Preparation of Cyclopentadienyltricarbonylrhenium Complexes Using a Double Ligand-Transfer Reaction

Todd W. Spradau and John A. Katzenellenbogen*

Department of Chemistry, University of Illinois, 600 South Mathews Avenue, Urbana, Illinois 61801

Received November 17, 1997

A unique double ligand-transfer reaction is described for the preparation of substituted cyclopentadienyltricarbonylrhenium complexes. In the reaction, potassium perrhenate(VII) is reduced and carbonylated by treatment with chromium trichloride and chromium hexacarbonyl to provide a proposed alkoxy carbonyl rhenium(I) intermediate. It is believed that this intermediate then undergoes a Cp ligand-transfer reaction with an acyl-substituted ferrocene to provide the corresponding (acyl-cyclopentadienyl)tricarbonylrhenium complex. A strongly coordinating solvent such as methanol is necessary to promote the reduction of perrhenate, and a carbonyl substituent conjugated to the Cp ring is necessary to activate it for transfer from iron to rhenium. This method has potential value for the synthesis of rhenium and technetium organometallic radiopharmaceuticals.

Introduction

A wide variety of radioactive isotopes are used for imaging or therapy in nuclear medicine.[1,2] By far, the most widely used radioisotope for imaging is Tc-99m (γ, $t_{1/2} = 6$ h); it is used in more than 80% of all nuclear medicine procedures.[3] For therapy, two isotopes of rhenium, Re-186 (β, $t_{1/2} = 91$ h) and Re-188 (β, $t_{1/2} = 17$ h), have shown great promise.[4−6] Because the physical properties of rhenium and technetium complexes are so similar, it has been proposed that the progress of a Re-186 treatment regimen could be monitored by imaging with the Tc-99m analogue of the rhenium compound used for the therapy.[7]

Despite the importance of Tc-99m to nuclear medicine, the chemistry of technetium is still relatively underdeveloped.[8] This can be attributed to the absence of any stable isotopes of technetium, and with respect to Tc-99m in particular, to the fact that standard Tc-99m generators produce this element in its highest oxidation state as pertechnetate, $^{99m}Tc(VII)O_4^-$. Therefore, all Tc-99m radiopharmaceuticals must be produced from this chemical form. The same holds true for the radioisotopes Re-186 and Re-188, which are available only as perrhenate, $Re(VII)O_4^-$.

Most, if not all, Tc-99m radiopharmaceuticals contain a polar Tc(V) oxo core (Figure 1), which is readily accessible from pertechnetate via $SnCl_2$ reduction followed by ligand exchange with a suitable chelate system. Because of the difficulty of controlling the reduction of $^{99m}TcO_4^-$ to a precursor in a suitably low oxidation state, few organometallic Tc radiopharmaceuticals exist—the most important being Tc(I)-99m-$(MIBI)_6^+$ (MIBI = 2-methoxyisobutylisonitrile), which has a variety of uses, among them heart imaging.[3]

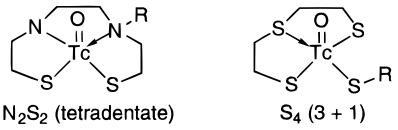
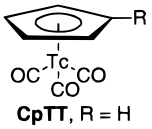


Figure 1. Common Tc-99m chelate systems.

An organometallic Tc complex which has intriguing potential for the development of Tc-99m imaging agents is cyclopentadienyltricarbonyltechnetium (CpTT). This



compound has a lipophilic core of high chemical stability and can be readily derivatized with substituents (R) connected to the Cp ring (e.g., for attaching Tc-99m-CpTT to a bioactive molecule). The goal of the present work was to find a convenient and efficient method for preparing Tc(I)-99m-CpTT complexes from Tc(VII)-99m-pertechnetate.

A major step toward an effective synthesis of Tc(I)-99m-CpTT was taken by Martin Wenzel, who in 1992 reported the transformation depicted in Scheme 1.[9] This reaction accomplished in one pot, the reduction, carbonylation, and cyclopentadienylation of $^{99m}TcO_4^-$ in a rapid and relatively mild manner. This transformation will be referred to as a double ligand-transfer (DLT) reaction, because two different ligands, Cp and CO, from two different metal atoms, Fe and Mn, were transferred

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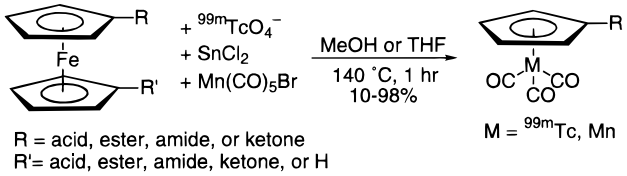
S0276-7333(97)01018-2 CCC: $15.00
Publication on Web 04/17/1998

Scheme 1. Double Ligand-Transfer (DLT) Reaction To Form CpTT

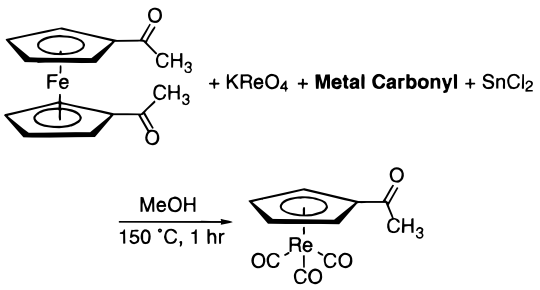


to a third metal atom, Tc. To our knowledge, this represents the first and only three metal/two ligand exchange reaction to be reported.[10−17]

Prior methods for the synthesis of CpTT from TcO_4^- required a time-consuming initial reduction/carbonylation reaction at extreme temperatures and CO pressures to produce $Tc_2(CO)_{10}$ or a related species,[18−20] followed by another step or steps to introduce the Cp ring. Recently, two new methods for the reduction/carbonylation of pertechnetate and perrhenate have appeared. These methods utilize the Lewis acidic hydride reagents BH_3/THF and DIBAL-H, respectively, to reduce $Tc(VII)O_4^-$ under milder conditions.[21,22] Whether such procedures could be used for the preparation of substituted Tc-99m CpTT compounds is still unknown, and the Wenzel procedure represents the only published method for the production of these complexes.

