Metathesis Reactions of Tris(adamantylimido)methylrhenium and Aldehydes and Imines

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The tris(imido)methylrhenium compound $CH_3Re(NAd)_3$ (Ad = 1-adamantyl) was prepared and characterized. It reacts with aromatic aldehydes ArCHO forming the imines ArCH=NAd. The reaction occurs in three stages, during which $CH_3Re(NAd)_2O$ and $CH_3Re(NAd)O_2$ could be detected. In the third and slowest stage CH_3ReO_3 (MTO) was formed, eventually in quantitative yield. The second-order rate constant for PhCHO in C_6D_6 at 298 K is 1.4×10^{-4} L mol^{-1} s^{-1}. Electron-donating substituents at the para-position of ArCHO cause a significant diminution in rate. Treated by the Hammett equation, the reaction constant is $\rho = +0.90$. The reactions between $CH_3Re(NAd)_3$ and linear aliphatic aldehydes occur much faster than do reactions of nonlinear aliphatic or aromatic aldehydes, indicating an important steric effect. Ketones do not react. The imidorhenium complex evidently undergoes a metathesis reaction with the aldehyde. Analogously, $CH_3Re(NAd)_3$ reacts with imines. Imine−imine metathesis is catalyzed by MTO homogeneously and by MTO supported on Nb_2O_5.

Introduction

Transfer of an oxygen atom from hydrogen peroxide is catalyzed by methyltrioxorhenium (CH_3ReO_3, abbreviated as MTO). Numerous substrates are able to accept the oxygen, including alkenes, organic sulfides, and phosphines. This area has been reviewed.[1−4] Recently, the transfer of a sulfur atom, catalyzed by a derivative of MTO, has been investigated.[5]

With this in mind, we invoked the isoelectronic principle to explore the possibility of nitrene (NR) transfer. In other contexts, nitrene transfer to olefins,[6−9] as well as to phosphines,[10−12] aldehydes,[11,13,14] and transition metal complexes,[15−17] has been explored previously. Transition metal imido species are involved or proposed as intermediates in nitrene transfer.[18,19] Toward this end, we have examined compounds of the formula $CH_3Re(NR)_3$. Compounds such as those with R = t-Bu and 2,6-diisopropylphenyl[20,21] are known; however, their nitrene transfer capabilities have not been investigated. Here, we would like to report our studies of nitrene transfer reactions with the compound $CH_3Re(NAd)_3$ (R = 1-adamantyl).

Experimental Section

Materials. The aldehydes and aniline derivatives for this study were used as received from commercial sources, except butyraldehyde (redistilled) and 4-methoxyaniline (recrystallized). 1-Adamantyl isocyanate was also used as received. The solvents toluene, benzene-d_6, and hexane were dried with sodium/benzophenone and stored in a nitrogen-filled glovebox. MTO[22] and the organic imines[23] were prepared according to the literature. MTO on niobia was available from a previous investigation.[24]

$CH_3Re(NAd)_3$. This previously unreported compound was prepared by refluxing a toluene solution of MTO with 3 equiv of AdNCO (Ad = 1-adamantyl), analogous to the literature procedure.[20] After removing most of the solvent by evaporation, the concentrated solution was cooled to −20 °C, whereupon a yellow solid was obtained. After filtration and washing with

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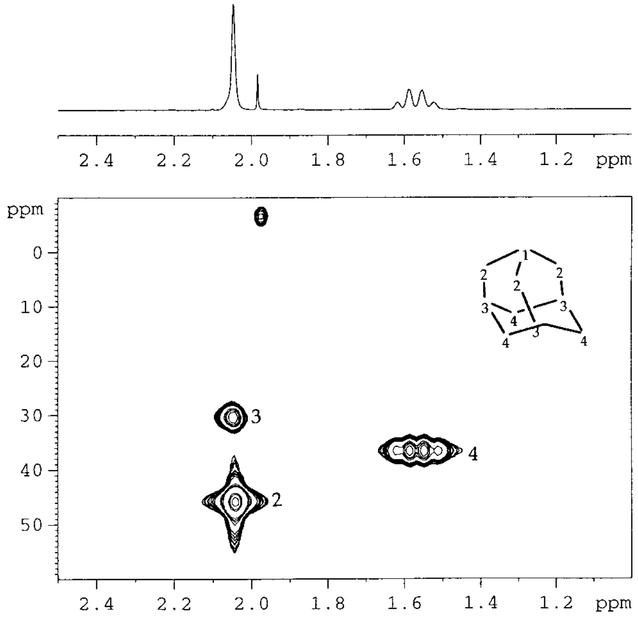

