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Reactions of Fluorenylidene Nitrile Ylides with (Salen)metal Complexes

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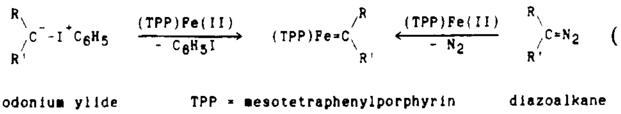
Nitrile ylides of fluorenylidene ($RR'C^--N^+C-R''$: $R'' = CH_3$ or C_6H_5; R, $R' = C_{12}H_8$) serve as carbene equivalents in reactions with (salen)metal complexes (salen = *N,N'*-ethylenebis(salicylideneaminato)) of first-row transition metals in acetonitrile or benzonitrile solvents. The microscopic rate constants for these reactions were obtained directly by flash photolysis experiments and were found to depend upon the nature, oxidation state, and ligation of the metal. Oxo(salen)chromium(V) triflate reacts with a rate constant close to the diffusional limit to form (salen)chromium(III) triflate and fluorenone. The reactivities of (salen)metal(III) cations are lower and decrease in the order V > Cr > Mn > Fe. The reactions of the ylides with metal(III) cations apparently form metallocarbenes or related species, and products resulting from carbene insertion into a metal–ligand bond (as identified for M = Cr) ultimately are obtained.

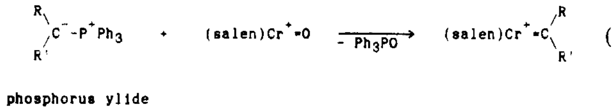
Introduction

Organometallic species are believed to be intermediates in oxidations mediated by cytochrome P450 and related model compounds.[1,2] Considerable evidence exists for formation of metal carbene and metal alkyl complexes in these reactions.[3,4] For example, recently Mansuy has prepared iron porphyrin carbene complexes almost quantitatively by reaction of ylides and diazoalkanes with iron porphyrin compounds (eq 1).[3] These species were demonstrated to be viable intermediates in reactions of oxometal complexes.



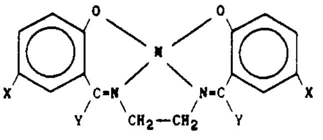
(1)

Alkynes and phosphorus ylides also serve as carbene equivalents with the oxo(salen)chromium(V) cation (salen = *N,N'*-ethylenebis(salicylideneaminato)), a cytochrome P450 model compound, and we have obtained evidence that carbene (or related) complexes of chromium are formed as intermediates (eq 2).[5] Such intermediates apparently are short-lived in this system, however, and no metallocarbene derivatives of the (salen)metal complexes were detected.



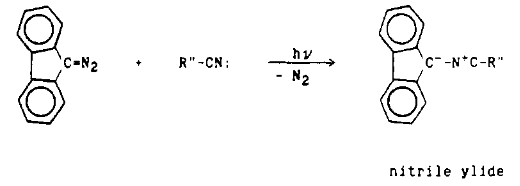
(2)

Thus, although reaction of coordinatively unsaturated metal complexes with an ylide appears to be a general route for synthesis of metallocarbene complexes,[3-6] the absolute reactivities for such processes have not been established. Therefore, we have directly examined the reaction of salen complexes of first-row transition metals (see I) with nitrile ylides using transient absorption techniques. (Salen)metal species are coordinatively unsaturated complexes that react with ylides and other carbene equivalents.[5] Ylides of fluorenylidene were selected as the carbene equivalents for this investigation for several reasons. Photolysis of diazofluorene in the near-UV region affords fluorenylidene, which in acetonitrile or benzonitrile solvent forms the nitrile ylide **1** or **2** in high yield (eq 3).[7] Nitrile ylides such as **1** and **2** resemble the phosphorus ylides used in our earlier studies (eq 2). The rates of reaction of the phosphorus ylides were too fast to measure by conventional techniques.[5] Furthermore, ylides **1** and **2** absorb at sufficiently low energy ($\lambda \geq 400$ nm[7]) that they may be observed optically in the presence of the colored (salen)metal complexes.



salen: X = Y = H
DClsalen: X = Cl, Y = H
DNO$_2$salen: X = NO$_2$, Y = H
DMesalen: X = H, Y = CH$_3$

I



(3)

1 R'' = CH$_3$
2 R'' = C$_6$H$_5$

We have found that the reaction of nitrile ylides **1** and **2** with (salen)metal derivatives leading to metallocarbenes or related species can be observed directly by flash photolysis. The results of our initial investigation are reported.

Experimental Section

Materials. 9-Diazofluorene[8] and the (salen)metal complexes[9] were prepared according to literature procedures. Acetonitrile (Fisher HPLC grade) and benzonitrile (MCB) were used as received; specially purified solvents (distilled first from CaH$_2$ and then from P$_2$O$_5$ under argon) were found to afford identical results.