Wenzel's original DLT reaction did, however, suffer from the drawback that the ring-substituted manganese analogue of the desired CpTT compound was produced as a byproduct in the reaction (Scheme 1, M = Mn). This contaminant was present in large excess compared to the trace amount of Tc-99m-CpTT produced and because the two compounds were not readily separable, the resulting radioligand had a very low effective specific activity.[23] This limits the usefulness of Wenzel's DLD reaction for the preparation of Tc-99m agents for receptor-based imaging, where high specific activities are essential; the Mn-containing impurity could compete with its Tc-99m congener for binding sites in a target tissue and thereby substantially diminish its uptake. In Wenzel's hands the replacement of the manganese component in the reaction by other carbonyl donors, such as $Fe_2(CO)_9$, $[CpFe(CO)_2]_2$, sodium formate, or oxalic acid, led to unacceptably low product yields.[9]

Table 1. Use of Various Metal Carbonyls in the DLT Reaction



metal carbonyl	% yield[a]
$Mn(CO)_5Br$	53
$Cr(CO)_6$, $Mo(CO)_6$ or $W(CO)_6$	45
$Fe(CO)_5$	20
$[Rh(CO)_2Cl]_2$ or $Na(diglyme)_2V(CO)_6$	5
others[b]	0

[a] Isolated yields. [b] Others: $[CpFe(CO)_2]_2$, oxalic acid, $Co_2(CO)_8$, $[Ru(CO)_3Cl_2]_2$, $(Ph_3P)_2Ni(CO)_2$, $Mn_2(CO)_{10}$, $(Piperidine)_2Mo(CO)_4$, or $Ru_3(CO)_{10}$.

Results

Our initial attempts to modify and optimize the DLT reaction also focused on carbonyl donors other than $Mn(CO)_5Br$, but reactions were performed with rhenium instead of technetium to avoid unnecessary handling of radioactivity. A broad survey of commercially available metal carbonyls was, therefore, undertaken to assess their ability to act as CO donors to rhenium in the DLT reaction. Table 1 summarizes the results of this investigation. Although none of the reagents tested performed as well as $Mn(CO)_5Br$, the group VI metal carbonyls provided reasonable yields of acetyl-CpTR and more importantly allowed its simple purification via column chromatography. These reactions also demonstrated, for the first time, that the double ligand-transfer reaction could be done with perrhenate as well as pertechnetate.

We next chose to investigate the role of $SnCl_2$ in the reaction and whether higher product yields could be attained with other metal halide reducing agents. Table 2 shows that the best reagents again came from group VI and that the use of $CrCl_3$ instead of $SnCl_2$ more than doubled the product yield. The success of the group VI chlorides can be attributed to the wide variety of stable oxo complexes, including oxo chlorides, known for those metals, which could be produced during their reactions with ReO_4^-.

It is noteworthy that the reaction proceeded even in the absence of $SnCl_2$ or any other metal halide and that the inclusion of some metal halides actually had a detrimental effect on the reaction, in some cases preventing the formation of any acetyl-CpTR at all. It appears that $Cr(CO)_6$ alone could (inefficiently) reduce and carbonylate ReO_4^-, perhaps via the formation of CO_2 and/or an oxide of chromium, but we did not search for such oxidation products. The reagents that inhibited the transformation likely underwent nonproductive side reactions. For instance, it is known that $RuCl_3$ reacts with ferrocene to produce ruthenocene.[24,25] This could

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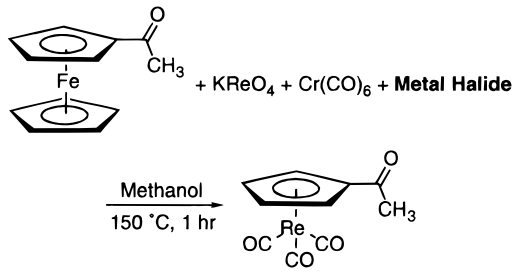
Table 2. DLT Reaction with Various Metal Halides



metal halide	% yield
none	5[b]
$SnCl_2$	36[b]
$CrCl_3$	83[a] (75)[b]
CrI_3 or MoI_2	10[b]
$CrCl_2$	65[b]
WCl_4	59[b]
$FeCl_2$	40[b]
VCl_3	14[b]
$RuCl_3$, SmI_2, CrF_2, or Cobaltocene	0

[a] Yield estimated based on ^{1}H NMR integration of partially purified product (see Experimental Section). [b] Isolated yield.

inhibit ring transfer to rhenium, as ruthenocene is thermodynamically more stable than ferrocene.[25,26]

The reaction schemes in Tables 1 and 2 reveal that both mono, and 1,1′-diacetylferrocene could be used in the reaction to generate approximately equal yields of acetyl-CpTR. Interestingly, with monoacetylferrocene, only the substituted ring was transferred to rhenium and no unsubstituted CpTR was observed. In fact, CpTR itself has never been detected as a product in the double ligand-transfer reaction when ferrocene, or a monosubstituted derivative thereof, was used as the Cp source. Furthermore, Wenzel found that it was necessary for a carbonyl group to be directly attached to a migrating Cp ring for the transformation to take place with Tc-99m,[27] and we observed a similar requirement for rhenium (Table 3). A possible mechanistic rationale for such a necessity is discussed below.

In most cases, when the ferrocenyl side chain was a methyl ester, a ketone, or an amide, the reaction proceeded in moderate to high yield. The yields were highest with the 1,1′-disubstituted ferrocenes (except the methyl ketone). This trend was especially evident with the ferrocene methyl esters, wherein no ring transfer took place from the monosubstituted ferrocene (entry 1), but the highest isolated product yield of all the reactions performed was obtained in the 1,1′-disubstituted case (entry 2).

In some reactions, the ferrocenyl side chains were altered during the course of the transformation, preventing the formation of the anticipated product. For example, as shown in Table 4, when the side chain was an ethynyl group (R = −C≡CH), the triple bond underwent hydration during the reaction, so that the isolated product was acetyl-CpTR (X = $COCH_3$). A transesterification reaction took place on the side chains of the ferrocenyl esters tested (methoxyethyl ester

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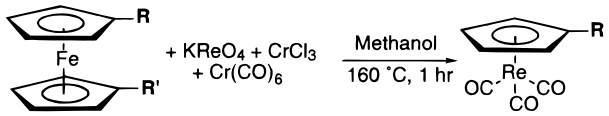
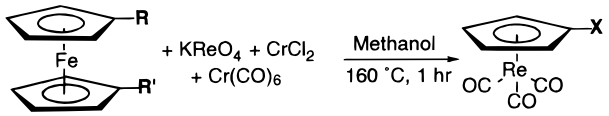
Table 3. Fc−Ketones, Esters, and Amides as Cp Donors in the DLT Reaction



entry	R	R′	% yield[a]
1	CO_2CH_3	H	0
2	CO_2CH_3	CO_2CH_3	88
3	CONH(*n*-Pr)	H	5
4	CONH(*n*-Pr)	CONH(*n*-Pr)	80
5	CON(*cyclo*-C_4H_8)	H	18
6	CON(*cyclo*-C_4H_8)	CON(*cyclo*-C_4H_8)	65
7	$COCH_3$	H	83
8	$COCH_3$	$COCH_3$	60
9	$COCH(Et)_2$	H	45
10	COC_3H_7	H	58
11	H	H	0

[a] Isolated yields.