Figure 1. ${}^1H-{}^{13}C$ 2-D NMR spectrum of $CH_3Re(NAd)_3$ (Ad = 1-adamantyl) in C_6D_6 at 298 K.

cold toluene, the yellow solid was dried under vacuum. Fine, needlelike yellow crystals were obtained through recrystallization from hexane. The compound was characterized by elemental analysis and spectroscopy. Anal. Found (calcd for $C_{31}H_{48}N_3Re$): C 57.24 (57.38), H 7.63 (7.46), N 6.48 (6.48). ${}^1H$ NMR (C_6D_6): 1.99 (s, 3 H), 2.06 (s, 27 H), 1.58 (m, 18 H). ${}^{13}C$ NMR (C_6D_6): −6.39 (CH_3Re), 30.80 (CH), 37.02 (CH_2), 46.14 (CH_2), 68.72 (CH_0). EI MS: *m/z* 649. The 2D-NMR spectrum of $CH_3Re(NAd)_3$ in C_6D_6 at room temperature is presented in Figure 1.

Kinetics Studies. Kinetics measurements, thermostated at 298 K, were carried out in C_6D_6 under N_2 by means of an NMR spectrometer. The initial rate method was used to determine the rate constants for the reactions of $CH_3Re(NAd)_3$ with $CH_3CH_2CH_2CHO$ and with $4\text{-}NO_2C_6H_4CHO$. The integrated intensities of aldehydes (C*H*O) and imines (C*H*N) were converted into concentrations using the known initial concentration of the aldehyde and mass conservation law. The concentration−time profile for the first 10% of the reaction is linear, and its slope is the initial rate (mol L^{-1} s^{-1}). A competition method was used to evaluate the rate constants for the reactions with other aromatic aldehydes. The rate constants, relative to that for $4\text{-}NO_2C_6H_4CHO$, were calculated according to the following equation:

$$\frac{k_{ArCHO}}{k_{4-NO_2C_6H_4CHO}} = \frac{[ArCH{=}NAd]_\infty}{[4\text{-}NO_2C_6H_4CH{=}NAd]_\infty} \times \frac{[4\text{-}NO_2C_6H_4CHO]_0}{[ArCHO]_0}$$

The integrated intensities for C*H*O of aldehydes and C*H*N of imines were used in the above calculations. For terephthaldehyde, the statistical factor of 2 and the intensity of the C*H*O protons contributed from two identical CHO groups were considered. The reactions with aliphatic aldehydes were not studied by the competition method because of the rapid exchange between aliphatic aldehydes and their imines.

Product Analysis. The products were characterized by NMR and mass spectrometry with Bruker DRX-400 and a Finnigan Magnum ion trap GC−mass spectrometer, in comparison with authentic samples obtained by refluxing $1\text{-}NH_2\text{-}Ad$ and RCHO in toluene for 3 h, during which time water was removed by a Dean−Stark trap. As summarized in the Supporting Information, the RC*H*=NAd moiety has characteristic ${}^1H$ and ${}^{13}C$ chemical shifts,[23] which were measured relative to the residual ${}^1H$ and ${}^{13}C$ resonances of the solvent (δ_H 7.16, δ_C 128.39 ppm).

Results

$CH_3Re(NAd)_3$. This compound proved to be moisture sensitive, but is not affected by oxygen, even in solution. The sample shows an absorption maximum at 374 nm (ϵ 720 L mol^{-1} cm^{-1}). The ${}^1H$ spectrum showed that the three imido groups are equivalent. Although the chemical shifts for the protons on the C2 and C3 groups are *coincidentally* the same, the carbons have different ${}^{13}C$ chemical shifts. The C1 carbon was observed in the regular proton-decoupled ${}^{13}C$ spectrum, which allowed the differentiation of C2 and C3 by an APT (attached proton test) experiment. The ${}^{13}C$ chemical shift of the methyl group on rhenium is −6.49 ppm, quite different from the value 17.4 ppm of MTO, but similar to the value of −6.08 ppm for $CH_3Re(N\text{-}t\text{-}Bu)_3$.[25]

A single-crystal X-ray analysis was performed on $CH_3Re(NAd)_3$, but no crystal was found that allowed a quantitative resolution of the structure owing to disorder problems and the small crystal size. The large *R*-factor precludes a meaningful comparison of bond lengths and angles with the reported structure of $CH_3Re(NAr)_3$.[21] Nonetheless, the low-precision results clearly show that the compound is a monomer with a structure analogous to that of $CH_3Re(NAr)_3$.

