11)	O3-C6-O4	117.7 (3)
N-Re-C1	175.23 (12)	C6-O4-C7	120.7 (3)
N-Re-C2	93.42 (12)	O4-C7-C8	109.7 (4)
C1-Re-C2	91.29 (15)		

[a] Esd's are in parentheses.

a solution of **8** in CH_3CN is treated with 1 equiv of Me_3NO, the nitrile complex **27** (R = Me) is formed virtually instantaneously and can be isolated in 99% yield (Scheme VIII). Although nitriles are usually considered to be labile ligands,[36] **27** can be handled in the air both as a solid and in solution with no apparent decomposition (solutions of **27** are only slightly moisture sensitive). Three inequivalent metal carbonyl signals are observed in the ^{13}C NMR spectrum of **27**, confirming the facial stereochemistry.

Unlike the similar tungsten enolate nitrile complex **29**, which dissociates CH_3CN to give the η^3-oxaallyl complex **30** upon dissolution in solvents other than CH_3CN[4a] (Scheme IX), solutions of **27** in solvents other than CH_3CN are stable at room temperature. At 80 °C in C_6H_6, however, the nitrile undergoes insertion into the rhenium–carbon bond and the tricarbonyl insertion product **28** is formed, along with **8** and **19** in a ratio of 6:1:1, and can be isolated in 35% yield. The last two compounds presumably result from loss of CO from **28**; the free CO displaces CH_3CN from **27** to give **8**, and the unsaturated rhenium species scavenges Ph_3P from the starting material or products to give **19**. That the CO ligand of **28** is labile at 80 °C is demonstrated by the conversion of **28** to **19** in 4 h in the presence of Ph_3P. This reaction also provides evidence that the sequence of **1** → **8** → **27** → **28** → **19** is possible.

Table III. Observed Rate Constants for the Disappearance of 27

[CD_3CN], M	k_{obs}, 10^{-4} s^{-1}	$t_{1/2}$, min	[CD_3CN], M	k_{obs}, 10^{-4} s^{-1}	$t_{1/2}$, min
0.114	4.29	26.9	0.912	2.39	48.4
0.190	4.00	28.9	1.418	1.80	64.3
0.190	3.76	30.8	1.741	1.50	76.8
0.485	3.52	32.9			

Kinetics. As was mentioned earlier, byproducts are obtained in the preparation of the tricarbonyl insertion product **28**. It was thought that the undesired formation of the tetracarbonyl enolate **8** could be suppressed by the addition of CH_3CN to compete with any free CO in the exchange with **27**. Toward this end, several qualitative experiments were performed by heating **27** in C_6H_6 at 80 °C for 2 h with increasing amounts of CH_3CN added to the reaction mixture. The crude reaction mixtures were examined by ^1H NMR spectroscopy, which revealed that the production of **8** was indeed suppressed at higher concentrations of CH_3CN. However, unchanged **27** was also observed in the crude reaction mixtures. The amount of **27** present was directly proportional to the amount of CH_3CN added, indicating a reduction of the reaction rate.

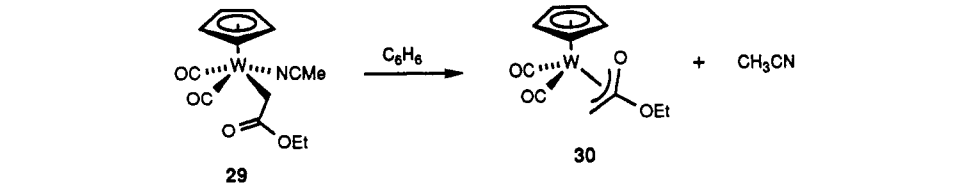
One possible explanation for the rate retardation caused by added acetonitrile is that coordinated CH_3CN might dissociate reversibly (perhaps to allow rearrangement of the C-bound η^1-enolate **31** to the O-bound η^3-enolate **32**) on the route to insertion product **28**. This mechanism is summarized in Scheme X, along with the rate law that can be derived for it by using the steady-state assumption. In order to investigate this possibility, a study of the rate of conversion of **27** to **28** was carried out with use of variable concentrations of acetonitrile in benzene solution. Kinetic data were obtained at 80 °C by monitoring the disappearance of of **27** by ^1H NMR spectroscopy with excess CD_3CN. Good pseudo-first-order kinetics were observed over 3 half-lives, and the data are presented in Table III.

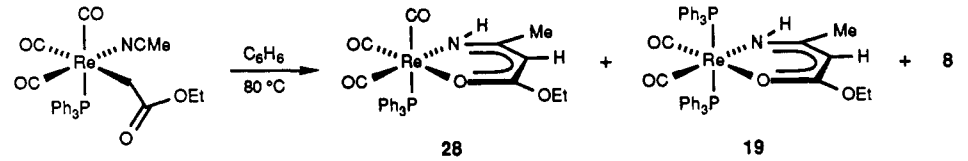
These measurements confirmed that added CH_3CN slows the rate of disappearance of **27** (Figure 2a). However, the effect is quite modest—the rate constant de-

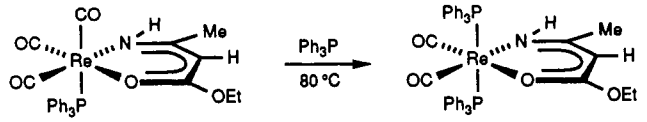
(35) (a) Blumer, D. S.; Barnett, K. W.; Brown, T. L. *J. Organomet. Chem.* **1979**, *173*, 71–76. (b) Koelle, U. *J. Organomet. Chem.* **1978**, *155*, 53–62. (c) Koelle, U. *J. Organomet. Chem.* **1977**, *133*, 53–8. For reviews, see: (d) Luh, T.-Y. *Coord. Chem. Rev.* **1984**, *60*, 255–76. (e) Albers, M. O.; Coville, N. J. *Coord. Chem. Rev.* **1984**, *53*, 227–59.

(36) Storhoff, B. N.; Lewis, H. C., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1–29.

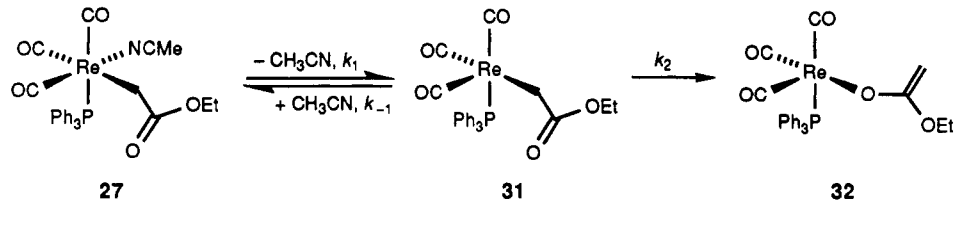
Scheme IX

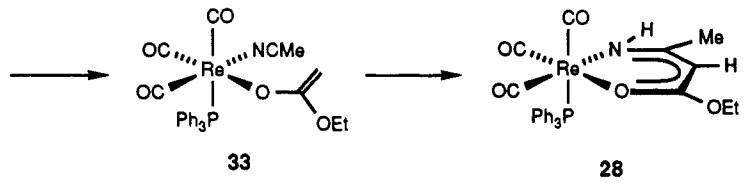




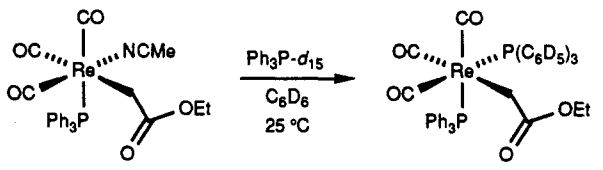


Scheme X





$$\text{Rate} = \frac{k_1 k_2 [27]}{k_{-1} + k_2 [CH_3CN]} = k_{obs} [27]$$



creases by only a factor of about 2.8 over a 15-fold increase in acetonitrile concentration. Furthermore, the maximum velocity (5.1×10^{-4} s^{-1} at 80 °C) of the insertion reactions, calculated by extrapolation of an inverse plot to zero acetonitrile concentration (Figure 2b), is much slower than the rate constant measured independently for dissociation of acetonitrile from the rhenium center in **27** (the presumed k_1 in Scheme X). This dissociation rate constant k_1 was estimated independently by measuring the rate of reaction of **27** with Ph_3P-d_{15}, which leads to phosphine-for-nitrile substitution product **15**-d_{15} (Scheme X). The maximum velocity for this reaction was not rigorously determined; however, as shown in Table IV, dissociation of the nitrile proceeds at a much faster rate ($\sim 4 \times 10^{-4}$ s^{-1} at 25 °C) than the nitrile insertion. The conversion of **27** to **28** proceeds very slowly at this temperature, and thus

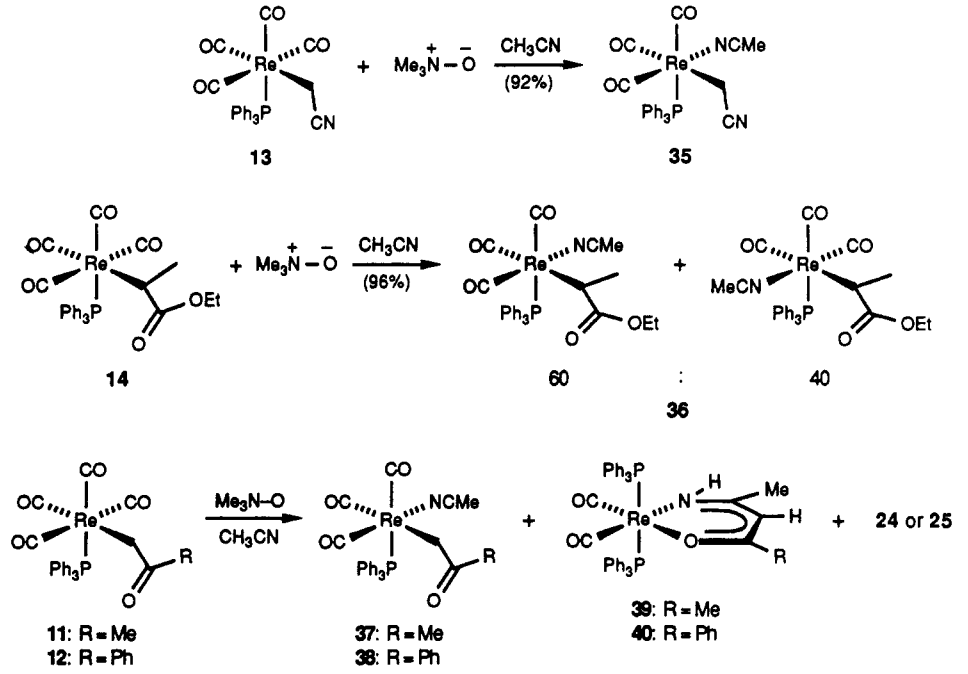
Table IV. Observed Rate Constants for the Reaction of 27 with Ph_3P-d_{15}

$[Ph_3P\text{-}d_{15}]$, M	k_{obs}, 10^{-4} s^{-1}	$t_{1/2}$, min
0.200	3.88	29.8
0.200	4.00	28.9
0.400	4.43	26.1

the simple acetonitrile dissociation pathway shown at the top of Scheme X cannot be the mechanism of this reaction.