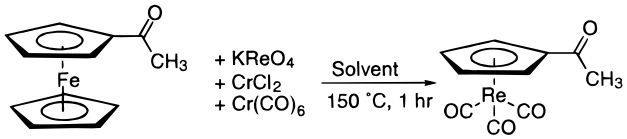
Table 4. Side Chain Modifications Caused by the DLT Reaction in Methanol



R	R′	X	% yield[a]
ethynyl	H	$COCH_3$	15
$CO_2(CH_2)_2OCH_3$	$CO_2(CH_2)_2OCH_3$	CO_2CH_3	85[b]
CHO	H	$CH(OCH_3)_2$	25

[a] Isolated yields. [b] Used $CrCl_3$ instead of $CrCl_2$.

Table 5. Effect of Solvent Variation on DLT Reaction



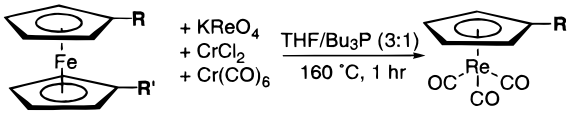
solvent	% yield[a]
DMF, DMSO, acetonitrile, pyridine, propylamine, benzene, acetone, THF, or DME	0
methanol	65
ethanol	21
Bu_3P	12
acetone/Bu_3P (3:1)	15
THF/Bu_3P (3:1)	33
DME/Bu_3P (3:1)	37
methanol/Bu_3P (3:1)	16
THF/$(CH_3O)_3P$ (3:1)	0

[a] Isolated yields.

shown, R = $CO_2(CH_2)_2OCH_3$), providing high yields of the rhenium methyl ester (X = CO_2CH_3). Finally, the carbonyl group of ferrocene carboxaldehyde (R = CHO) was transformed into its methyl acetal under the reaction conditions (X = $CH(OCH_3)_2$).

In each of these cases, the solvent, methanol, was reacting with the susceptible side chains; therefore, alternate solvents were tested. As shown in Table 5, most other solvents were unsuitable hosts for the double ligand-transfer reaction. In fact, of the solvents tried, only the alcohols and Bu_3P provided measurable yields of acetyl-CpTR from acetylferrocene. It was found that

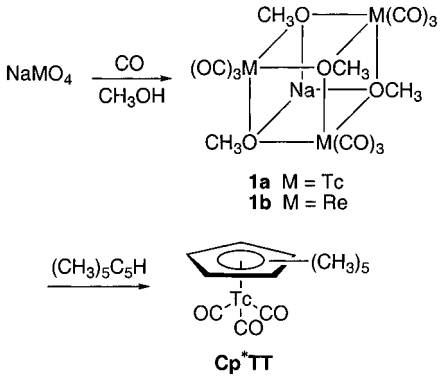
Table 6. THF/Bu_3P (3:1) as an Alternative Solvent for the DLT Reaction



R	R′	% yield[a]
CON(*cyclo*-C_4H_8)	H	40
$COCH_3$	H	33
CONH(*n*-Pr)	H	5
$COOCH_3$	$COOCH_3$	0[b]
COH	H	0
ethynyl	H	0

[a] Isolated yields. [b] Used $CrCl_3$ instead of $CrCl_2$.

Scheme 2. Carbonylation of $M(VII)O_4^-$ (M = Tc, Re) in Methanol



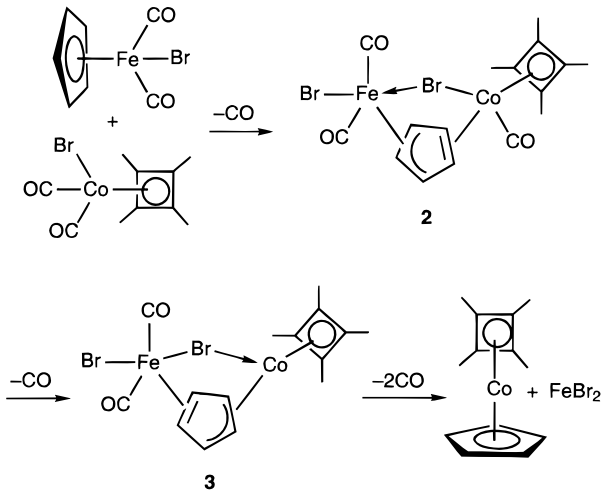
the use of Bu_3P as a cosolvent enabled the DLT reaction to be performed in otherwise unsuitable solvents such as THF, and it was hoped that the methanol-induced side chain modifications encountered earlier could be eliminated using this solvent system. However, as shown in Table 6, the DLT reaction in THF/Bu_3P was not as efficient as in methanol.

Discussion

The mechanism of this unusual reaction deserves some comment. Although rigorous mechanistic studies were not done, some general deductions and inferences can be made on the basis of our data and by analogy to the work of others. As suggested by Wenzel,[27] the DLT reaction can be thought of as taking place in two steps: First, reduction/carbonylation of $Re(VII)O_4^-$ to provide a $Re(I)(CO)_3^+$ donor, and second, Cp ring transfer from an acyl−ferrocene to that intermediate.

A possible candidate for the key $Re(I)(CO)_3^+$ donor is $[Re_3(CO)_9(OCH_3)_4]^-$ (**1b**, Scheme 2). Alkoxy carbonyls of rhenium were first reported by Ioganson and co-workers in 1974[28] and were synthesized from $Re(CO)_5$-Cl and KOH/alcohol. More recently, Herrmann and co-workers described the isolation of **1a** and **1b** as products of the incomplete carbonylation of $M(VII)O_4^-$ (M = Tc, Re, respectively) in methanol.[29,30] The reaction conditions were more vigorous but still very similar to those

Scheme 3. Mechanism of Cp Ring Transfer from Iron to Cobalt



of the DLT reaction (50 bar, 230 °C, 2 days for Re; 70 bar, 150 °C, 4 days for Tc). Furthermore, the methoxy carbonyl complex contained the metal in the +1 oxidation state, and technetium compound **1a** was shown to be a $Tc(I)(CO)_3$ donor in its reaction with pentamethylcyclopentadiene to form Cp*TT (Scheme 2). These results lend strong support to the intermediacy of an alkoxy carbonyl like **1** in the DLT reaction and also help explain the pronounced solvent restrictions of the transformation.