Reactions with Aldehydes. The reaction between 4-nitrobenzaldehyde (δ_{CHO} 9.30 ppm) and $CH_3Re(NAd)_3$ (δ_{CH3} 1.99 ppm) was studied with ${}^1H$ NMR. The loss of intensity of the aldehyde proton and the buildup of the characteristic imine proton of $4\text{-}NO_2C_6H_4CH{=}NAd$ were followed with time. Concurrent with these changes, a new signal grew in at δ 1.91 ppm, assigned as the methyl resonance of $CH_3Re(NAd)_2O$; see below. The rate constant for reaction 1 with 4-nitrobenzaldehyde is $k_1 = 7 \times 10^{-4}$ L mol^{-1} s^{-1} at 298 K. When a large excess of the aldehyde was used, the buildup of $CH_3Re(NAd)(O)_2$ was detected at δ 1.75 ppm. When that solution was allowed to stand for an even longer period, 40 h and more, the buildup of MTO itself was noted at δ 1.21 ppm. This suggests these reactions:

$$CH_3Re(NAd)_3 + ArCHO \rightarrow CH_3Re(NAd)_2O + ArCH{=}NAd \quad (1)$$

$$CH_3Re(NAd)_2O + ArCHO \rightarrow CH_3Re(NAd)O_2 + ArCH{=}NAd \quad (2)$$

$$CH_3Re(NAd)O_2 + ArCHO \rightarrow CH_3ReO_3 + ArCH{=}NAd \quad (3)$$

The ${}^1H$ signal attributed to $CH_3Re(NAd)_2O$ in the first stage of this experiment matched exactly that from the product of this reaction:

$$CH_3ReO_3 + 2CH_3Re(NAd)_3 \rightarrow 3CH_3Re(NAd)_2O \quad (4)$$

For example, when a C_6D_6 solution of 10 mM CH_3ReO_3 was added into a solution containing 2 equiv of CH_3-

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Table 1. Rate Constants and Hammett Substituent Constants According to Eq 1 for the Reaction of Aromatic Aldehydes with $CH_3Re(NAd)_3$ in C_6D_6 at 298 K

$4\text{-}XC_6H_4CHO$, X =	$k_1/10^{-4}$ L mol^{-1} s^{-1}	σ_X
$4\text{-}NO_2$	7.0[a]	0.78
CHO	5.6[b]	0.45
MeOC(O)	3.2[b]	0.45
H	1.4[b]	0
MeO	0.4_2[b]	−0.27
Me_2N	0.2_8[b]	−0.83

[a] Determined directly. [b] Determined in competition experiments relative to the value for 4-nitrobenzaldehyde.

$Re(NAd)_3$, the predominant resonance in 5 min was from $CH_3Re(NAd)_2O$. As reported for $MeRe(NAr)_2O$,[21] compound $CH_3Re(NAd)_2O$ could also be prepared by refluxing a toluene solution of MTO and 2 equiv of AdNCO. Also, the spectrum of $CH_3Re(NAd)O_2$ obtained from the second stage of the reaction is the same as that from this reaction:

$$2CH_3ReO_3 + CH_3Re(NAd)_3 \rightarrow 3CH_3Re(NAd)O_2 \quad (5)$$

The chemical shifts of the methyl group bound to rhenium change systematically with the number of oxygen atoms. For $CH_3Re(NAd)_{3-x}O_x$, the values are δ 1.99, 1.91, 1.75, and 1.21 ppm for the series with $x = 0$ to 3, respectively. For the same series, the ^{13}C chemical shifts are −6.49, 0.80, 8.10, and 17.40 ppm.