We conclude that the modest rate inhibition produced by added acetonitrile in the conversion of **27** to **28** at 80 °C is *not* due to inhibition of nitrile dissociation from the rhenium center in the starting material but instead is a weak solvent effect caused by the marked difference in polarity between CH_3CN and benzene. This suggests that the rate-determining transition state(s) for the nitrile in-

Scheme XI

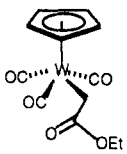


sertion (which perhaps involves direct conversion of C-bound enolate **27** to its O-bound isomer **33**, without CH_3CN dissociation) must be slightly less polar than the ground state. We do not yet understand the exact physical source of this difference in polarity. This behavior is precedented in the reactions of lithium enolates with aldehydes.[37]

An O-bound enolate is an attractive intermediate for two reasons. Unlike main-group-metal carbon-bound enolates that act as nucleophiles toward carbonyl compounds[15] (Reformatsky reaction) or nitriles[38] (Blaise reaction), the carbon-bound rhenium enolates do not exhibit any nucleophilic or basic tendencies. In fact, electron-withdrawing groups such as CO_2R normally retard the rate of migratory insertion reactions (which can be considered a type of nucleophilic attack on coordinated CO) of substituted transition-metal alkyls.[39] Additionally, there are several instances where oxygen-bound transition-metal enolates are known to react as nucleophiles or have been implicated as nucleophilic intermediates.[40]

Synthesis of Nitrile Complexes. The introduction of the labile nitrile ligand into the coordination sphere of the rhenium ester enolate complex could provide additional reactivity of the enolates under mild conditions. The successful synthesis of **27** prompted an investigation of the synthesis of nitrile complexes of other enolates. Under the same conditions used for the preparation of **27**, the nitrile enolate **13** and the secondary ester enolate **14** are converted into their respective nitrile complexes **35** and **36** in 92% and 95% yields (Scheme XI). Two diastereomers of **36** are obtained in approximately equal amounts; no attempt was made to separate these isomers.

Table V. Selected Spectroscopic Data for Rhenium and Tungsten η^1- and η^3-Enolates

compd	$\delta_{MCH_2{}^{13}COR}$	$\delta_{^{31}P}$	IR ν_{C-O}, cm^{-1}
8	183.09	9.5	1693
	181.25		1691
27	182.51	19.7	1673
30	159.2		*a*
10	182.35	9.1	1576
41	187.55	22.8	1551
42		19.2	1595
43	179.29		1605
44	163.17		1548

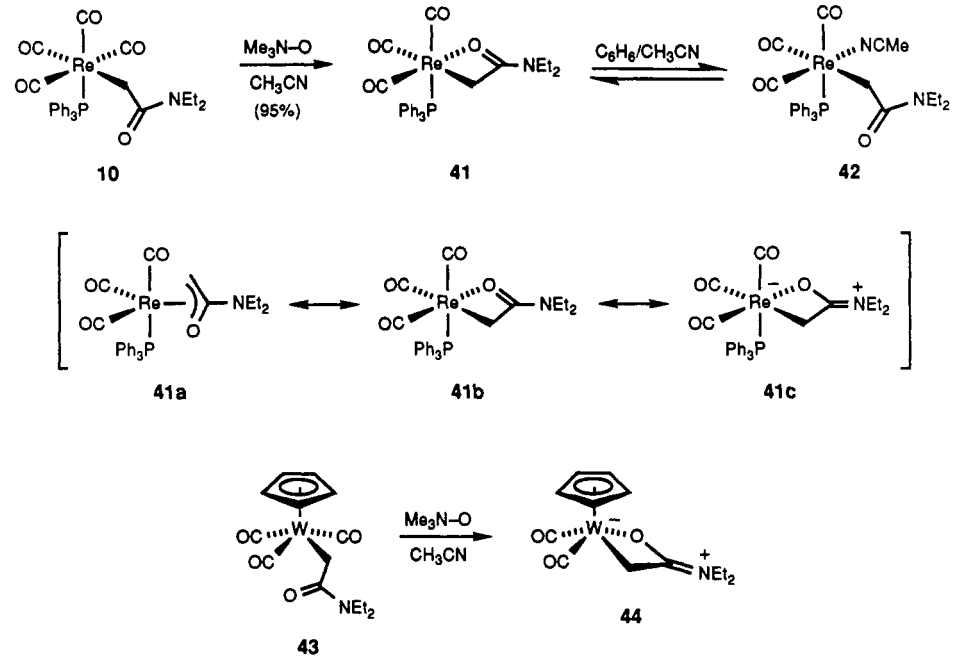
[a] No organic C=O observed.

Attempts to prepare the analogous nitrile complexes of the ketone enolates **11** and **12** were not successful. Addition of 1 equiv of Me_3NO to CH_3CN solutions of **11** or **12** removes one CO as desired, but the ketone enolates proved to be significantly more reactive toward nitrile insertion than the ester or amide enolates (Scheme XI). Crude reaction mixtures were examined by ^1H NMR spectroscopy, which indicated the presence (albeit in low yield) of the desired nitrile complexes **37** and **38**, along with significant amounts of the nitrile insertion products **39** and **40** and **24** and **25**.

The amide enolate **10** does not give a nitrile complex when treated with Me_3NO in CH_3CN (Scheme XII). The amine oxide removes one molecule of CO, but the product **41**, which can be isolated in 95% yield, does not incorporate CH_3CN; the absence of CH_3CN was confirmed by ^1H and ^{13}C NMR, IR, and mass spectrometry as well as by combustion analysis. The exact structure of this complex has not been determined, due to our inability to obtain single crystals suitable for X-ray analysis. The spectroscopic data allow assignment of the following structural features. In the ^1H NMR spectrum, the α-CH_2 protons appear as two double doublets, indicating a diastereotopic environment found only in the tricarbonyl facial isomer.

(37) Heathcock, C. H.; Lampe, J. *J. Org. Chem.* **1983**, *48*, 4330–7.
(38) (a) Blaise, E. E. *C. R. Hebd. Seances Acad. Sci.* **1901**, *132*, 478. (b) Hannick, S. M.; Kishi, Y. *J. Org. Chem.* **1983**, *48*, 3833–5 and references cited therein. For the use of lithium rather than zinc enolates, see: Overman, L. E.; Osawa, T. *J. Am. Chem. Soc.* **1985**, *107*, 1698–701.
(39) Cawse, J. N.; Fiato, R. A.; Pruett, R. L. *J. Organomet. Chem.* **1979**, *172*, 405–13.
(40) (a) Hirao, T.; Fujihara, Y.; Tsuno, S. *Chem. Lett.* **1984**, 367–8. (b) Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 1664–5. (c) Evans, D. A.; McGee, L. R. *Tetrahedron Lett.* **1980**, 3975–8. (d) Yamamoto, Y.; Maruyama, K. *Tetrahedron Lett.* **1980**, *21*, 4607–10. (e) Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 61–6.

Scheme XII



This assignment is also confirmed by the three inequivalent CO ligands observed in the ^{13}C NMR and IR spectra.

The spectroscopic data for **41** suggest η^3-coordination of the enolate ligand. The three resonance structures **41a–c** can be drawn for the η^3-coordinated amide and are shown in Scheme XII. By a comparison of similar tungsten derivatives, the relative contribution of each resonance structure can be assessed. The tungsten η^3-oxaallyl complexes (e.g. **30**; Scheme IX) analogous to **41a** do not display an IR absorption for the organic carbonyl due to the allylic delocalization of the ligand. Additionally, in the ^{13}C NMR spectra of these complexes, the central carbon is observed upfield from the η^1-enolate (Table V). The tungsten amide enolate $Cp(CO)_3WCH_2CONEt_2$ (**43**) can be decarbonylated to give the η^3 complex **44**, which has been characterized by single-crystal X-ray analysis[4a] and has a structure similar to resonance form **41c**. Although the rhenium complex **41** has an IR absorption that appears at lower energy than that of its η^1 derivative, the effect is not as pronounced as in **44** (Table V). Also, the upfield shift of the organic carbonyl in the ^{13}C NMR spectrum of **44** is not observed in **41**. The considerable C–N double-bond character (1.333 (4) Å) in the tungsten complex **44** results in a partial negative charge on tungsten and is reflected in the intense red color of the charge-transfer complex; the rhenium complex **41** does not show any intense coloration.

Unlike the tungsten complex **44**, which reacts sluggishly with dative ligands,[4a] treatment of a C_6H_6 solution of **41** with 100 equiv of CH_3CN immediately produces an equilibrium mixture of **41** and the nitrile complex **42**. The IR spectrum (Table I) of this solution clearly shows the amide carbonyl of **41** and that of **42**. Addition of 50 equiv of CD_3CN to a solution of **41** in C_6D_6 gives a 41:59 mixture of the deuterated nitrile analogues of **41** and **42**. Evidence for the structure of the nitrile complex is found in the ^{31}P NMR spectrum (Table V). The ^{31}P resonance observed for **42** is nearly identical with that observed for **27**. Increasing the amount of CD_3CN to 100 equiv leads to a 35:65 mixture of **41** and **42**. That the equilibrium constant $K_{eq} < 1$ is demonstrated by the addition of only 5 equiv of CD_3CN to **41**, which gives **42** in nearly undetectable amounts. On the basis of the reactivity and spectroscopic properties of **41**, it appears that **41** has a large contribution from the resonance form **41b** and little or no contribution from **41a** or **41c**.