Transient Absorption Spectra. The flash photolysis apparatus and curve-fitting routines have been described previously.[10] The frequen-

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Table I. Rate Constants for Reactions of Fluorenylidene Ylides with (Salen)metal Complexes

metal complex[a]	λ (ϵ)[b]	rate const, M^{-1} s^{-1}[c] CH$_3$CN	rate const, M^{-1} s^{-1}[c] C$_6$H$_5$CN
$OCr^{V}salen(CF_3SO_3)$	580 (1800)	5.5×10^9	6.3×10^8
$OV^{IV}salen$	580 (160)	1.0×10^6	
$Cl_2V^{IV}salen$	580 (4800)	1.7×10^8	
$ClV^{III}salen$	580 (850)	6.7×10^8	2.5×10^7
$ClCr^{III}salen(H_2O)_2$	500 (400)	6×10^7	*d*
$(PF_6)Cr^{III}salen(H_2O)_2$	500 (370)	5×10^7	6×10^7
$(CF_3SO_3)Cr^{III}salen(H_2O)_2$	500 (430)	7.3×10^7	7.7×10^7
$(CF_3SO_3)Cr^{III}DMesalen(H_2O)_2$	500 (220)	6.1×10^7	4.3×10^7
$(CF_3SO_3)Cr^{III}DClsalen(H_2O)_2$	500 (530)	2.6×10^8	1.5×10^8
$(CF_3SO_3)Cr^{III}DNO_2salen(H_2O)_2$	500 (1300)	5.4×10^8	1.9×10^8
$(BF_4)Mn^{III}salen$	500 (780)	1.6×10^7	9.3×10^6
$ClFe^{III}salen$	500 (4200)	1×10^6	
$(PF_6)Fe^{III}salen$		$\sim 5 \times 10^6$	4.1×10^6
$Mn^{II}salen$	500 (2200)	$<2 \times 10^{7}$[d]	
$Co^{II}salen$	500 (1800)	$<3 \times 10^{6}$[d]	
$Ni^{II}salen$	500 (570)	$<1 \times 10^{6}$[d]	
$Cu^{II}salen$	580 (350)	$\sim 1 \times 10^7$	
$Zn^{II}salen$	*e*	*e*	

[a] See structure I. [b] Absorption bands (nm) and molar extinction coefficients (M^{-1} cm^{-1}) of the metal complexes. [c] Standard deviations ±15%. [d] No quenching observed. [e] Complex insoluble.

cy-doubled (532 nm) emission from a Quantel YG481 Nd:YAG laser (11 ns, Q-switched) was passed through wire-mesh filters (4%–100% transmission), which attenuated light intensity and varied the concentration of transients to test kinetic order. A fluorescence cuvette (l = 0.5 cm) containing solution was purged gently with nitrogen for about 25 min preceding and throughout the measurements. The difference transient absorption spectra and decays of **1** and **2** were monitored at 400–420 nm at 22 ± 1 °C. The decay of **1** in the absence of additives could be reproduced satisfactorily by assumption of competing first- and second-order processes, with rate constants $k_1 = 3 \times 10^3$ s^{-1} and $k_2/\epsilon = 5 \times 10^5$ cm s^{-1}. The decays in the quenching experiments were determined under pseudo-first-order conditions using (salen)metal complexes in excess, and rates were determined to be independent of the concentration of diazofluorene over the range 0.02–0.5 mM. Standard deviations for two or three repetitive runs were ±15% or less.

The concentrations of metal complexes were determined optically by using an HP8450A diode-array spectrophotometer. Extinction coefficients (Table I) of freshly prepared (salen)metal complexes were determined on an HP8452A spectrophotometer. Absorption maxima and molar extinction coefficients in acetonitrile determined for the (salen)metal complexes are listed in Table I. The solubilities of (salen)metal(II) derivatives were relatively low, and their quenching behavior was examined over a smaller concentration range extending to the limit of their solubilities. Generally, the solubilities of the (salen)metal complexes also were lower in benzonitrile and in THF than in acetonitrile.

The 9-fluorenyl radical, prepared by photolysis in cyclohexane for comparison,[11] exhibits characteristic absorptions near 500 and ~350 nm. The formation of small amounts of this radical in nitrile solvents does not interfere with observation of the ylides. The absorptions of the radical were too small to obtain information concerning reaction of the radical with the (salen)metal complexes, however.

Product Studies. Preparative-scale experiments were performed by irradiation of equimolar solutions of metal complexes and diazofluorene in degassed acetonitrile using a 450-W medium-pressure Hanovia mercury lamp (Pyrex filter). No reaction between diazofluorene itself and the (salen)metal complexes occurred in the dark under the conditions of the irradiations. Organic products were separated by extraction with benzene and were analyzed by proton NMR spectroscopy (using a Varian FT-80A spectrophotometer) and GC/MS (using a cross-linked 5% phenylmethylsilicone capillary column and EI with a Finnigan TSQ 45 GC/MS/MS/DS instrument). The benzene-insoluble metal complexes were characterized by UV/vis spectroscopy. Recovered (salen)chromium(III) complexes were either oxidized with iodosobenzene to the oxo(salen)chromium(V) species, which were tested for activity, or demetalated as described below.