To overcome the complications from the succession of reactions in eqs 1−3, the rate constants for the first stage of the reactions between $CH_3Re(NAd)_3$ and aromatic aldehydes were evaluated by a competition method. Details about data collection and analyses are given in the Experimental Section. These reactions were carried out using a mixture of 4-nitrobenzaldehyde (for which k_1 was independently determined) and a given ArCHO. The intensities of the aldehydes and imines were measured at least three times during the reaction of eq 1. From these measurements, the values of k_1 could be determined. The data are presented in Table 1. It is clear that a change in substituent X of the compound $4\text{-}XC_6H_4CHO$ has a substantial effect on the rate, with electron-donating X groups slowing the reaction and vice versa.

The reactions of linear aliphatic aldehydes with $CH_3Re(NAd)_3$ proceed much more rapidly than those of aromatic aldehydes. The reaction of t-BuCHO takes place slowly, and the imine formed is stable. However, the other aliphatic organic imines produced are not stable. When 2 mM $n\text{-}C_3H_7C\mathbf{H}O$ (δ_{CHO} 9.26 ppm; $^3J_{HH}$ 1.6 Hz) was added to a 1 mM C_6D_6 solution of $CH_3Re(NAd)_3$, a triplet (δ 7.47 ppm, $^3J_{HH}$ 4.8 Hz) was observed, corresponding to $n\text{-}C_3H_7C\mathbf{H}{=}NAd$. The rate constants for the first and second stages are $k_1 = 3.2 \times 10^{-2}$ L mol^{-1} s^{-1} and $k_2 = 6.4 \times 10^{-4}$ L mol^{-1} s^{-1} at 298 K.

Reactivity of $MeRe(NAd)_3$ and $MeRe(NAr)_3$. Redistribution reactions between $MeRe(NAd)_3$ and $MeRe(NAr)_3$ were not observed. The only imine noted was $4\text{-}NO_2C_6H_4CH{=}NAd$ after a large excess of $4\text{-}NO_2C_6H_4CHO$ was added to a C_6D_6 solution of $MeRe(NAd)_3$ and $MeRe(NAr)_3$ (1:5). We assumed that the other possible imine, $4\text{-}NO_2C_6H_4CH{=}NAr$, was formed, but it amounted to less than 5% of $4\text{-}NO_2C_6H_4CH{=}NAd$ and thus was not detectable by the ^1H NMR technique. One can conclude that $MeRe(NAd)_3$ is at least 100 times more reactive than $MeRe(NAr)_3$ toward $4\text{-}NO_2C_6H_4CHO$. It is worth noting that a mixture of $MeRe(NAr)_3$ and $MeRe(NAr)_2O$ was observed from the above sample after 2 days; however, the corresponding imine $4\text{-}NO_2C_6H_4CH{=}NAr$ was not observed. The formation of $MeRe(NAr)_2O$ is presumed to result from the reaction of $MeRe(NAr)_3$ with MTO, according to eqs 1−3. The redistribution reactions between $MeRe(NAr)_3$ and MTO have been reported by Herrmann and co-workers.[21]

Reaction with Imines. Addition of $PhC\mathbf{H}{=}NPh$ ($\delta_{CH=N}$ 8.13 ppm) to a solution of $CH_3Re(NAd)_3$ in C_6D_6 gave rise to a new imine resonance at 8.47 ppm, assigned as $PhC\mathbf{H}{=}NAd$. Likewise, use of $(4\text{-}NMe)_2C_6H_4CH{=}NC_6H_4(4\text{-}OMe)$ (δ 8.40 ppm) gave rise to a new resonance for $(4\text{-}NMe_2)C_6\mathbf{H}_4CH{=}NAd$ at 8.32 ppm.

The reactions of $CH_3Re(NAd)_3$ with imines are slower than those of the aldehydes. Since $CH_3Re(NAd)_3$ is moisture sensitive, it is reasonable to ask whether the reaction really involves $AdNH_2$, a hydrolysis product of the parent. It should be noted that neither $AdNH_2$ nor H_2O was observed in the spectra taken during the reactions of $CH_3Re(NAd)_3$ with imines. An attempted reaction of $AdNH_2$ (25 mM) with $(4\text{-}OMe)C_6H_4CH{=}NC_6H_4(4\text{-}t\text{-}Bu)$ required many weeks to reach equilibrium ($K_{298} \approx 2.7$).

Other reagents that do not react with $CH_3Re(NAd)_3$ at 298 K in C_6D_6 are the *N*,*N*-dimethylhydrazones of 2-pyridinecarboxaldehyde and cyclohexanecarboxaldehyde.