Summary and Conclusions

Several carbon-bound rhenium enolates, based on $(CO)_5Re$ and $(Ph_3P)(CO)_4Re$, can be prepared by alkylation of the corresponding carbonylmetalate anions with α-chloro carbonyl or α-sulfonyloxy carbonyl compounds. These materials can be isolated by standard chromatographic methods and are air-stable in solution and the solid state. Irradiation of the $(CO)_5Re$ derivatives led to decomposition. Thermal activation of these compounds required elevated temperatures, which in the presence of Ph_3P and a nitrile resulted in the formation of a carbon–carbon bond between the enolate and nitrile carbon atoms. The ketone enolates are unstable under these conditions and lead only to products of metal–carbon bond cleavage.

The mechanism of the nitrile/enolate condensation has been examined and is proposed to proceed through a Ph_3P-substituted nitrile complex. This complex was synthesized independently, and its efficacy as an intermediate was demonstrated. Kinetic studies of the insertion step were inconclusive with respect to the existence of an oxygen-bound enolate, but a weak solvent effect was observed upon addition of CH_3CN. At higher concentrations of CH_3CN, a deceleration of the rate of the insertion reaction was found to occur.

Labile derivatives of the Ph_3P-substituted enolates were prepared by reaction of the enolates with Me_3NO in CH_3CN. Acetonitrile complexes are obtained for the ester and nitrile enolates. The amide enolate does not give a nitrile complex when treated in this fashion; rather, the amide oxygen coordinates to rhenium. The reactivity of these labile enolate derivatives will be described in a subsequent paper.

Experimental Section

General Considerations. All manipulations involving air-sensitive material were performed under nitrogen or argon with use of Schlenk or vacuum line techniques[41] or in a Vacuum At-

(41) Shriver, D. F.; Dredzdon, M. A. *The Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

mospheres HE 43-2 inert-atmosphere glovebox equipped with an HE-493 Dri-Train inert-gas purifier.

All solvents were thoroughly dried and degassed before use in all reactions. Tetrahydrofuran (THF) was distilled from Na/benzophenone under a nitrogen atmosphere. Acetonitrile (CH_3CN), benzene (C_6H_6), pentane, toluene ($PhCH_3$), and dichloromethane (CH_2Cl_2) were distilled from CaH_2 under a nitrogen atmosphere; chloroform ($CHCl_3$) was distilled from P_2O_5 under a nitrogen atmosphere. Other solvents were reagent grade and were used without purification. All NMR solvents were dried and transferred under vacuum before use: benzene-d_6 (C_6D_6) was stirred over Na/benzophenone, chloroform-d ($CDCl_3$) was stirred over P_2O_5, and dichloromethane-d_2 (CD_2Cl_2) was stirred over CaH_2. Ethyl chloroacetate (MCB), chloroacetone (Aldrich), and chloroacetonitrile (MCB) were distilled and degassed (three freeze–pump–thaw cycles) prior to use; 2-chloroacetophenone (Aldrich) was used as received. Ethyl lactate (Aldrich) was distilled before use. Propionitrile (Aldrich) and isobutyronitrile (Aldrich) were distilled from CaH_2 and degassed prior to use. Benzonitrile (Aldrich) was distilled from P_2O_5 and degassed before use. $Re_2(CO)_{10}$ was used as received from Strem Chemicals; $(CO)_5ReBr$ was prepared according to the published procedure.[22] Triphenylphosphine (Ph_3P) (Aldrich) was recrystallized from ethanol. Anhydrous trimethylamine N-oxide (Me_3NO) was prepared from $Me_3NO{\cdot}2H_2O$ (Aldrich) by azeotropic removal of H_2O with dimethylformamide.[42] Preparation of 1% sodium amalgam (Na/Hg) was effected by adding 0.5 g of Na to 49.5 g of Hg in the glovebox. Other reagents were used as received.

Solution infrared spectra were recorded in 0.1-mm NaCl sealed cells; IR data are reported as (solvent) cm^{-1} (intensity: vs, very strong; s, strong; m, medium; w, weak) and are calibrated with the 1601-cm^{-1} band of polystyrene. Data for complex ^1H NMR spin systems are reported in the manner suggested by Jackman and Sternhell.[43] When necessary, coupling constants for these systems (given in hertz) were obtained through simulation of the spin system. ^{13}C NMR spectra are referenced by using the ^{13}C resonance of the solvent as an internal standard (C_6D_6, 128.0 ppm; $CDCl_3$, 77.0 ppm; CD_2Cl_2, 53.8 ppm); all ^{13}C resonances are singlets unless otherwise noted. The ^{31}P NMR (121.5 or 82 MHz) spectra were recorded with proton decoupling and are reported in units of parts per million (δ) downfield from external 85% H_3PO_4. Electron impact and chemical ionization mass spectra are reported as the most intense peak of the isotope envelope. Melting points are reported uncorrected.

Flash column chromatographic separations by the method of Still, Kahn, and Mitra[44] were carried out on silica gel under nitrogen pressure. Solvents for chromatography were reagent grade (Fisher) and were not purified before use.

The X-ray crystal structure was solved by Patterson methods and refined by standard least-squares and Fourier techniques. Peaks corresponding to the expected positions of most of the hydrogen atoms were found by difference Fourier techniques; hydrogens were included in the structure factor calculations in their expected positions but were not refined in least squares.[45]

Ethyl 2-[((Trifluoromethyl)sulfonyl)oxy]propanoate. This procedure is based on that of Vedejs and co-workers.[46] A solution of 0.85 mL (831 mg; 10.5 mmol) of pyridine in 35 mL of CH_2Cl_2 under N_2 was cooled in a CCl_4/CO_2 bath (−23 °C), and 1.70 mL (2.85 g; 10.1 mmol) of trifluoromethanesulfonic anhydride was added by syringe. The resulting white precipitate was stirred for 10 min, and 1.15 mL (1.20 g; 10.1 mmol) of ethyl lactate was also added by syringe. The heterogeneous mixture was stirred for 10 min, the −23 °C bath was exchanged for an ambient-temperature H_2O bath, and the mixture was stirred an additional 20 min. The solids were filtered, and the solvent was removed under reduced pressure (N.B.: the product is volatile, and pressures less than 20 mmHg and/or temperatures greater than 30 °C will result in substantial product loss) to obtain a pale pink residue. This residue was extracted with 4 × 20 mL of pentane, and the extracts were filtered through a 2-cm silica gel plug. Evaporation of the pentane gave 2.14 g (84%) of colorless liquid. IR ($CHCl_3$): 1762 (s), 1425 (vs), 1155 (vs) cm^{-1}. ^1H NMR (250 MHz; $CDCl_3$): δ 1.33 (t, 3, J = 7.2), 1.71 (d, 3, J = 7.0), 4.31 (q, 2, J = 7.2), 5.22 (q, 1, 7.0). ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 13.92, 18.06, 62.76, 80.09, 118.42 (q, J = 319.2), 167.32. Anal. Calcd for $C_6H_9F_3O_5S$: C, 28.80; H, 3.63; S, 12.81. Found: C, 28.91; H, 3.67; S, 12.91.

General Procedure for the Preparation of Compounds 1–3. To a rapidly stirred solution of 5.22 g (8.0 mmol) of $Re_2(CO)_{10}$ in 100 mL of THF was added 40.4 g of 1% Na/Hg. After 4 h, consumption of the starting material and the generation of $[(CO)_5Re]^-$ was confirmed by IR spectroscopy (1908 (vs), 1862 (s), 1832 (s) cm^{-1}; lit.[47] 1911 (s), 1864 (s), 1835 (sh) cm^{-1}) by removing aliquots under air-free conditions. The deep red solution of the anion was transferred via cannula under a positive pressure of Ar to a 125-mL Schlenk flask containing 16.0 mmol of $ClCH_2COR$. The color of the anion was immediately discharged to give a yellow solution and a white precipitate of NaCl. The mixture was stirred until the anion could no longer be detected by IR spectroscopy (4–12 h) of an aliquot removed from the solution under air-free conditions. THF was removed under high vacuum, the resulting orange residue was extracted repeatedly (6 × 15 mL) with pentane (1 and 2) or a pentane/Et_2O mixture (3), and the solid NaCl was removed by filtration. Concentration of the filtrate with a rotary evaporator gave orange oils that were purified as described below.

Pentacarbonyl(2-ethoxy-2-oxoethyl)rhenium (1). Flash chromatography (6:1 hexane/THF) gave 4.18 g (63%) of a pale yellow oil, which solidifies slightly below ambient temperature. IR (THF): 2021 (s), 1985 (m), 1696 (w) cm^{-1}. ^1H NMR (250 MHz; C_6D_6): δ 1.05 (t, 3, J = 7.0), 1.66 (s, 2), 4.04 (q, 2, J = 7.0). ^{13}C NMR (75.5 MHz; C_6D_6): δ −8.14, 14.6, 59.1, 180.2, 180.8, 183.0. MS (EI, 70 eV): m/z 414 (M^+), 286 (base). Anal. Calcd for $C_9H_7O_7Re$: C, 26.15; H, 1.71. Found: C, 26.06; H, 1.69.

Pentacarbonyl(2-oxopropyl)rhenium (2). Flash chromatography (3:1 hexane/THF) gave 3.38 g (55%) of a yellow oil. IR (THF): 2022 (s), 1978 (m), 1922 (vs), 1663 (m) cm^{-1}. ^1H NMR (250 MHz; C_6D_6): δ 1.85 (q, 2, J = 0.5), 1.88 (t, 3, J = 0.5). ^{13}C NMR (75.5 MHz; C_6D_6): δ 7.90, 28.0, 180.2, 183.4, 210.0. MS (EI, 70 eV): m/z 384 (M^+), 43 (base). Anal. Calcd for $C_8H_5O_6Re$: C, 25.07; H, 1.32. Found: C, 25.21; H, 1.27.