With respect to the second ligand transfer, that of the Cp ring from iron to rhenium, there is considerable literature precedent for $AlCl_3$-induced Fe−Cp bond breakage but these reactions generally involve Cp ring replacement by an arene (e.g. benzene)[31−33] or ring interchange between differentially substituted ferrocene molecules.[34−38] Outside of the DLT reaction, the only example of Cp ring transfer from ferrocene to another metal is the reaction of ferrocene with $RuCl_3$ to produce ruthenocene.[24,25]

The family of reactions that are perhaps most similar to the DLT are those involving Cp ring transfer to various metals from $[CpFe(CO)_2]_2$ or $CpFe(CO)_2Br$. Recipient metals include Pd, Ni, Co, and Ti.[10,12,16,39] In the case of the transfer to cobalt, a mechanism was proposed which involved $\eta^5 \rightarrow \eta^0$ ring slippage via η^3/η^2 intermediates **2** and **3** (Scheme 3).[10]

Cyclopentadienyl ring slippage is by no means uncommon.[11] For example, it has been used to explain the nonstatistical deuterium incorporation patterns of certain substituted ferrocenes in refluxing pyridine.[40] Slocum and co-workers found that the only deuterium-

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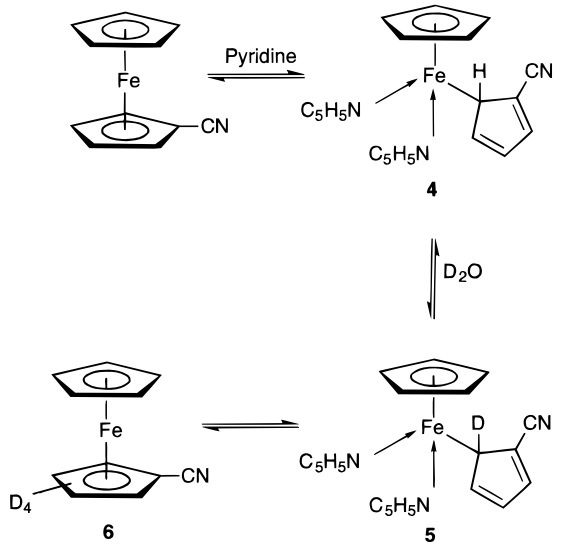
Scheme 4. Mechanism of Deuterium Exchange in Cyanoferrocene



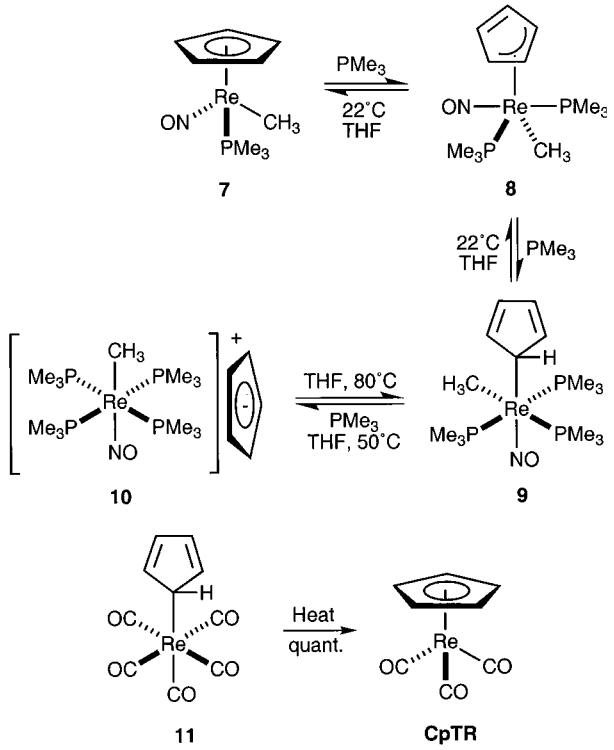
exchanged derivative of cyanoferrocene was the tetrasubstituted complex **6** (Scheme 4), and they rationalized its formation via a variety of ring-slipped intermediates, including **4** and **5**. Significantly, it was observed that exchange occurred only in the electron-deficient rings of other substituted ferrocenes (e.g., acetyl) as well and that rings without such substituents were essentially inert. The mechanism of side chain activation that they proposed nicely accounts for the pronounced side chain restrictions (viz., electron-withdrawing groups) of the DLT reaction.

Two final pieces of evidence supporting ring-slipped intermediates in the DLT reaction involve studies with two different Cp−rhenium complexes. First, Me_3P-induced $\eta^5 \rightarrow \eta^0$ ring slippage in compound **7** (Scheme 5) produced intermediates **9** and **10**, which were directly observable; the formation of **8** was inferred.[41] Second, $\eta^1 \rightarrow \eta^5$ ring slippage generated CpTR itself upon gentle heating of η^1-$CpRe(CO)_5$ (**11**) (Scheme 5).[42]

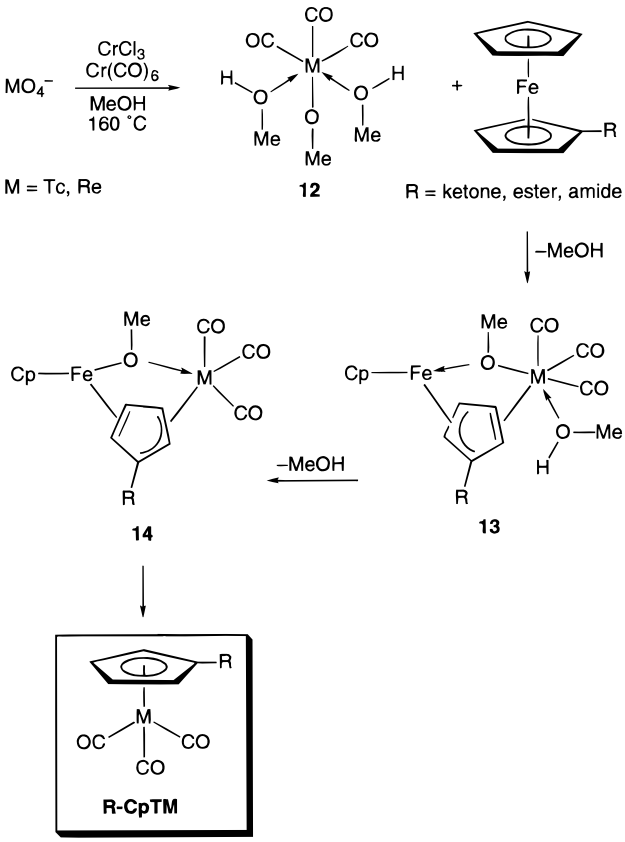
On the basis of this evidence, we propose a scenario such as that shown in Scheme 6 for the DLT reaction of substituted ferrocenes and ReO_4^- or TcO_4^-. The first step involves reduction and carbonylation of the oxo metal with $CrCl_3$ and/or $Cr(CO)_6$ to form an intermediate such as **12**, similar to the known cubane **1b** (Scheme 2). It is thought that the pronounced solvent dependence of the DLT reaction has its root in the role that hydroxyl solvents play in the formation of this key intermediate.