Reactions with Other Donors. Cyclic ketones, acetophenone, nitrosobenzene, and methylphenylsulfoxide do not react with $CH_3Re(NAd)_3$. Nor do *cis*- and *trans*-stilbene oxides, styrene oxide, and pyridine-*N*-oxide. Indeed, MTO is the best oxygen transfer system, as first reported for $CH_3Re(NAr)_3$, Ar = 2,6-diisopropylphenyl.[21] Thus $CH_3Re(NAd)_3$ reacts with MTO to give $CH_3Re(NAd)_2O$ and/or $CH_3Re(NAd)O_2$, according to the proportions used.

Reactions between $CH_3Re(NAd)_3$ and phosphines were attempted, since certain imido metal complexes produce phosphinimines.[11,12] This met with no success for PPh_3, $PPhMe_2$, and $P(n\text{-}Bu)_3$.

Imine−Imine Metathesis. Although the products of the metathesis reaction between organic imines and $CH_3Re(NAd)_3$ have been observed, this rhenium compound does not catalyze the metathesis reaction between two imines.

On the other hand, MTO itself does catalyze the imine−imine metathesis process, both as the dissolved complex in benzene and MTO supported on Nb_2O_5, the preparation of which has been described.[24] This uncatalyzed reaction was very slow:

$$PhCH{=}NPh + ArCH{=}NAr' \rightleftarrows PhCH{=}NAr' + ArCH{=}NPh \quad (6)$$

Upon addition of MTO (11 mM), equilibrium was reached in 40 h at room temperature and in >60 h when 1.8 mM MTO was used, Figure 3. The intensities of the resonances for the reaction at equilibrium lead to a value of the equilibrium constant of $K_6 = 1.1$ at room temperature in benzene.

The heterogeneous catalyst, MTO supported on niobium oxide,[24,26] proved much more active. Equilibrium was attained in reaction 6 within 2 h when 5 mg of MTO/Nb_2O_5 was added to 0.7 mL of C_6D_6 containing

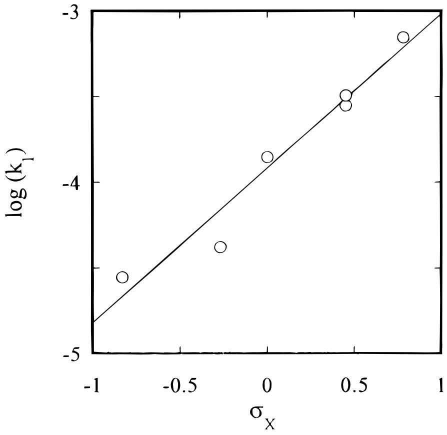


Figure 2. Correlation of the rate constants for the reaction between $CH_3Re(NAd)_3$ (Ad = 1-adamantyl) and para-substituted benzaldehydes, with the Hammett substituent constant σ.

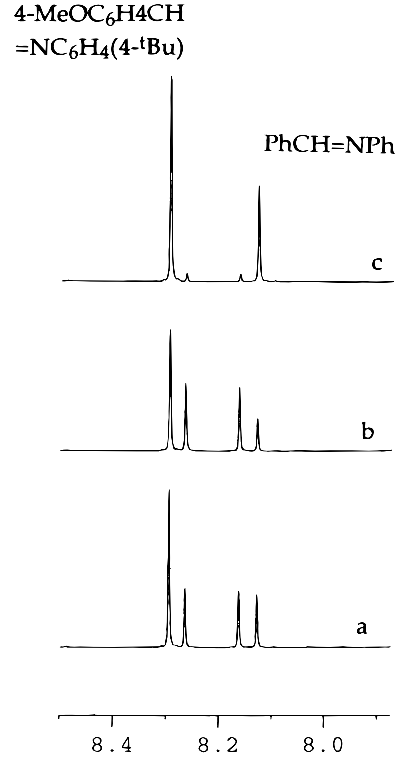


Figure 3. ^{1}H spectra taken of reactions between PhCH=NPh (10 mM) and $(4\text{-MeO})C_6H_4CH{=}NC_6H_4(4\text{-t-Bu})$ (20 mM) in the presence of (a) 1.8 mM MTO, (b) 11 mM MTO, and (c) in the absence of MTO.