Pentacarbonyl(2-phenyl-2-oxoethyl)rhenium (3). Flash chromatography (85:15 hexane/THF) gave 4.19 g (59%) of yellow solid, mp 54–57 °C. IR (THF): 2143 (m), 2078 (m), 2039 (vs), 1990 (vs), 1644 (s) cm^{-1}. ^1H NMR (250 MHz; C_6D_6): δ 2.47 (s, 2), 7.13–7.16 (m, 3), 7.98–8.02 (m, 2). ^{13}C NMR (75.5 MHz; C_6D_6): δ 2.57, 128.16, 128.59, 131.84, 137.75, 179.92, 183.21, 203.31. Anal. Calcd for $C_{13}H_7O_6Re$: C, 35.06; H, 1.58. Found: C, 35.44; H, 1.56.

Pentacarbonyl(2-ethoxy-1-methyl-2-oxoethyl)rhenium (4). The Re anion was generated as above from 657 mg (1.01 mmol) of $Re_2(CO)_{10}$ and 7.21 g of Na/Hg in 30 mL of THF. The red solution was transferred as above to a 50-mL Schlenk flask containing 409 mg (3.14 mmol) of $MsOCH(CH_3)CO_2Et$.[48] After the mixture was stirred for 15 h, the solvent was removed with a rotary evaporator and the residue was extracted with 3 × 20 mL of 1:1 Et_2O/pentane and then with 5 mL of THF. The solids were removed by suction filtration, and the filtrate was evaporated to yield an orange oil. Purification by flash chromatography (12:1 hexane/THF) gave 406 mg (47%) of a pale yellow oil. IR ($CHCl_3$): 2148 (w), 2079 (w), 2041 (vs), 1994 (s), 1690 (m) cm^{-1}. ^1H NMR (250 MHz; C_6D_6): δ 1.04 (t, 3, J = 7.1), 1.86 (d, 3, J = 6.9), 2.37 (q, 1, J = 6.9), 4.01–4.15 (m, 2). ^{13}C NMR (121.5 MHz; C_6D_6): δ 6.26, 14.54, 24.20, 58.81, 180.27, 182.39, 184.12. Anal. Calcd for $C_{10}H_9O_7Re$: C, 28.10; H, 2.12. Found: C, 28.05; H, 2.07.

***cis*-Bromotetracarbonyl(triphenylphosphine)rhenium (6).** This procedure is essentially that of Jolly and Stone[23] with minor modifications. A 1-L, round-bottomed flask containing 6.36 g (15.7

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mmol) of $(CO)_5ReBr$, 4.20 g (16.0 mmol) of Ph_3P, and a stirring bar was fitted with a reflux condenser and a nitrogen inlet, and the system was then flushed with N_2. To the flask was added 750 mL of $CHCl_3$, and the resulting solution was heated at reflux for 18 h. IR spectroscopy confirmed the absence of starting material. The solvent was evaporated with a rotary evaporator to yield a white solid. The solid was collected on a fritted disk, washed with pentane, and dried under reduced pressure (water aspirator) to give 9.92 g (99%) of a white, microcrystalline solid, mp 146–148 °C (lit.[23] mp 146 °C). IR ($CHCl_3$): 2129 (s), 2024 (vs), 1951 (s) cm^{-1}. ^1H NMR (250 MHz; C_6D_6): δ 6.92–7.00 (m, 9), 7.58–7.66 (m, 6). ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 128.67 (d, J = 10.2), 131.00 (d, J = 2.0), 131.74 (d, J = 48.5), 133.53 (d, J = 10.5), 182.00 (d, J = 56.0), 182.75 (d, J = 5.6), 184.80 (d, J = 9.4). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 1.5. Anal. Calcd for $C_{22}H_{15}BrO_4PRe$: C, 41.26; H, 2.36. Found: C, 41.59; H, 2.35.

General Procedure for the Preparation of Enolates 8–14. Example: Tetracarbonyl(2-ethoxy-2-oxoethyl)(triphenylphosphine)rhenium (8). A 0.2 M solution of NaNp was generated by stirring (glass stirring bar) under Ar a solution of 1.28 g (9.99 mmol) of naphthalene and 420 mg (18.3 mg atom) of Na in 50 mL of THF for 1 h. A 100-mL Schlenk flask was charged with 1.92 g (3.00 mmol) of **6** and a glass stirbar and then degassed (two vacuum–Ar backfills). To the flask was added 25 mL of THF, and the solution was cooled to −78 °C (acetone/CO_2 bath). The NaNp solution was added by syringe until the green color of the NaNp persisted (ca. 30–35 mL was added). After 15 min, 500 μL (579 mg; 4.72 mmol) of ethyl chloroacetate was added by syringe. The resulting orange mixture was stirred for 1–2 h at −78 °C and then placed in a −20 °C freezer for 12 h. The flask was warmed to ambient temperature, and the reaction mixture was transferred to a separatory funnel with an equal volume of Et_2O. The organic layer was washed with 3 × 20 mL of H_2O to remove the NaX salts. The combined aqueous layers were extracted with 3 × 25 mL of Et_2O. The organic layers were combined, washed with 20 mL of saturated NaCl solution, dried over $MgSO_4$, and removed on a rotary evaporator to give 3.20 g of yellow residue. Purification of the residue by flash chromatography (97.5:2.5 CH_2Cl_2/Et_2O) gave 1.68 g (86%) of off-white solid, mp 111–112 °C, containing a 97:3 mixture of **8a** and **8b**. Data for cis isomer **8a**: IR (THF) 2090 (m), 1977 (sh), 1983 (vs), 1895 (m), 1693 (m) cm^{-1}; ^1H NMR (250 MHz; C_6D_6) δ 1.16 (t, 3, J = 7.1), 1.81 (d, 2, J = 6.9), 4.21 (q, 2, J = 7.1), 6.91–7.02 (m, 9), 7.43–7.51 (m, 6); ^{13}C NMR (75.5 MHz; $CDCl_3$) δ −1.45 (d, J = 5.4), 14.55, 58.65, 128.73 (d, J = 10.1), 130.81 (d, J = 1.9), 132.17 (d, J = 46.7), 133.23 (d, J = 10.8), 183.09 (d, J = 3.9), 186.42 (d, J = 7.0), 186.74 (d, J = 51.0), 189.39 (d, J = 9.6); ^{31}P NMR (82 MHz; $CDCl_3$) δ 9.5; MS (EI, 70 eV) m/z 649 (M^+), 561 (base). Anal. Calcd for $C_{26}H_{22}O_6PRe$: C, 48.22; H, 3.42. Found: C, 48.50; H, 3.52.

Tetracarbonyl[2-(1,1-dimethylethoxy)-2-oxoethyl](triphenylphosphine)rhenium (9). Reaction of 961 mg (1.50 mmol) of **6** and 450 μL (474 mg; 3.15 mmol) of *tert*-butyl chloroacetate by the foregoing method yielded 1.70 g of crude product. Flash chromatography (98:2 CH_2Cl_2/Et_2O) gave a 699-mg (69%) yield of off-white solid, mp 129–131 °C, containing a 95:5 mixture of **9a** and **9b**. Data for cis isomer **9a**: IR ($CHCl_3$) 2106 (s), 2008 (sh), 1988 (vs), 1947 (s), 1670 (m) cm^{-1}; ^1H NMR (250 MHz; C_6D_6) δ 1.60 (s, 9), 1.81 (d, 2, J = 7.3), 6.89–7.03 (m, 9), 7.44–7.52 (m, 6); ^{13}C NMR (75.5 MHz; $CDCl_3$) δ −0.08 (d, J = 5.8), 28.39, 77.62, 128.70 (d, J = 10.1), 130.75 (d, J = 2.0), 132.29 (d, J = 46.5), 133.24 (d, J = 10.8), 182.58 (d, J = 3.6), 186.38 (d, J = 6.6), 186.96 (d, J = 51.1), 189.54 (d, J = 9.7); ^{31}P NMR (121.5 MHz; $CDCl_3$) δ 9.2. Anal. Calcd for $C_{28}H_{26}O_6PRe$: C, 49.77; H, 3.88. Found: C, 50.04; H, 3.95.

Tetracarbonyl[2-(diethylamino)-2-oxoethyl](triphenylphosphine)rhenium (10). Reaction of 640 mg (1.00 mmol) of **6** and 250 μL (272 mg; 1.82 mmol) of 2-chloro-*N*,*N*-diethylacetamide[49] by the foregoing method yielded 1.09 g of crude product. Flash chromatography (2:1 CH_2Cl_2/Et_2O) gave 546 mg (81%) of white, crystalline product, mp 127–128 °C, containing a 97:3 mixture of **10a** and **10b**. Data for cis isomer **10a**: IR ($CHCl_3$) 2107 (m), 2003 (vs), 1982 (vs), 1943 (s), 1578 (w) cm^{-1}; ^1H NMR (250 MHz; C_6D_6) δ 0.87 (t, 3, J = 7.0), 1.16 (t, 3, J = 7.0), 1.80 (d, 2, J = 6.9), 3.08 (q, 2, J = 7.0), 3.43 (q, 2, J = 7.0), 6.89–7.04 (m, 9), 7.56–7.64 (m, 6); ^{13}C NMR (75.5 MHz; $CDCl_3$) δ 0.08 (d, J = 5.4), 13.45, 14.14, 39.54, 43.00, 128.68 (d, J = 10.0), 130.71 (d, J = 2.0), 132.19 (d, J = 46.3), 133.26 (d, J = 10.8), 182.35 (d, J = 4.2), 186.34 (d, J = 7.7), 187.48 (d, J = 48.6); ^{31}P NMR (82 MHz; $CDCl_3$) δ 9.1. Anal. Calcd for $C_{28}H_{27}NO_5PRe$: C, 49.85; H, 4.03; N, 2.08. Found: C, 49.95; H, 4.10; N, 2.04.