We propose that intermediate **12** then reacts with a substituted ferrocene to provide the corresponding CpTM via ring-slipped, bridged intermediates such as **13** and **14**, in direct analogy with the proposal of Slocum et al.[40] Only the ring substituted with an electron-withdrawing group is transferred to rhenium because it stabilizes the transition state of the initial $\eta^5 \rightarrow \eta^3$ ring slip of ferrocene, as documented in kinetic studies on CO substitution reactions in a related system (η^5-cyclopentadienyldicarbonylrhodium(I)) by Basolo and

Scheme 5. Examples of Ring Slippage in Cp−Re Compounds



Scheme 6. Proposed Mechanism for DLT Reaction



Rerek.[43] Possible byproducts of the reaction include Cr_2O_3, $CpFe(CO)_2Cl$, $FeCl_2$, and/or $[CpFeCl_2]_2$.[44]

(41) Casey, C. P.; O'Connor, J. M.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 1241.
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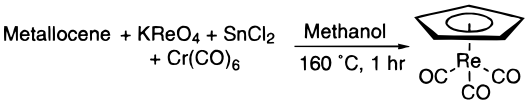
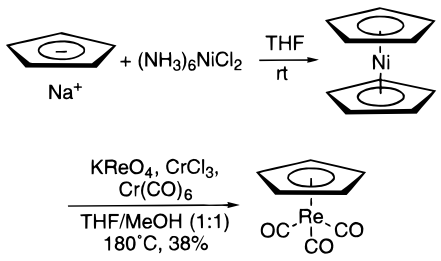
Table 7. Various Metallocenes as Cp Donors in the DLT Reaction



metallocene	% yield[a]
Cp_2Ni	32
Cp_2VCl_2	10
Cp_2Cr, Cp_2Mg, or Cp_3Nd	5
others[b]	0

[a] Isolated yields. [b] Others: Cp_2V, Cp_2Co, Cp_2TiCl_2, $CpFe(CO)_2I$, $[CpMo(CO)_3]_2$.

Scheme 7. DLT Reaction with Nickelocene Prepared from Cp⁻



The fact that only acyl-substituted Cp rings could be transferred from ferrocene to rhenium in the DLT reaction led us to investigate other metallocenes as potential Cp donors (Table 7). It was found that unsubstituted Cp rings could, indeed, be transferred to rhenium in the DLT reaction, albeit in modest yields. Nickelocene performed the best of the metallocenes tested, consistent with its proven capability in π-ligand-transfer reactions.[10,45−47] Furthermore, it was shown that nickelocene could be freshly generated from Cp^- and then used directly in the DLT reaction without purification (Scheme 7). Although the yield was again modest, this sequence could potentially be used to prepare any desired CpTM compound from an appropriately substituted cyclopentadiene derivative.

Conclusion

We have described the optimization and defined the scope of a unique double ligand-transfer reaction for the preparation of substituted cyclopentadienyltricarbonylrhenium complexes. The use of $Cr(CO)_6$ instead of $Mn(CO)_5Br$ as the carbonyl donor in the reaction eliminated the formation of the inseparable manganese-containing impurities encountered by Wenzel in the original report of this transformation.[9] Furthermore, yields improved significantly upon substitution of $CrCl_3$ for $SnCl_2$ as the reducing agent in the reaction.

The transformation was found to be general for a variety of acylated ferrocenes, but other substituted and unsubstituted ferrocenes were inert. The side chain restrictions of the transferred Cp ring in the DLT reaction were explained in terms of a difficult $\eta^5 \rightarrow \eta^3$ ring slippage that could be promoted by an acyl side chain, while the pronounced solvent dependence of the reaction was derived from its role in the formation of the key $Re(I)(CO)_3^+$ donor, **12**, from $Re(VII)O_4^-$.

A promising new line of inquiry was opened up when nickelocene replaced ferrocene in the DLT reaction. It was found that unactivated Cp rings could be transferred to rhenium and that freshly prepared nickelocene could be used without purification. It is possible that a wide variety of substituted CpTR complexes could be synthesized via this technique that would not be possible using ferrocene, thereby expanding the scope of the DLT reaction. The application of the DLT reaction for the labeling of protein and peptides with CpTM (M = Tc, Re) will be reported elsewhere.

Experimental Section

General Comments. The compounds used in this study were purchased from commercial sources (mainly Strem and Aldrich) unless otherwise indicated and were used without further purification. Reactions were performed in either 4 or 15 mL threaded pressure tubes sealed with Teflon screw caps with O-rings (all purchased from Ace Glass). An egg-shaped (1 cm) stir bar was used to stir each reaction. ***Cautionary Note:*** *Pressure tubes were placed within a specially made solid aluminum block containing holes drilled deep enough to admit the tubes to about $^3/_4$ of their height and wide enough to allow room for the addition of some mineral oil to ensure good thermal contact. The tubes and aluminum base were covered with a matching hollow aluminum screw cap, equipped with a small hole aligned with one drilled in the base (to the same depth as those for the pressure tubes) to hold a metal thermometer. This containment device minimized the potential danger of explosions during heating, allowed for the efficient stirring of the reactions, and enabled the reaction temperature to be monitored readily. All manipulation of sealed reaction tubes during and after the reactions were done in a fume hood with suitable protective equipment: blast shield, full-face visor, heavy gloves.*

General Procedure 1: For Metal Carbonyl Optimization in Double Ligand-Transfer Reactions (Table 1). $KReO_4$ (0.123 g, 0.424 mmol), 1,1′-diacetylferrocene (0.349 g, 1.29 mmol), $Cr(CO)_6$ (0.612 g, 2.78 mmol), and $SnCl_2$ (0.1 g, 0.5 mmol) were combined in an oven-dried 15 mL pressure tube containing a magnetic stir bar. Dry (Na-distilled) methanol (5 mL) was added, and the tube was sealed with an O-ring-equipped Teflon screw cap. (See Cautionary Note under General Comments.) The tube was inserted into the aluminum block described above along with a few drops of mineral oil, and stirring was initiated with a stirrer/hot plate. Note: It is very important that the reaction be stirred vigorously, as it is heterogeneous. The temperature was increased rapidly to 140 °C and then to 155 °C over the course of an hour. The pressure tube was (carefully) removed from the heating block and cooled first in a water/ice bath for 10 min and then in a dry ice/2-propanol bath for another 10 min. The cap was removed, and the solvent was evaporated under a stream of N_2 at 30 °C. The mixture was dissolved in a minimum of CH_2Cl_2 and purified by flash column chromatography (3:1 hexane:ethyl acetate) to give 0.72 g (45% based on $KReO_4$) of tricarbonyl(acetylcyclopen-

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tadienyl)rhenium.[48] ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.98 (t, J = 2.29 Hz, 2H, $CH_3CO-Cp-H_2(\alpha)$), 5.40 (t, J = 2.29 Hz, 2H, $CH_3CO-Cp-H_2(\beta)$), 2.34 (s, 3H, $Cp-COCH_3$). MS (CI): m/z 379 $(M + H)^+$. Anal. Calcd for $C_{10}H_7O_4Re$: C, 31.75; H, 1.87; Re, 49.46. Found: C, 32.13; H, 1.92; Re, 49.41.