10 mM PhCH=NPh and 20 mM ArCH=NAr′. It has been established that MTO/Nb_2O_5 is superior to the homogeneous catalyst for olefin metathesis.[26]

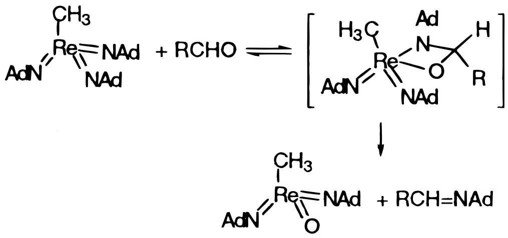
Amine−Imine Exchange. Such a reactions, eq 7, might be considered as a method for preparing imines of sterically hindered ketones.[27]

$$RNH_2 + R''CH{=}NR' \rightleftarrows R'CH{=}NR + R'NH_2 \quad (7)$$

To see if amines can initiate imine−imine exchange reactions, $PhCH_2NH_2$ was added to a solution containing PhCH=NPh and $ArCH{=}NCH_2Ar'$. Besides the four imines shown in eq 6, the following two imines were found as well: $PhCH{=}NCH_2Ph$ and $ArCH{=}NCH_2Ph$. It seems that the amine/imine exchange reaction is governed not only by the basicity of the amine but also by its steric demand. The sterically less hindered amines, $PhCH_2NH_2$ and $4\text{-MeOC}_6H_4NH_2$, react with $4\text{-MeO}{-}C_6H_4CH{=}NC_6H_4(4\text{-}t\text{-Bu})$ much faster than sterically demanding amines such as 1-NH_2Ad and $2,6\text{-Me}_2C_6H_3NH_2$. These equilibrium constants were obtained for reaction 7 for $4\text{-MeO}{-}C_6H_4CH{=}NC_6H_4(4\text{-}t\text{-Bu})$. The least favorable reactions required ~3 weeks to attain equilibrium, and the values of $K_7(C_6D_6, 298\ K)$ given below may be less precise:

amine:	$PhCH_2NH_2$	$4\text{-MeOC}_6H_4NH_2$	$AdNH_2$	$2,6\text{-Me}_2\text{-}C_6H_3NH_2$
$K_7(rt, C_6D_6)$	27	5	~2.7	~0.04

Scheme 1



Discussion

Aldehyde Reactions: Kinetics. The triphasic steps (reactions 1−3) are not well enough separated in time to allow a simple resolution of the kinetics. The times at which the spectroscopic intensities appeared were sufficient to allow one to state that the steps 1−3 decrease in rate in succession. As a typical example, the reactions of $n\text{-}C_3H_7CHO$ for stages 1 and 2 are in the ratio 50:1. Because of the concurrent nature of this reaction trio, resolution of the rate constants, even for the first stage, may lead to large and perhaps systematic errors.

With the series of benzaldehydes, the rate constants were determined for the first stage, as given in Table 1. It is clear that there is a systematic effect of the para substituent of benzaldehydes, such that electron-withdrawing groups accelerate the reaction. This series was examined by Hammett's linear free-energy correlation. Figure 2 depicts a plot of log k versus the substituent constants σ. The data define a reasonable straight line (correlation coefficient 0.976) with a slope that gives the reaction constant $\rho = +0.90 \pm 0.10$; the relatively low precision arises from the nature of the kinetic data and analysis. In any event, this value of ρ implicates a mechanism in which the reaction center, here the carbonyl carbon, becomes less positive in the transition state as compared to the starting material.

The mechanism proposed for the reaction between $CH_3Re(NAd)_3$ and aldehydes, Scheme 1, is analogous to the olefin metathesis. The involvement of a four-center transition state is generally accepted for many related (2+2) exchange reactions.[18,19] The final step is irreversible since no tris(imido)metal complex was formed from $CH_3Re(NAd)_2O$ and an excess of any imine.[28] In support of the structure proposed for the reaction intermediate, two imidomethylrhenium com-

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plexes with bridging oxo ligands have been identified.[21] A similar intermediate can be postulated for the imido-oxo exchange reactions between $CH_3Re(NAd)_3$ and MTO.