Tetracarbonyl(2-oxopropyl)(triphenylphosphine)rhenium (11). Reaction of 640 mg (1.00 mmol) of **6** and 160 μL (186 mg; 2.01 mmol) of chloroacetone by the foregoing method yielded 1.12 g of crude product. Flash chromatography (9:1 CH_2Cl_2/Et_2O) gave 509 mg (82%) of off-white solid, mp 134–136 °C dec, containing a 91:9 mixture of **11a** and **11b**. Data for cis isomer **11a**: IR ($CHCl_3$) 2102 (s), 2006 (vs), 1986 (vs), 1632 (m) cm^{-1}; ^1H NMR (250 MHz; C_6D_6) δ 2.02 (d, 2, J = 7.2), 2.09 (s, 3), 6.91–7.01 (m, 9), 7.43–7.51 (m, 6); ^{13}C NMR (75.5 MHz; $CDCl_3$) δ 16.33 (d, J = 4.5), 28.35 (s), 128.77 (d, J = 10.1), 130.89 (d, J = 2.1), 131.92 (d, J = 46.78), 133.18 (d, J = 10.8), 186.17 (d, J = 7.4), 187.43 (d, J = 49.9), 189.57 (d, J = 9.5), 213.24 (d, J = 4.1); ^{31}P NMR (121.5 MHz; $CDCl_3$) δ 9.0. Anal. Calcd for $C_{25}H_{20}O_5PRe$: C, 48.62; H, 3.26. Found: C, 48.39; H, 3.28.

Tetracarbonyl(2-phenyl-2-oxoethyl)(triphenylphosphine)rhenium (12). Reaction of 320 mg (0.50 mmol) of **6** and 125 mg (0.80 mmol) of 2-chloroacetophenone (in 1.0 mL of THF) by the foregoing method yielded 0.60 g of crude product. Flash chromatography (95:5 CH_2Cl_2/Et_2O) gave 273 mg (80%) of off-white solid, mp 135–137 °C dec, containing a 85:15 mixture of **12a** and **12b**. Data for cis isomer **12a**: IR ($CHCl_3$) 2104 (s), 2008 (sh), 1987 (vs), 1947 (s), 1662 (m) cm^{-1}; ^1H NMR (250 MHz; C_6D_6) δ 2.63 (d, 2, J = 6.8), 6.87–7.05 (m, 12), 7.48–7.56 (m, 6), 8.09–8.13 (m, 2); ^{13}C NMR (75.5 MHz; $CDCl_3$) δ 10.87 (d, J = 4.5), 127.50, 127.98, 128.80 (d, J = 10.1), 130.89 (d, J = 2.2), 131.10, 131.96 (d, J = 46.7), 133.20 (d, J = 10.8), 138.53, 185.97 (d, J = 7.5), 186.54 (d, J = 51.1), 189.41 (d, J = 9.4), 206.07 (d, J = 4.0); ^{31}P NMR (82 MHz; $CDCl_3$) δ 9.4. Anal. Calcd for $C_{30}H_{22}O_5PRe$: C, 53.01; H, 3.26. Found: C, 53.16; H, 3.39.

Tetracarbonyl(cyanomethyl)(triphenylphosphine)rhenium (13). Reaction of 320 mg (0.50 mmol) of **6** and 65 μL (78 mg; 1.03 mmol) of chloroacetonitrile by the foregoing method yielded 0.51 g of crude product. Flash chromatography (CH_2Cl_2) gave 171 mg (57%) of white solid, containing a 98:2 mixture of **13a** and **13b**. Data for cis isomer **13a**: IR ($CHCl_3$) 2208 (m), 2103 (s), 2012 (vs), 1989 (vs), 1948 (s) cm^{-1}; ^1H NMR (250 MHz; C_6D_6) δ 0.75 (d, 2, J = 7.0), 6.89–6.99 (m, 9), 7.30 (m, 6); ^{13}C NMR (75.5 MHz; $CDCl_3$) δ −31.18 (d, J = 6.2), 128.96 (d, J = 10.1), 130.13 (d, J = 3.3), 131.09 (d, J = 2.0), 131.51 (d, J = 47.6), 132.51 (d, J = 10.9), 185.60 (d, J = 50.2), 185.99 (d, J = 7.4), 188.22 (d, J = 9.6); ^{31}P NMR (121.5 MHz; $CDCl_3$) δ 10.4. Anal. Calcd for $C_{24}H_{17}NO_4PRe \cdot 0.2C_5H_{12}$: C, 48.82; H, 3.18; N, 2.28. Found: C, 48.82; H, 3.17; N, 2.30. (Prolonged evacuation did not remove 0.2 equiv of pentane, which was confirmed quantitatively by ^1H NMR spectroscopy.)

Tetracarbonyl(2-ethoxy-1-methyl-2-oxoethyl)(triphenylphosphine)rhenium (14). Reaction of 1.28 g (2.00 mmol) of **6** and 551 mg (2.20 mmol) of ethyl 2-[((trifluoromethyl)sulfonyl)oxy]propanoate by the foregoing method yielded 2.00 g of crude product. Flash chromatography (99:1 CH_2Cl_2/Et_2O) gave 997 mg (75%) of off-white solid, mp 113–114 °C, containing a 96:4 mixture of **14a** and **14b**. Data for cis isomer **14a**: IR ($CHCl_3$) 2102 (s), 2000 (sh), 1946 (s), 1673 (m) cm^{-1}; ^1H NMR (250 MHz; C_6D_6) δ 1.17 (t, 3, J = 7.1), 1.87 (d, 3, J = 6.8), 2.37 (dq, 1, J = 6.8, J_{PH} = 10.9), 4.10–4.37 (m, 2), 6.91–7.05 (m, 9), 7.53–7.62 (m, 6); ^{13}C NMR (75.5 MHz; $CDCl_3$) δ 10.97 (d, J = 5.3), 14.52, 23.21 (d, J = 0.9), 58.39, 128.63 (d, J = 10.0), 130.76 (d, J = 2.1), 132.22 (d, J = 46.5), 133.25 (d, J = 10.8), 184.74 (d, J = 2.3), 186.19 (d, J = 6.5), 187.37 (d, J = 51.2), 189.53 (d, J = 10.2), 190.05 (d, J = 9.6); ^{31}P NMR (82 MHz; $CDCl_3$) δ 9.5. Anal. Calcd for $C_{27}H_{24}O_6PRe$: C, 49.01; H, 3.66. Found: C, 49.14; H, 3.60.

***fac*-Tricarbonyl(2-ethoxy-2-oxoethyl)bis(triphenylphosphine)rhenium (15).** A solution of 33 mg (0.05 mmol) of **27** and 26 mg (0.10 mmol) of Ph_3P in 1.0 mL of C_6H_6 was allowed to stand for 18 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (98:2 CH_2Cl_2/Et_2O) to give 37 mg (84%) of white powder, mp 151–155 °C dec, that was identical (^1H NMR spectroscopy) with that observed in the reaction of **1** with Ph_3P. IR ($CHCl_3$): 2035

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(s), 1941 (2), 1898 (s), 1667 (m) cm^{-1}. ^1H NMR (250 MHz; C_6D_6): δ 1.20 (t, 3, J = 7.1), 1.80 (m, 2), 4.26 (q, 2, J = 7.1), 6.93–6.95 (m, 18), 7.48–7.56 (m, 12). ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 7.63 (t, J = 5.8), 14.67, 58.18, 128.16 (t, J = 4.7), 132.90 (t, J = 13.7), 133.46 (t, J = 13.8), 134.03 (t, J = 5.3), 183.75 (t, J = 3.9), 192.05 (t, J = 19.8), 192.63 (t, J = 23.9), 193.13 (t, J = 7.7). Anal. Calcd for $C_{43}H_{37}O_5P_2Re$: C, 58.56; H, 4.23. Found: C, 58.26; H, 4.29.

Tetracarbonyl(carboxymethyl)(triphenylphosphine)-rhenium (17). A 5-mL flask was charged with 135 mg (0.20 mmol) of **9** and 1.0 mL of CH_2Cl_2. The solution was concentrated under a stream of N_2 to 0.5 mL, and 23 μL (34 mg; 0.30 mmol) of CF_3CO_2H was added. After 2 days, TLC (9:1 CH_2Cl_2/Et_2O) indicated consumption of **9**. The reaction mixture was diluted with 5 mL of CH_2Cl_2 and washed with 2 × 2 mL of H_2O and 2 mL of saturated NaCl solution, dried over $MgSO_4$, and evaporated to give 99 mg (80%) of white solid, mp 174–176 °C dec. IR ($CHCl_3$): 2104 (s), 2011 (sh), 1987 (vs), 1946 (s), 1647 (m) cm^{-1}; ^1H NMR (250 MHz; C_6D_6): δ 1.77 (d, J = 6.7), 6.89–6.97 (m, 9), 7.38–7.47 (m, 6); ^{13}C NMR (75.5 MHz; CD_2Cl_2): δ −0.58 (d, J = 5.2), 129.12 (d, J = 10.1), 131.21 (d, J = 2.0), 132.50 (d, J = 46.9), 133.62 (d, J = 10.8), 186.93 (d, J = 7.0), 187.11 (d, J = 50.7), 189.75 (d, J = 10.4), 189.79 (d, J = 3.5); ^{31}P NMR (121.5 MHz; CD_2Cl_2): δ 9.6. Anal. Calcd for $C_{24}H_{18}O_6PRe$: C, 46.53; H, 2.93. Found: C, 46.68; H, 3.03.

***fac*-Tricarbonyl(2-ethoxy-2-oxoethyl)[1,2-bis(diphenylphosphino)ethane]rhenium (18). Method A.** In a 50-mL round-bottomed flask equipped with a reflux condenser and a magnetic stirrer was placed 216 mg (0.52 mmol) of **1**, 212 mg (0.53 mmol) of 1,2-bis(diphenylphosphino)ethane (dppe), and 20 mL of toluene. The solution was brought to reflux while a slow stream of N_2 was maintained over the solution. After the mixture was heated for 45 h, the toluene was removed under high vacuum. Pentane (20 mL) was added to the solid brown residue, and the white solid was collected on a fritted disk and washed with pentane to give 228 mg (58%) of off-white solid, mp 188–194 °C dec, that was >95% pure by ^1H and ^{13}C NMR spectroscopies. An analytical sample was obtained by flash chromatography (95:5 CH_2Cl_2/Et_2O). IR ($PhCH_3$): 2021 (s), 1942 (s), 1904 (m), 1679 (w) cm^{-1}. ^1H NMR (250 MHz; C_6D_6): δ 1.08 (m, 2), 1.23 (t, 3, J = 7.1), 2.13 (br m, 4), 4.24 (q, 2, J = 7.1), 6.94 (m, 8), 7.10 (m, 4), 7.57 (m, 8). ^{13}C NMR (75.5 MHz; C_6D_6): δ 2.11 (t, J = 4.0), 15.0, 27.8 (m), 58.1, 129.0 (m), 130.4, 131.5–132.6 (m), 135.7 (d, J = 46.2), 182.6 (t, J = 3.9), 191.6 (t, J = 6.2), 195.9 (dd, J = 9.5, 56.3). ^{31}P NMR (75.5 MHz; C_6D_6): δ 33.9. Anal. Calcd for $C_{33}H_{31}O_5P_2Re$: C, 52.45; H, 4.13. Found: C, 52.66; H, 4.47.