General Procedure 2: For Double Ligand-Transfer Reactions in Tables 2−7. $KReO_4$ (0.0479 g, 0.166 mmol), acetylferrocene (0.118 g, 0.519 mmol), $Cr(CO)_6$ (0.205 g, 0.932 mmol), and $CrCl_3$ (0.0529 g, 0.334 mmol) were combined in an oven-dried 4 mL pressure tube containing a magnetic stir bar. Dry methanol (1 mL) was added, and the tube was sealed, heated (to 165 °C), and cooled as above. (See Cautionary Note under General Comments above.) The reaction mixture was transferred to a 15 mL disposable vial with CH_2Cl_2, and the solvent was evaporated under a stream of N_2 at 30 °C. The mixture was dissolved in a minimum of CH_2Cl_2 and purified by flash column chromatography (4:1 hexane:ethyl acetate) to give 0.0559 g of a 7.33:1 mixture of tricarbonyl(acetylcyclopentadienyl)rhenium (83% yield based on $KReO_4$) and acetylferrocene, determined from the ^{1}H NMR (300 MHz, $CDCl_3$) spectrum by integration of the peaks at 5.99 ppm {Re−[$CH_3CO-Cp-H_2(\alpha)$]} and 5.41 ppm (Re−[$CH_3CO-Cp-H_2(\beta)$]) versus the signals at 4.51 ppm (CpFe−[$CH_3CO-Cp-H_2(\alpha)$]) and 4.21 ppm (CpFe−[$CH_3CO-Cp-H_2(\beta)$]). The mixture was purified further by flash column chromatography (95:5 benzene:ethyl acetate) to give 0.047 g (75%) of tricarbonyl(acetylcyclopentadienyl)rhenium.

Preparation of Substituted Ferrocenes in Tables 3 and 4. 1,1′-Bis(carbomethoxy)ferrocene. Trimethyl orthoformate (5 mL, 46 mmol), methanol (1.5 mL, 37 mmol), and sulfuric acid (1.3 mL) were added to 1,1′-ferrocenedicarboxylic acid[49] (1.55 g, 5.6 mmol) in a 25 mL round-bottomed flask equipped with a reflux condenser. The mixture was stirred and heated at reflux overnight. The reaction was diluted with CH_2Cl_2 and washed (3×) with saturated $NaHCO_3$. The organic phase was dried ($MgSO_4$), concentrated, and purified by flash column chromatography (4:1 hexane: ethyl acetate) to give 1 g (60%) of 1,1′-bis(carbomethoxy)-ferrocene.[50] ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.83 (t, J = 1.87 Hz, 4H, $[CH_3COO-Cp-H_2(\alpha)]_2$), 4.41 (t, J = 1.91 Hz, 4H, $[CH_3COO-Cp-H_2(\beta)]_2$), 3.82 (s, 6H, $(Cp-COOCH_3)_2$). MS (EI): m/z 302 (M^+).

[(2-Ethyl)butyro]ferrocene. Sodium hydride (60% dispersion in mineral oil, 0.17 g, 4.3 mmol) was added to acetylferrocene (0.746 g, 3.27 mmol) in 20 mL of dry (Na/benzophenone) THF at −78 °C. The solution was allowed to warm to room temperature over the course of 2−3 h, and then ethyl iodide (350 μL, 4.4 mmol) was added dropwise. After the mixture was stirred overnight, the reaction was diluted with ethyl acetate and washed with water. The organic phase was concentrated, and flash column chromatography (95:5 hexane: ethyl acetate) provided 0.28 g (30%) of [(2-ethyl)butyro]-ferrocene[51] followed by 0.21 g (25%) of butyroferrocene[52] (commercially available). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.7 (2H, $-CO-Cp-H_2(\alpha)$), 4.5 (2H, $-CO-Cp-H_2(\beta)$), 4.2 (5H, $Cp-H_5$), 2.7 (1H, $CpCOC-H$), 1.75 and 1.5 (4H, $CpCOCH(CH_2CH_3)_2$), 0.9 (6H, $CpCOCH(CH_2CH_3)_2$). HREIMS m/z calcd for $C_{16}H_{20}OFe$ 284.0864, found 284.0863 (Δ 0.1 ppm, M^+).

1,1′-Bis(*N*−propyl)ferrocene Carboxamide. 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (EDC, 0.957 g, 4.99 mmol) was added to a solution of 1,1′-ferrocenedicarboxylic acid[49] (0.554 g, 2.02 mmol), triethylamine (700 μL, 5.02 mmol), propylamine (500 μL, 6.08 mmol), and 1-hydroxybenzotriazole (HOBt, 0.584 g, 4.32 mmol) in DMF (20 mL) at room temperature. The reaction was stirred for 30 min, then diluted with CH_2Cl_2, and washed with HCl (1%) and then saturated $NaHCO_3$. The organic phase was dried ($MgSO_4$), concentrated, and purified by flash column chromatography (3:1 ethyl acetate:hexane) to give 0.43 g (60%) of 1,1′-bis(*N*-propyl)ferrocene carboxamide. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.79 (s, 2H, $(-CONHC_3H_7)_2$), 4.48 (s, 4H, $(-CO-Cp-H_2(\alpha))_2$), 4.36 (s, 4H, $(-CO-Cp-H_2(\beta))_2$), 3.36 (q, J = 6.67 Hz, 4H, $(-CONHCH_2CH_2CH_3)_2$), 1.67 (m, 4H, $(-CONHCH_2CH_2CH_3)_2$), 1.00 (t, J = 7.29 Hz, 6H, $(-CONHCH_2CH_2CH_3)_2$). HREIMS m/z calcd for $C_{18}H_{24}N_2O_2Fe$ 356.1187, found 356.1190 (Δ −0.8 ppm, M^+).

(*N*−Propyl)ferrocene Carboxamide. To a solution of ferrocene carboxylic acid (0.884 g, 3.84 mmol) in $CHCl_3$ (3 mL) were added DMF (2 drops) and thionyl chloride (450 μL, 6.2 mmol). The reaction was stirred for 3 h, and then propylamine (1.6 mL, 19.5 mmol) was added, and the reaction was stirred overnight. The reaction was then diluted with CH_2Cl_2 and washed with HCl (5%) and then saturated K_2CO_3. The organic phase was dried ($MgSO_4$), concentrated, and purified by flash column chromatography (5% acetic acid in 3:1 hexane: ethyl acetate) to give 0.3 g (30%) of (*N*-propyl)ferrocene carboxamide.[53] ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.79 (s, 1H, $-CONHC_3H_7$), 4.67 (s, 2H, $-CO-Cp-H_2(\alpha)$), 4.33 (s, 2H, $-CO-Cp-H_2(\beta)$), 4.20 (s, 5H, $Cp-H_5$), 3.35 (q, J = 6.08 Hz, 2H, $-CONHCH_2CH_2CH_3$), 1.62 (m, 2H, $-CONHCH_2CH_2CH_3$), 0.99 (t, J = 6.97 Hz, 3H, $-CONHCH_2CH_2CH_3$). HREIMS m/z calcd for $C_{14}H_{17}NOFe$ 271.0660, found 271.0659 (Δ 0.3 ppm, M^+).