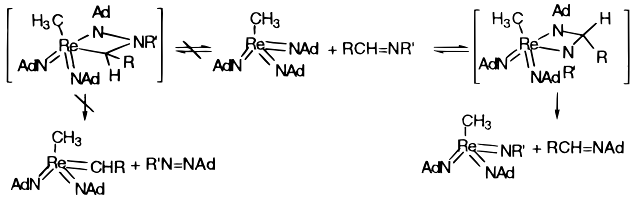
In the reaction of $CH_3Re(NAd)_3$ and RCHO, neither a nitroso compound, AdNO, nor a rhenium carbene, Re═CHAr, was observed. Thus the reaction is regiospecific. The electrophilic carbon of the aldehyde interacts with the nitrogen atom of the imidorhenium compound, forming the cyclic intermediate shown in Scheme 1. Quite likely, the oxygen atom initially attacks the Re(VII) center. The large substituent effect is consistent with a polar cycloaddition mechanism, as observed in Wittig reactions.[29] The positive value of ρ suggests that electrophilic attack of the nitrogen of the imido group by the carbon of the aldehyde is rate-controlling. As it turns out, $CH_3Re(NAd)_3$ is a much weaker Lewis acid than MTO. Pyridine, for example, which binds appreciably to MTO ($K = 2 \times 10^2$ L mol^{-1}),[30] does not coordinate to the imido complex to a detectable extent.

Although an ortho substituent of an aromatic aldehyde does not lead to a steric effect, the reactivity of sterically hindered aliphatic aldehydes is significantly diminished. Thus, n-C_3H_7CHO is much more reactive than $(CH_3)_3CCHO$. We suggest that ketones do not react with $CH_3Re(NAd)_3$ for steric reasons. Whereas MTO reacts with $CH_3Re(NAd)_3$, $CH_3Re(NAr)_3$ does not because of the steric hindrance in forming an intermediate with μ-NAd and μ-NAr bridges.

Thermodynamic Considerations. It is useful to estimate a value for the Re═NAd bond enthalpy in $CH_3Re(NAd)_3$. The first stage of the reaction between it and an aldehyde, in which $CH_3Re(NAd)_2O$ is formed, is much faster than the final stage that forms MTO (i.e., $k_1 \gg k_3$). The values of ΔH are roughly the same for each, implying the difference resides in the values of ΔS. The values of ΔS for the two steps could be much different, since $CH_3Re(NAd)_3$ imposes a much greater steric demand than $CH_3Re(NAd)O_2$. The C═O bond of the aldehyde is stronger than the C═N bond of the imine by about 30 kcal mol^{-1},[31] so that the driving force for the imide/aldehyde reaction derives from the strength of the Re═O interaction. The bond dissociation free energy of the first Re═O bond of MTO is 111 kcal mol^{-1}, as measured against V^{2+}/VO^{2+} in aqueous solution.[32] If the entropy change is ignored for the conversion of $CH_3Re(NAd)O_2$ to MTO, then the bond enthalpy for the Re═NAd bond is less than ca. 80 kcal mol^{-1}.

Catalytic Formation of Imines. The compound $CH_3Re(NAd)_3$ can be prepared according to eq 8, and its overall reaction with aromatic aldehydes is described by eq 9. Thus reaction 10, the combination of eqs 8 and 9, should be catalyzed by MTO. Indeed, the formation of $4\text{-}NO_2C_6H_4CH{=}NAd$ from the reaction of AdNCO and $4\text{-}NO_2C_6H_4CHO$ is catalyzed by MTO or $MeRe(NAd)_3$.

Scheme 2



Although reaction 10 is not practical at room temperature due to the low activities of the catalysts, this water-free method to prepare imines may be useful at elevated temperature. For example, $4\text{-}NO_2C_6H_4CH{=}NAd$ was obtained quantitatively when a solution of AdNCO (1 mmol), $4\text{-}NO_2C_6H_4CHO$ (1 mmol), and MTO (0.02 mmol) was refluxed in toluene for 4 h. Organic imine was not observed when the reaction was carried out in the absence of MTO.

$$CH_3ReO_3 + 3AdNCO \rightarrow CH_3Re(NAd)_3 + 3CO_2 \quad (8)$$

$$CH_3Re(NAd)_3 + 3ArCHO \rightarrow CH_3ReO_3 + 3ArCH{=}NAd \quad (9)$$

$$AdNCO + ArCHO \rightarrow ArCH{=}NAd + CO_2 \quad (10)$$

Reactions with Imines. It seems reasonable to adopt the mechanism for aldehydes, Scheme 1, to the reactions between $CH_3Re(NAd)_3$ and imines. If so, the imidorhenium/imine reaction would also be regiospecific. Consistent with that, no diazene was formed, Scheme 2.