Method B. In a 5-mL, round-bottomed flask equipped with a reflux condenser and a magnetic stirrer was placed 453 mg (1.10 mmol) of **1** and 456 mg (1.10 mmol) of dppe, under N_2. The flask was placed in an oil bath maintained at 130–135 °C while a slow stream of N_2 was passed over the mixture. After the molten yellow mixture was heated for 12 h, the mixture was cooled to ambient temperature. The resulting brown solid was broken up with 20 mL of pentane, collected on a fritted disk, and dried in vacuo to give 712 mg (86%) of cream-colored solid that was identical (^1H NMR spectroscopy) with that prepared by method A.

***trans*-Dicarbonyl(ethyl 3-iminobutanoato-*N,O'*)bis(triphenylphosphine)rhenium (19). Method A.** In an NMR tube was placed 140 mg of **1** (0.34 mmol), 140 mg of Ph_3P (0.53 mmol), and 1 mL of CH_3CN. After the NMR tube was sealed with Parafilm, the tube was placed in an oil bath at 110 °C. After 1 day, crystals began to appear in the reaction mixture. After 6 days at 110 °C, 132 mg (44%) of light yellow crystals, mp 213–215 °C dec, was collected by filtration. The compound was judged to be >95% pure by ^1H and ^{13}C NMR spectroscopies. IR (THF): 1915 (s), 1834 (s), 1590 (m) cm^{-1}. ^1H NMR (300 MHz; C_6D_6; 75 °C): δ 0.86 (t, 3, J = 7), 3.45 (q, 2, J = 7), 4.05 (s, 1), 4.97 (br s, 1), 7.04 (m, 18), 7.83 (m, 12). ^{13}C NMR (75.5 MHz; C_6D_6; 75 °C): δ 14.6, 58.9, 78.7 (d, J = 5), 128.2 (t, J = 4.5), 129.4, 134.6 (t, J = 5.5), 135.2 (t, J = 21), 167.8, 168.3 (d, J = 5.5), 202.5 (t, J = 8), 204.5 (t, J = 8). ^{31}P NMR (121.5 MHz; C_6D_6; 75 °C): δ 29.1. MS (EI, 70 eV): m/z 898 (M^+), 185 (base). High-resolution mass spectrum: m/z 895.1988 (M^+) (calcd for $C_{44}H_{40}NO_4P_2Re$, 895.1990).

Method B. A solution of 165 mg (0.40 mmol) of **1**, 262 mg (1.00 mmol) of Ph_3P, and 250 μL (194 mg; 4.73 mmol) of CH_3CN in 5.0 mL of toluene was heated under N_2 at reflux for 2.5 days; the consumption of **1** was confirmed by TLC (98:2 CH_2Cl_2/Et_2O). When the reaction mixture was cooled to ambient temperature, a pale yellow powder separated from the solution. The solvent was concentrated slightly, and the solid was collected on a fritted disk, washed with a minimum of Et_2O and pentane, and dried in vacuo to give 256 mg of pale yellow powder. The filtrate was concentrated to ~0.5–1.0 mL, and Et_2O was added. Cooling to −20 °C for 8 h produced a second crop of yellow powder (43 mg), for an overall yield of 299 mg (84%), that was identical (^1H NMR spectroscopy) with that prepared by method A. Anal. Calcd for $C_{44}H_{40}NO_4P_2Re$: C, 59.09; H, 4.50; N, 1.57. Found: C, 58.85; H, 4.52; N, 1.65.

General Procedure for the Preparation of Nitrile Insertion Products 20–23. A solution of 0.10 mmol of **1** or **4** and 58 mg (0.22 mmol) of Ph_3P in 0.50 mL of the nitrile was placed in an NMR tube. The tube was capped, wrapped with Parafilm, and placed in an oil bath maintained at 120 °C for 3 days; crystals generally began to form in the tube after 2 days of heating. The tubes were allowed to stand at ambient temperature several hours or overnight. The tubes were then opened, and the solid was collected on a fritted disk, washed with hexane or pentane, and dried in vacuo to give analytically pure, crystalline solids.

***trans*-Dicarbonyl(ethyl 3-iminopentanoato-*N,O'*)bis(triphenylphosphine)rhenium (20).** Yield: 74 mg (81%) of yellow solid, mp 215–217 °C dec. IR (THF): 1915 (s), 1835 (s), 1593 (m) cm^{-1}. ^1H NMR (250 MHz; C_6D_6): δ 0.25 (t, 3, J = 7.6), 0.86 (t, 3, J = 7.1), 1.26 (q, 2, J = 7.6), 3.21 (q, 2, J = 7.1), 4.21 (d, 1, J = 1.7), 5.22 (br s, 1), 6.92–7.06 (m, 18), 7.85–7.92 (m, 12). ^{13}C NMR (75.5 MHz; C_6D_6; 40 °C): δ 10.60, 14.49, 34.50, 58.84, 77.49, 128.20 (t, J = 6.3), 129.39, 134.57 (t, J = 5.5), 135.08 (t, J = 21.0), 167.86, 172.96, 202.80 (t, J = 8.5), 204.65 (t, J = 8.6). ^{31}P NMR (121.5 MHz; C_6D_6): δ 30.3. Anal. Calcd for $C_{45}H_{42}NO_4P_2Re$: C, 59.46; H, 4.66; N, 1.54. Found: C, 59.62; H, 4.52; N, 1.64.

***trans*-Dicarbonyl(ethyl 3-imino-4-methylpentanoato-*N,O'*)bis(triphenylphosphine)rhenium (21).** Yield: 72 mg (78%) of yellow solid, mp 199–203 °C dec. IR ($CHCl_3$): 1964 (s), 1829 (s), 1600 (m) cm^{-1}. ^1H NMR (250 MHz; C_6D_6): δ 0.32 (d, 6, J = 6.9), 0.83 (t, 3, J = 7.1), 1.50 (septet, 1, J = 6.9), 2.90 (q, 2, J = 7.1), 4.30 (d, 1, J = 1.9), 5.45 (br s, 1), 6.92–7.07 (m, 18), 7.89–7.96 (m, 12). ^{13}C NMR (75.5 MHz; C_6D_6; 75 °C): δ 14.36, 20.27, 39.71, 58.76, 76.77, 128.23 (t, J = 8.6), 129.38, 134.64 (t, J = 5.4), 135.45 (t, J = 20.6), 168.44, 177.01, 197.94, 204.79. ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 29.8. Anal. Calcd for $C_{46}H_{44}NO_4P_2Re$: C, 59.86; H, 4.80; N, 1.52. Found: C, 59.63; H, 4.78; N, 1.54.

***trans*-Dicarbonyl(ethyl 3-imino-3-phenylpropanoato-*N,O'*)bis(triphenylphosphine)rhenium (22).** Yield: 43 mg (45%) of yellow-orange solid, mp 214–219 °C dec. IR (THF): 1919 (s), 1840 (s), 1596 (m) cm^{-1}. ^1H NMR (300 MHz; C_6D_6; 70 °C): δ 0.88 (t, 3, J = 7.1), 3.33 (q, 2, J = 7.1), 4.63 (d, 1, J = 2.1), 5.67 (br s, 1), 6.56–6.58 (m, 2), 6.86–7.05 (m, 21), 7.84–7.90 (m, 12). ^{13}C NMR (75.5 MHz; C_6D_6; 30 °C): δ 14.40, 59.13, 78.47, 125.77, 127.87, 128.10, 128.44 (t, J = 5.9), 129.40, 134.50 (t, J = 5.5), 134.87 (t, J = 21.0), 143.36, 168.20, 169.04, 196.57, 202.81 (t, J = 8.3). ^{31}P NMR (121.5 MHz; C_6D_6): δ 30.1. Anal. Calcd for $C_{49}H_{42}NO_4P_2Re$: C, 61.50; H, 4.12; N, 1.46. Found: C, 61.68; H, 4.18; N, 1.72.

***trans*-Dicarbonyl(ethyl 3-imino-2-methylpentanoato-*N,O'*)bis(triphenylphosphine)rhenium (23).** Yield: 74 mg (80%) of yellow solid, mp 200–204 °C dec. IR ($CHCl_3$): 1910 (s), 1824 (s), 1598 (m) cm^{-1}. ^1H NMR (250 MHz; C_6D_6): δ 0.17 (t, 3, J = 7.5), 0.87 (t, 3, J = 7.1), 1.17 (q, 2, J = 7.6), 1.61 (s, 3), 3.21 (q, 2, J = 7.1), 5.40 (br s, 1), 6.92–7.06 (m, 18), 7.85–7.91 (m, 12). ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 9.06, 12.08, 14.29, 32.05, 58.59, 80.87, 127.72 (t, J = 4.4), 129.10, 134.06 (t, J = 5.5), 134.31 (t, J = 21.0), 164.59, 171.51, 202.80 (t, J = 7.9), 204.58 (t, J = 7.9). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 27.9. Anal. Calcd for $C_{46}H_{44}NO_4P_2Re \cdot 0.3C_3H_5N$: C, 59.97; H, 4.89; N, 1.98. Found: C, 59.82; H, 4.87; N, 2.23. (Prolonged evacuation of the sample did not remove 0.3 equiv of propionitrile, which was confirmed by ^1H NMR spectroscopy.)