1,1′-Bis(pyrrolidinylcarbonyl)ferrocene. 1,1′-Ferrocenedicarboxylic acid (0.81 g, 3.52 mmol) was heated overnight at reflux in phosphorus trichloride (40 mL). The PCl_3 was removed in vacuo, pyrrolidine (20 mL) was added, and the solution was heated overnight at 50−70 °C. The pyrrolidine was removed in vacuo, and the mixture was purified by flash column chromatography (95:5 methylene chloride:methanol) to give 0.4 g (30%) of 1,1′-bis(pyrrolidinylcarbonyl)ferrocene.[54] ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.77 (d, J = 1.74 Hz, 4H, $(-CO-Cp-H_2(\alpha))_2$), 4.36 (d, J = 1.53 Hz, 4H, $(-CO-Cp-H_2(\beta))_2$), 3.53−3.64 (m, 8H, $(-CO-cyclo-NCH_2CH_2CH_2CH_2)_2$), 1.85−1.97 (m, 8H, $(-CO-cyclo-NCH_2CH_2CH_2CH_2)_2$).

(Pyrrolidinylcarbonyl)ferrocene. To a solution of ferrocene carboxylic acid (0.77 g, 3.35 mmol) in chloroform (2 mL) were added thionyl chloride (350 μL, 4.8

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(49) Rausch, M. D.; Ciappenelli, D. J. *J. Organomet. Chem.* **1967**, *10*, 127.
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(52) DeYoung, E. L. *J. Org. Chem.* **1961**, *26*, 1312.
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(54) Kishore, K.; Lyanar, K.; Pandureng, L. P. *Fuel* **1994**, *73*, 1583.

mmol) and DMF (1 drop). The reaction was heated at reflux for 1 h, pyrrolidine (1 mL, 12 mmol) was added, and the reaction was heated at reflux overnight. The reaction was diluted with CH_2Cl_2 and washed with HCl (5%) and then saturated K_2CO_3. The organic phase was dried ($MgSO_4$), concentrated, and purified by flash column chromatography (2:1 hexane:ethyl acetate) to give 0.25 g (27%) of (pyrrolidinylcarbonyl)ferrocene. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.74 (s, 2H, $-$CO$-$Cp$-H_2$-(α)), 4.33 (s, 2H, $-$CO$-$Cp$-H_2(\beta)$), 4.21 (s, 5H, Cp$-H_5$), 3.70 and 3.61 (m, 4H, $-$CO$-$*cyclo*-NCH_2CH_2CH_2CH_2), 1.90$-$1.97 (m, 4H, $-$CO$-$*cyclo*-NCH_2CH_2CH_2CH_2). MS (EI): *m*/*z* 283 (M^+). Anal. Calcd for $C_{15}H_{17}NOFe$: C, 63.59; H, 6.05; N, 4.95; Fe, 19.76. Found: C, 63.46; H, 5.79; N, 5.30; Fe, 19.46.

1,1′-Bis(2-methoxyethyl) Ferrocenoate. 1,1′-Ferrocenedicarboxylic acid (0.84 g, 3.65 mmol) was heated overnight at reflux in phosphorus trichloride (40 mL). The PCl_3 was removed in vacuo, 2-methoxyethanol (10 mL) was added at 0 °C, and the solution was heated for 48 h at 70 °C. The 2-methoxyethanol was removed in vacuo, and the mixture was purified by flash column chromatography (2:1 hexane:ethyl acetate) to give 0.71 g (50%) of 1,1′-bis(2-methoxyethyl) ferrocenoate. ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 4.87 (s, 4H, (CO$-$Cp$-H_2$(α))$_2$), 4.43 (s, 4H, (CO$-$Cp$-H_2(\beta)$)$_2$), 4.40 (t, *J* = 4.67 Hz, 4H, Cp(CO$_2$CH_2CH_2OCH_3)$_2$), 3.70 (t, *J* = 4.73 Hz, 4H, Cp(CO$_2$CH_2CH_2OCH_3)$_2$), 3.44 (s, 6H, Cp(CO$_2$-CH_2CH_2OCH_3)$_2$). HREIMS *m*/*z* calcd for $C_{18}H_{22}O_6Fe$ 390.0766, found 390.0764 (Δ 0.4 ppm, M^+).

Double Ligand-Transfer Reaction. Tricarbonyl(carbomethoxycyclopentadienyl)rhenium. The reaction was performed according to General Procedure 2 and purified by flash column chromatography (1:1 hexane:(95:5 benzene:ethyl acetate)) to give 0.056 g (88%) of tricarbonyl(carbomethoxycyclopentadienyl)-rhenium[55] from 1,1′-bis(carbomethoxy)ferrocene. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.01 (t, *J* = 1.98 Hz, 2H, $-$CO$-$Cp$-H_2$(α)), 5.37 (t, *J* = 1.77 Hz, 2H, $-$CO$-$Cp$-H_2(\beta)$), 3.81 (s, 3H, CpCOOCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.90 (Re(CO)$_3$), 164.18 (*C*OOCH$_3$), 88.87, 84.90 (C_5H_4), 88.02 (C ipso), 52.36 (COO*C*H$_3$). HREIMS *m*/*z* calcd for $C_{10}H_7O_5Re$ 393.9851, found 393.9836 (Δ 3.9 ppm, M^+).

Tricarbonyl(butyrocyclopentadienyl)rhenium. The reaction was performed according to General Procedure 2 and purified by flash column chromatography (9:1 hexane:ethyl acetate) to give 0.039 g (58%) of tricarbonyl(butyrocyclopentadienyl)rhenium from butyroferrocene. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.99 (s, 2H, $-$CO$-$Cp$-H_2$(α)), 5.40 (s, 2H, $-$CO$-$Cp$-H_2(\beta)$), 2.57 (t, *J* = 7.17 Hz, 2H, $-$COCH_2CH_2CH_3), 1.68$-$1.76 (m, 2H, $-$COCH_2CH_2CH_3), 0.97 (t, *J* = 7.40 Hz, 3H, $-$COCH_2CH_2CH_3). HREIMS *m*/*z* calcd for $C_{12}H_{11}O_4Re$ 404.0187, found 404.0190 (Δ $-$0.7 ppm, M^+).