Certain examples of imido/imine reactions have been reported.[33−38] Isolation of such a material, $Cp_2Zr(Bu^tNCHPhNPh)$, from the reaction of $Cp_2Zr(N\text{-}t\text{-}Bu)$ and PhCH═NPh supports a cycloaddition processes.[34] Kinetic studies on $Py_3Cl_2Ti{=}N\text{-}t\text{-}Bu$, however, suggest an alternative mechanism.[35]

Although amines ($AdNH_2$ or $ArNH_2$) and water were not detected in the reactions of $CH_3Re(NAd)_3$ with imines, it is difficult to rule out that trace amounts of them might be involved:

$$CH_3Re(NAd)_3 + H_2O \rightarrow CH_3Re(NAd)_2O + AdNH_2 \quad (11)$$

$$AdNH_2 + ArCH{=}NAr' \rightleftarrows ArCH{=}NAd + Ar'NH_2 \quad (12)$$

$$Ar'NH_2 + CH_3Re(NAd)_3 \rightleftarrows CH_3Re(NAd)_2(NAr') + AdNH_2 \quad (13)$$

The involvement of $AdNH_2$ was shown to be unimportant by demonstrating that its reactions with imines are very slow. Thus the contributions of reactions 11−13 are negligible.

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(28) The C_6D_6 solution of $MeRe(NAd)_2O$ was prepared by mixing $MeRe(NAd)_3$ and MTO in a 2:1 ratio. The imines used here were $4\text{-}NO_2C_6H_4CH{=}NAd$ and $4\text{-}MeOC_6H_4{=}NC_6H_4(4\text{-}t\text{-}Bu)$.

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Imine−Imine Metathesis. The chemical shift of $C\mathbf{H}_3ReO_3$ changes significantly when pyridine is coordinated.[30] In contrast, it barely changes at all when an imine is added. The weak imine interaction thus indicated appears to be responsible for the slowness of the MTO-catalyzed metathesis at room temperature. A metal-mediated mechanism for catalytic imine metathesis has been suggested.[38] MTO is very likely involved because the metathesis rate increases with its concentration. It remains unresolved whether MTO simply catalyzes the hydrolysis of the imines, eqs 14 and 15, or if it is directly involved in the exchange.

$$\mathrm{PhN{=}CHPh + H_2O \xrightleftharpoons{MTO} PhCHO + PhNH_2} \qquad (14)$$

$$\mathrm{ArN{=}CHAr' + H_2O \xrightleftharpoons{MTO} Ar'CHO + ArNH_2} \qquad (15)$$

As shown in eq 7, the anilines thus formed (eqs 14 and 15) will rapidly react with imines to produce the same products as those given from the direct metathesis reaction. The imine alone is stable in solution for at least a week under these conditions; however, small amounts of aldehydes were observed when MTO/Nb_2O_5 was used as a catalyst.

Olefin metathesis (eq 16) is catalyzed by MTO, but imine metathesis (eq 17) is not. An attempt to reverse the latter process was attempted with MTO, but the reaction did not occur in that direction either.

$$\mathrm{2RCH{=}CHR' \rightleftarrows RCH{=}CHR + R'CH{=}CHR'} \qquad (16)$$

$$\mathrm{2RCH{=}NR' \rightleftarrows RCH{=}CHR + R'N{=}NR'} \qquad (17)$$

Conclusions

Admantylimidorhenium complexes react with aldehydes and imines through a metathesis mechanism. Sterically hindered aliphatic aldehydes react much more slowly than linear ones. Electronic effects also play an important role in the imido−aldehyde metathesis reactions. Tris(admantylimido)methylrhenium is much more reactive toward aldehydes than tris(2,6-diisopropylphenylimido)methylrhenium. MTO catalyzes imine−imine exchange reactions, as well as the water-free imine formation from aromatic isocyanates and aldehydes.

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Supporting Information Available: ^1H and ^{13}C NMR chemical shifts for imines. This material is available free of charge via the Internet at http://pubs.acs.org.

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