***trans*-Dicarbonyl(4-imino-2-pentanonato-*N,O*)bis(triphenylphosphine)rhenium (24).** To a stirred solution of 62 mg (0.10 mmol) of **11** and 39 mg (0.15 mmol) of Ph_3P in 1.5 mL of CH_3CN was added a solution of 8 mg (0.11 mmol) of Me_3NO in 2.5 mL of CH_3CN. The solution was allowed to stand for 1 h and then was heated in an oil bath maintained at 80 °C for 6

h, resulting in the precipitation of a light yellow solid. The reaction mixture was cooled to ambient temperature, and the solid was collected on a fritted disk, washed with a minimum amount of Et_2O and pentane, and dried in vacuo to give 64 mg (74%) of light yellow powder, mp 210–213 °C dec. IR ($CHCl_3$): 1911 (s), 1823 (s), 1592 (m) cm^{-1}. ^1H NMR (250 MHz; C_6D_6): δ 0.84 (s, 2), 1.41 (s, 3), 4.22 (d, 1, J = 2.1), 5.68 (br s, 1), 6.92–7.05 (m, 18), 7.80–7.88 (m, 12). ^{13}C NMR (75.5 MHz; C_6D_6; 35 °C): δ 26.54, 27.75, 96.48, 127.79 (t, J = 4.5), 129.14, 134.21 (t, J = 5.6), 134.30 (t, J = 21.0), 164.82, 177.42 (the almost complete insolubility of **24** in all solvents prevented the observation of the CO ligands). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 25.8. Anal. Calcd for $C_{43}H_{38}NO_3P_2Re$: C, 59.71; H, 4.43; N, 1.62. Found: C, 59.63; H, 4.42; N, 1.77.

***trans*-Dicarbonyl(3-imino-1-phenyl-1-butanonato-*N*,*O*)-bis(triphenylphosphine)rhenium (25).** To a stirred solution of 61 mg (0.09 mmol) of **12** and 37 mg (0.14 mmol) of Ph_3P in 1.0 mL of CH_3CN was added a solution of 8 mg (0.11 mmol) of Me_3NO in 2.0 mL of CH_3CN, resulting in the intermediate color change of the solution to yellow-orange. The solution was allowed to stand for 1 h and then was heated in an oil bath maintained at 80 °C for 8 h, yielding an orange precipitate. The reaction mixture was cooled to ambient temperature, and the solid was collected on a fritted disk, washed with a minimum amount of Et_2O and pentane, and dried in vacuo to give 57 mg (69%) of orange powder, mp 209–212 °C dec. IR ($CHCl_3$): 1913 (s), 1828 (s), 1597 (w), 1578 (w) cm^{-1}. ^1H NMR (250 MHz; C_6D_6): δ 0.88 (s, 3), 4.90 (d, 1, J = 1.8), 5.96 (br s, 1), 6.89–7.01 (m, 18), 7.05–7.11 (m, 3), 7.45–7.49 (m, 2), 7.78–7.85 (m, 12). ^{13}C NMR (75.5 MHz; $CDCl_3$; 30 °C): δ 28.23, 94.53 (d, J = 1.6), 126.37, 127.08, 127.81 (t, J = 4.4), 128.39, 129.11, 134.12 (t, J = 5.4), 134.15 (t, J = 21.1), 140.42, 165.48, 171.66, 202.48 (t, J = 8.1), 204.34 (t, J = 9.0). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 25.1. Anal. Calcd for $C_{48}H_{40}NO_3P_2Re$: C, 62.19; H, 4.35; N, 1.51. Found: C, 61.85; H, 4.33; N, 1.63.

***trans*-Dicarbonyl[3-imino-1-(diethylamino)-1-butanona-to-*N*,*O*]bis(triphenylphosphine)rhenium (26).** To a stirred solution of 54 mg (0.08 mmol) of **10** and 35 mg (0.13 mmol) of Ph_3P in 1.0 mL of CH_3CN was added a solution of 7 mg (0.09 mmol) of Me_3NO in 1.6 mL of CH_3CN. The solution was allowed to stand for 1 h and then was heated in an oil bath maintained at 80 °C for 12 h, resulting in the precipitation of a yellow solid. The reaction mixture was cooled to ambient temperature, and the solid was collected on a fritted disk, washed with a minimum amount of Et_2O and pentane, and dried in vacuo to give 60 mg (81%) of yellow powder, mp 195–199 °C dec. IR ($CHCl_3$): 1903 (s), 1818 (s), 1584 (m) cm^{-1}. ^1H NMR (250 MHz; C_6D_6): δ 0.57 (t, 6, J = 7.0), 1.00 (s, 3), 2.78 (q, 4, J = 7.0), 3.72 (s, 1), 4.57 (br s, 1), 6.95–7.08 (m, 18), 7.86–7.90 (m, 12). ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 13.71, 28.42, 40.03, 77.24, 127.68 (t, J = 4.3), 128.87, 134.17 (t, J = 5.4), 134.67 (t, J = 20.8), 163.66, 164.10, 202.61 (t, J = 8.1), 204.88 (t, J = 8.5). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 25.9. Anal. Calcd for $C_{46}H_{45}N_2O_3P_2Re$: C, 59.92; H, 4.92; N, 3.04. Found: C, 59.54; H, 5.03; N, 3.20.

***fac*-(Acetonitrile)tricarbonyl(2-ethoxy-2-oxoethyl)(tri-phenylphosphine)rhenium (27).** To a stirred solution of 648 mg (1.00 mmol) of **8** in 30 mL of CH_3CN was added a solution of 79 mg (1.05 mmol) of Me_3NO in 10 mL of CH_3CN. After 1 h at ambient temperature, IR spectroscopy confirmed consumption of **8**. The solution was concentrated with a rotary evaporator to a clear, glassy residue, which yielded white crystals upon adding hexane and cooling to −20 °C. The solid was collected on a fritted disk, washed with a minimum of pentane, and dried in vacuo to give 653 mg (99%) of white solid, dec pt >130 °C. IR (CH_3CN): 2028, 1928, 1896, 1673 (m) cm^{-1}. ^1H NMR (250 MHz; C_6D_6): δ 0.56 (d, 3, J = 1.2), 1.28 (t, 3, J = 7.1), 1.80 (*ABX* (X = ^{31}P), 2, ν_{AB} = 261.6, J_{AB} = −7.5, J_{AX} = 5.7, J_{BX} = 8.0), 4.29 (q, 2, J = 7.1), 6.90–7.02 (m, 9), 7.62–7.70 (m, 6). ^{13}C NMR (75.5 MHz; C_6D_6): δ 1.63, 10.08 (d, J = 5.9), 15.20, 58.13, 120.57, 128.63 (d, J = 9.6), 130.20, 132.90 (d, J = 42.9), 134.15 (d, J = 10.7), 182.51 (d, J = 4.2), 192.26 (d, J = 6.8), 193.58 (d, J = 65.3), 197.35 (d, J = 8.8). ^{31}P NMR (121.5 MHz; C_6D_6): δ 19.7. MS (CI): m/z 661 (M^+), 185 (base). Anal. Calcd for $C_{27}H_{25}NO_5PRe$: C, 49.09; H, 3.81; N, 2.12. Found: C, 48.88; H, 3.82; N, 1.99.

***fac*-Tricarbonyl(ethyl 3-iminobutanoato-*N*,*O*')(triphe-nylphosphine)rhenium (28).** A resealable pressure bottle was charged with 66 mg (0.10 mmol) of **27**, 50 μL (38 mg; 0.94 mmol) of CH_3CN, a stirbar, and 5.0 mL of C_6H_6. The bottle was placed in an oil bath maintained at 70 °C for 7 h. The reaction mixture was cooled, and the bottle was opened under a stream of CO admitted by a syringe needle. The needle was then placed in the solution, and CO was bubbled through the solution for 5 min. The bottle was resealed and returned to the oil bath for 18 h. The solvent was removed under reduced pressure, and the resulting residue was purified by flash chromatography (1.5:1 C_6H_6/hexane that had been saturated with N_2) to give 23 mg (35%) of cream-colored solid, mp 187–190 °C dec. IR ($CHCl_3$): 2040 (vs), 1927 (vs), 1884 (vs), 1602 (s) cm^{-1}. ^1H NMR (250 MHz; C_6D_6): δ 0.92 (t, 3, J = 7.1), 1.10 (s, 3), 3.50–3.87 (m, 2), 4.32 (d, 1, J = 2.0), 4.90 (br s, 1), 6.96–7.00 (m, 9), 7.53–7.61 (m, 6). ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 14.63, 27.93, 59.63, 77.59, 128.33 (d, J = 9.4), 130.12 (d, J = 1.9), 131.21 (d, J = 41.5), 133.92 (d, J = 10.7), 168.24, 170.46, 191.99 (d, J = 82.2), 196.02 (d, J = 7.0), 196.70 (d, J = 8.2). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 21.4. Anal. Calcd for $C_{27}H_{25}NO_5PRe$: C, 49.09; H, 3.81; N, 2.12. Found: C, 49.09; H, 3.87; N, 2.12.

***fac*-(Acetonitrile)tricarbonyl(cyanomethyl)(triphenyl-phosphine)rhenium (35).** By a method identical with that used for the preparation of **27**, reaction of 120 mg (0.20 mmol) of **13** and 16 mg (0.21 mmol) of Me_3NO in 10 mL of CH_3CN gave an off-white residue, which crystallized upon addition of Et_2O. The cream-colored solid was collected on a fritted disk, washed with a minimum of pentane, and dried in vacuo to give 113 mg (92%) of pure product, dec pt >137 °C. ^1H NMR (250 MHz; C_6D_6): δ 0.74 (d, 3, J = 1.2), 0.80–0.90 (m, 1), 1.45–1.54 (m, 1), 6.89–7.00 (m, 9), 7.53–7.61 (m, 6). ^{13}C NMR (75.5 MHz; $CDCl_3$): δ −21.19 (d, J = 6.9), 3.66, 120.34, 128.57 (d, J = 9.7), 130.32 (d, J = 1.7), 130.88 (d, J = 2.9), 131.63 (d, J = 43.6), 133.53 (d, J = 10.7), 191.14 (d, J = 7.9), 191.15 (d, J = 63.7), 195.39. ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 19.8. Anal. Calcd for $C_{25}H_{20}N_2O_3PRe$: C, 48.93; H, 3.29; N, 4.57. Found: C, 49.15; H, 3.51; N, 4.45.