Tricarbonyl{[(2-ethyl)butyro]cyclopentadienyl}-rhenium. The reaction was performed according to General Procedure 2. After aqueous workup (see above), the reaction mixture was partially purified by flash column chromatography using only 2 in. of silica gel and eluting with 95:5 benzene:ethyl acetate (200 mL). The eluent collected was removed in vacuo, and flash column chromatography (9:1 hexane:ethyl acetate) provided 0.033 g (45%) of tricarbonyl{[(2-ethyl)butyro]cyclopentadienyl}rhenium from [(2-ethyl)butyro]ferrocene. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.00 (t, *J* = 1.94 Hz, 2H, $-$CO$-$Cp$-H_2$(α)), 5.40 (t, *J* = 1.96 Hz, 2H, $-$CO$-$Cp$-H_2(\beta)$), 2.52 (m, 1H, CpCOC*H*(CH$_2$CH$_3$)$_2$), 1.48$-$1.61 and 1.66$-$1.79 (m, 4H, CpCOCH(CH_2CH$_3$)$_2$), 0.91 (t, *J* = 7.42 Hz, 6H, CpCOCH(CH$_2$CH_3)$_2$). HREIMS *m*/*z* calcd for $C_{14}H_{15}O_4Re$ 432.0500, found 432.0501 (Δ $-$0.3 ppm, M^+).

Tricarbonyl[(propylamido)cyclopentadienyl]-rhenium. The reactions were performed according to General Procedure 2 and purified by flash column chromatography (3:2 hexane:ethyl acetate) to give 0.054 g (80%) of tricarbonyl[(propylamido)cyclopentadienyl]-rhenium from 1,1′-bis(*N*-propyl)ferrocene carboxamide and 0.003 g (5%) from (*N*-propyl)ferrocene carboxamide. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.88 (s, 2H, $-$CO$-$Cp$-H_2$(α)), 5.36 (s, 2H, $-$CO$-$Cp$-H_2(\beta)$), 3.28$-$3.34 (m, 2H, $-$CONHCH_2CH_2CH_3), 1.54$-$1.61 (m, 2H, $-$CONH-CH_2CH_2CH_3), 0.95 (t, *J* = 7.35 Hz, 3H, $-$CONHCH_2-CH_2CH_3). MS (EI): *m*/*z* 421 (M^+).

Tricarbonyl[(pyrrolidinylcarbonyl)cyclopentadienyl]rhenium. The reactions were performed according to General Procedure 2 and purified by flash column chromatography (98:2 methylene chloride:methanol) to give 0.031 g (65%) of tricarbonyl[(pyrrolidinylcarbonyl)cyclopentadienyl]rhenium from 1,1′-bis-(pyrrolidinylcarbonyl)ferrocene and 0.014 g (30%) from (pyrrolidinylcarbonyl)ferrocene. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.92 (s, 2H, $-$CO$-$Cp$-H_2$(α)), 5.37 (s, 2H, $-$CO$-$Cp$-H_2(\beta)$), 3.51$-$3.60 (m, 4H, $-$CO$-$*cyclo*-NCH_2-CH_2CH_2CH_2), 1.87$-$1.93 and 1.98$-$2.05 (m, 4H, $-$CO$-$*cyclo*-NCH_2CH_2CH_2CH_2). HREIMS *m*/*z* calcd for $C_{13}H_{12}$-NO_4Re 433.0324, found 433.0330 (Δ $-$1.4 ppm, M^+). Anal. Calcd for $C_{13}H_{12}NO_4Re$: C, 36.11; H, 2.80; N, 3.24. Found: C, 36.83; H, 2.98; N, 3.15.

Tricarbonyl[(dimethoxymethyl)cyclopentadienyl]-rhenium. The reaction was performed according to General Procedure 2 and purified by flash column chromatography (100% benzene) to give 0.02 g (25%) of tricarbonyl[(dimethoxymethyl)cyclopentadienyl]-rhenium from ferrocene carboxaldehyde. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.49 (t, *J* = 2.02 Hz, 2H, (CH$_3$O)$_2$CH$-$Cp$-H_2$(α)), 5.30 (t, *J* = 2.03 Hz, 2H, (CH$_3$O)$_2$CH$-$Cp$-H_2(\beta)$), 5.16 (s, 1H, (CH$_3$O)$_2$C*H*-Cp), 3.34 (s, 6H, (CH_3O)$_2$-CH$-$Cp).

Cyclopentadienyltricarbonylrhenium. The reactions were performed according to General Procedure 2 and purified by flash column chromatography (4:1 hexane:benzene) to give 0.021 g (32%) of cyclopentadienyltricarbonylrhenium[56] from nickelocene, 0.006 g (10%) from biscyclopentadienylvanadium dichloride, and 0.005 g (5%) from biscyclopentadienylchromium, biscyclopentadienylmagnesium, and triscyclopentadienylneodymium. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.37 (s, 5H, Cp$-H_5$). Anal. Calcd for $C_8H_5O_3Re$: C, 28.57; H, 1.50; Re, 55.64. Found: C, 28.64; H, 1.31; Re, 55.48.

Cyclopentadienyltricarbonylrhenium from NaCp/(NH$_3$)$_6$NiCl$_2$. A 2 M solution of sodium cyclopentadienylide in THF (700 μL, 1.4 mmol) was added to hexaaminenickel(II) chloride, and the solution was

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stirred under N_2 for 2 h at room temperature. Methanol (700 μL) was added, and the resulting solution was transferred to an oven-dried 4 mL pressure tube containing $KReO_4$ (0.0248 g, 0.086 mmol), $Cr(CO)_6$ (0.108 g, 0.486 mmol), and $CrCl_3$ (0.0347 g, 0.219 mmol). The tube was sealed, heated (to 195 °C), cooled and concentrated as described in the General Procedure. (See Cautionary Note under General Comments.) The reaction mixture was dissolved in methylene chloride and eluted from a 1 in. silica gel plug with 95:5 hexane:ethyl acetate. The eluent was concentrated and purified by flash column chromatography (4:1 hexane:benzene) to give 0.011 g (38%) of cyclopentadienyltricarbonylrhenium. (The same procedure, performed without added methanol (in 100% THF) and with lithium cyclopentadienylide instead of sodium cyclopentadienylide, provided 0.004 g (18%) of cyclopentadienyltricarbonylrhenium.)

Acknowledgment. We are grateful for support of this research through grants from the Department of Energy (Grant No. DE FG02 86ER60401) and the National Institutes of Health (Grant No. PHS 5R01 CA25836). NMR spectra were obtained in the Varian Oxford Instrument Center for Excellence in the NMR Laboratory. Funding for this instrumentation was provided in part from the W. M. Keck Foundation, the National Institutes of Health (Grant No. PHS 1 S10 RR104444-01), and the National Science Foundation (Grant No. NSF CHE 96-10502).

OM971018U