***fac*-(Acetonitrile)tricarbonyl(2-ethoxy-1-methyl-2-oxo-ethyl)(triphenylphosphine)rhenium (36).** By a method identical with that for **27**, reaction of 666 mg (1.01 mmol) of **14** and 78 mg (1.04 mmol) of Me_3NO gave an off-white syrup. Repeated trituration with hexane yielded an off-white solid, which was collected on a fritted disk, washed with a minimum of pentane, and dried in vacuo to give 644 mg (95%) of pure product, dec pt >100 °C, as a ~60:40 mixture of two diastereomers that were not separated. IR (CH_3CN): 235 (m), 2030, 1928, 1895 (vs), 1685 (m) cm^{-1}. ^1H NMR (250 MHz; C_6D_6): major diastereomer, δ 0.73 (d, 3, J = 1.3), 1.19 (t, 3, J = 7.1), 2.24 (d, 3, J = 6.5), 2.58–2.69 (m, 1), 4.02–4.16 (m, 2), 6.91–7.06 (m, 9), 7.64–7.77 (m, 6); minor diastereomer, δ 0.28 (d, 3, J = 1.0), 1.40 (t, 3, J = 7.1), 1.42 (d, 3, J = 6.8), 3.02–3.23 (m, 1), 4.42–4.58 (m, 2), 6.91–7.06 (m, 9), 7.64–7.77 (m, 6). ^{13}C NMR (75.5 MHz; $CDCl_3$): major diaste-reomer, δ 3.41, 14.67, 19.50 (d, J = 5.3), 22.29 (d, J = 2.1), 57.70, 119.69, 128.29 (d, J = 9.5), 130.06, 132.07 (d, J = 42.6), 133.74 (d, J = 10.4), 183.71 (d, J = 2.0), 191.61 (d, J = 7.1), 192.98 (d, J = 64.8), 197.00 (d, J = 7.9); minor diastereomer, δ 2.82, 14.84, 15.24 (d, J = 5.6), 18.49 (d, J = 1.3), 57.98, 119.47, 128.32 (d, J = 9.6), 130.06, 132.49 (d, J = 42.5), 133.74 (d, J = 9.7), 185.44 (d, J = 2.7), 191.25 (d, J = 6.3), 192.86 (d, J = 65.2), 196.21 (d, J = 8.8). ^{31}P NMR (82 MHz; $CDCl_3$): δ 19.3. Anal. Calcd for $C_{28}H_{27}NO_5PRe$: C, 49.85; H, 4.03; N, 2.08. Found: C, 49.67; H, 4.11; N, 1.97.

***fac*-Tricarbonyl[2-(diethylamino)-2-oxoethyl](tri-phenylphosphine)rhenium (41).** By a method identical with that for **27**, reaction of 337 mg (0.50 mmol) of **10** and 41 mg (0.55 mmol) of Me_3NO in 25 mL of CH_3CN gave a clear, glassy residue. Repeated trituration of the residue with hexane gave an off-white solid. The solid was collected on a fritted disk, washed with a minimum of pentane, and dried in vacuo to give 306 mg (95%) of off-white powder, mp 150–153 °C dec. IR (C_6H_6): 2018 (vs), 1909 (vs), 1870 (vs), 1551 (m) cm^{-1}. ^1H NMR (250 MHz; C_6D_6): δ 0.38 (t, 3, J = 7.2), 0.58 (t, 3, J = 7.2), 0.93–1.03 (m, 1), 1.73–1.81 (m, 1), 2.39 (q, 2, J = 7.2), 2.47–2.68 (m, 2), 6.93–7.10 (m, 9), 7.59–7.67 (m, 6). ^{13}C NMR (75.5 MHz; $CDCl_3$) δ −1.00 (d, J = 4.1), 12.92, 13.11, 37.93, 40.52, 128.24 (d, J = 9.4), 130.02 (d, J = 1.8), 131.87 (d, J = 41.5), 134.22 (d, J = 10.8), 187.55 (d, J = 0.9), 196.13 (d, J = 7.2), 197.70 (d, J = 63.3), 199.51 (d, J = 7.6). ^{13}P NMR (121.5 MHz; $CDCl_3$): δ 22.8. Anal. Calcd: C, 50.15; H, 4.21; N, 2.17. Found: C, 50.16; H, 4.40; N, 2.51.

Kinetics. Nitrile Insertion. A 2.00×10^{-2} M solution of **27** was prepared by dissolving 66 mg (1.00×10^{-1} mmol) of **27** and 15 mg of acenaphthene (internal standard) in C_6D_6 to attain a final volume of 5.00 mL. Each kinetic run was performed by withdrawing a 0.50-mL aliquot of the stock solution, adding a known volume of CD_3CN via a pipet, and then placing the solution in an NMR tube. The tube was frozen at −196 °C and sealed under vacuum. The tubes were heated in a constant-temperature bath maintained at 80 ± 0.2 °C, and the disappearance of **27** was monitored by ^1H NMR spectroscopy at 300 MHz. Each spectrum was obtained with four scans, allowing an appropriately long (60-s) delay time between each scan. Integration of the 2.30–2.35 ppm multiplet vs the 3.08 ppm singlet of acenaphthene gave the relative concentration of **27**. Standard least-squares analysis of the data obtained afforded k_{obs} for each run (Table III).

Reaction of 27 with Ph_3P-d_{15}. A 4.01×10^{-1} M stock solution of **27** was prepared by dissolving 53 mg (8.02×10^{-2} mmol) of **27** and 12.0 mg (7.78×10^{-2} mmol) of acenaphthene (internal standard) in C_6D_6 to attain a final volume 2.00 mL. A 1.60 M stock solution of Ph_3P-d_{15} was prepared by dissolving 444 mg (1.60 mmol) of Ph_3P-d_{15}[50] in C_6D_6 to attain a final volume of 1.00 mL. This solution was used to prepare solutions of 8.00×10^{-1} and 4.00×10^{-1} M by successive dilution of 0.50-mL aliquots of the 1.60 and 8.00×10^{-1} M solutions to 1.00 mL. Each kinetic run was performed by transferring a 0.25-mL aliquot of the solution of **27** to septum-capped NMR tube and adding a 0.25-mL aliquot of 8.00×10^{-1} or 4.00×10^{-1} M Ph_3P-d_{15} solution by syringe. The solutions were mixed quickly, and the tube was immediately placed in the NMR probe maintained at 25 ± 0.5 °C. The initial spectrum was obtained after allowing temperature stabilization of the solution. All spectra were obtained at 300 MHz with one scan at appropriate time intervals and were analyzed identically with those above. Rate constants are given in Table IV.

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Registry No. **1**, 96413-81-9; **2**, 104067-89-2; **3**, 124342-53-6; **4**, 124342-54-7; **5**, 14220-21-4; **6**, 15259-18-4; **7**, 124378-87-6; **8a**, 96413-82-0; **8b**, 124378-88-7; **9a**, 124342-55-8; **9b**, 124378-89-8; **10a**, 124342-56-9; **10b**, 124378-90-1; **11a**, 124342-57-0; **11b**, 124378-91-2; **12a**, 124342-58-1; **12b**, 124378-92-3; **13a**, 124342-59-2; **13b**, 124378-93-4; **14a**, 124342-60-5; **14b**, 124378-94-5; **15**, 124342-61-6; **17**, 124342-62-7; **18**, 124342-63-8; **19**, 96427-38-2; **20**, 124342-64-9; **21**, 124342-65-0; **22**, 124342-66-1; **23**, 124354-99-0; **24**, 124342-67-2; **25**, 124342-68-3; **26**, 124342-69-4; **27**, 124342-70-7; **28**, 124342-71-8; **35**, 124342-72-9; **36**, 124342-73-0; **41**, 124342-74-1; $TfOCH(CH_3)CO_2Et$, 77902-90-0; $Re_2(CO)_{10}$, 14285-68-8; $MsOCH(CH_3)CO_2Et$, 58742-64-6; CH_3CH_2CN, 107-12-0; CH_3CN, 75-05-8; $(CH_3)_2CHCN$, 78-82-0; C_6H_5CN, 100-47-0; trifluoromethanesulfonic anhydride, 358-23-6; ethyl lactate, 97-64-3; ethyl chloroacetate, 105-39-5; chloroacetone, 78-95-5; 2-chloroacetophenone, 532-27-4; *tert*-butyl chloroacetate, 107-59-5; 2-chloro-*N*,*N*-diethylacetamide, 2315-36-8; chloroacetonitrile, 107-14-2.

Insertion, H/D Exchange, and σ-Bond Metathesis Reactions of Acetylene with Cl_2ScH

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Correlated ab initio theoretical calculations at the valence double-ζ plus polarization level are used to study reaction paths for the reaction of acetylene with Cl_2ScH. The paths studied are the classic insertion pathway and two σ-bond metathesis pathways, one resulting in H/D exchange and the other resulting in formation of a scandium acetylide. The insertion process is calculated to have a barrier of 6.3 kcal/mol with respect to the complexed acetylene (−9.1 kcal/mol with respect to free acetylene) and to be 36.5 kcal/mol exothermic with respect to free acetylene. The direct H/D exchange reaction is calculated to have a barrier of 13.7 kcal/mol with respect to free acetylene. The acetylide-forming reaction is calculated to have a barrier of 6.2 kcal/mol with respect to free acetylene and to be 15.2 kcal/mol exothermic with respect to free acetylene. Given the reversibility of this reaction, H/D exchange could occur through sequential formation and reduction of the acetylide complex. The insertion pathway is the only one calculated to proceed through a metal acetylene complex. The two σ-bond metathesis pathways are each calculated to proceed through a direct interaction with the Sc–H bond. In addition, the overall reaction energetics are calculated for the insertion and acetylide formation reactions of Cl_2ScCH_3 with acetylene. In contrast to the hydride reactions, the insertion and acetylide formation reactions for the methyl complex are found to be equivalently exothermic. The insertion reaction is calculated to be 39.1 kcal/mol exothermic and the acetylide formation reaction is calculated to be 40.9 kcal/mol exothermic.

Introduction

The activation of carbon–carbon and carbon–hydrogen bonds of saturated and unsaturated hydrocarbons by transition metals is a major goal of experimental organometallic chemistry.[1-6] This activation would provide synthetic organic chemists with a new array of reagents for selective syntheses as well as providing new schemes for the upgrading of fuel stocks. There have been recent successes in the activation of carbon–hydrogen bonds.[1,2] For example, degenerate methane exchange or σ-bond

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