Irradiation of diazofluorene ($C_{12}H_8C{=}N_2$, 0.18 g, 1.0 mmol) in acetonitrile (100 mL) in the absence of metal complexes afforded a mixture of products characteristic of the carbene fluorenylidene ($C_{12}H_8C$:), mostly 9-(cyanomethyl)fluorene ($C_{12}H_8CH{-}CH_2CN$)[7] and fluorenone ketazine ($C_{12}H_8C{=}N{-}N{=}CC_{12}H_8$)[7] together with small amounts of 9,9′-bifluorenylidene ($C_{12}H_8C{=}CC_{12}H_8$), 9,9′-bifluorenyl ($C_{12}H_8CH{-}CHC_{12}H_8$), and 9-fluorenol ($C_{12}H_8CHOH$). Photochemical reaction of diazofluorene (0.18 g, 1.0 mmol) in the presence of oxo(salen)chromium(V) triflate (0.22 g, 0.5 mmol) in acetonitrile (100 mL) afforded (salen)chromium(III) triflate and fluorenone only in yields of 80 ± 10% and 83 ± 5%, respectively (based on oxometal). About 90% of the original amount of oxo(salen)chromium(V) triflate could be regenerated by addition of iodosobenzene. Irradiation of diazofluorene (0.36 g, 2.0 mmol) with a stoichiometric amount of (salen)chromium(III) triflate (0.97 g) in acetonitrile (200 mL) also resulted in consumption of the diazofluorene and the production of a brown solid. Only about 50% of the recovered metal-containing products could be oxidized to oxo(salen)chromium(III) triflate, however. Treatment of the crude material with boiling concentrated HCl liberated the ligand. The aqueous solution was decanted from undissolved residue, neutralized, and extracted with chloroform. The organic layer contained two principal products identified as adducts of fluorene to the ligand: 9-((2-aminoethyl)amino)fluorene (**4**) and 9-((2-(salicylideneamino)ethyl)amino)fluorene (**3**) (Scheme I). A third product, formed in trace amount, was identified as 1,2-bis(fluorenylamino)ethane. 9-(Cyanomethyl)fluorene and fluorenone ketazine also were formed in this reaction.

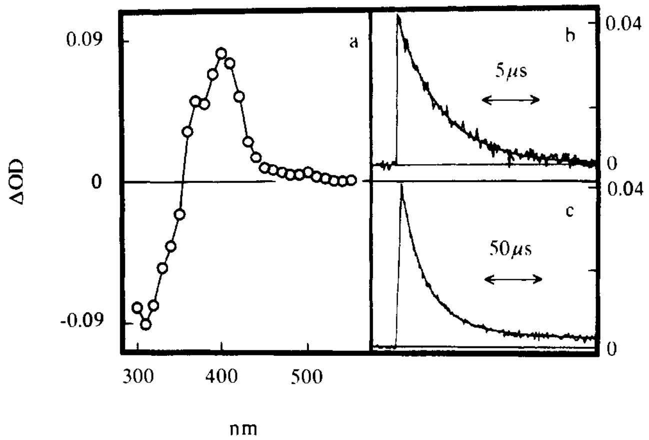

Figure 1. Difference transient absorption spectrum observed 100 ns following 355-nm excitation of diazofluorene in acetonitrile (a) and least-squares fits (solid traces) to observed decays of **1** monitored at 400 nm in the presence of 6.0×10^{-5} M $OCr^{V}salen(CF_3SO_3)$ (b) or 2.8×10^{-4} M $(CF_3SO_3)Cr^{III}salen(H_2O)_2$ (c).

Results

In nitrile solvents, carbenes react with the solvent to form nitrile ylides. Flash photolysis of diazofluorene at 355 nm in deaerated acetonitrile was found to produce a broad transient absorption near 400 nm (Figure 1a) due to formation of the acetonitrile ylide **1** of fluorenylidene[7] (eq 3). The ylide decays nonexponentially in the absence of additives, and analysis of the photolysate indicates formation of a number of products. Three of the products, 9-(cyanomethyl)fluorene, fluorenone ketazine, and an apparent dinitrile adduct of fluorenylidene, previously were reported to have formed following irradiation of dilute solutions of diazofluorene.[7] Three other products, 9-fluorenol, 9,9′-bifluorenyl, and 9,9′-bifluorenylidene, were observed in small amounts under our conditions. No fluorenone could be detected from deaerated solutions. The ylide absorptions were quenched efficiently by dioxygen, however, and fluorenone is the principal product formed in the presence of air. The presence of oxygen does not reduce the initial absorbance of the ylide, so that the fluorenone must be produced mostly by reaction of **1** with O_2.

Addition of salen complexes of first-row transition metals to deaerated, dilute solutions of diazofluorene resulted in strictly monoexponential decays for the ylide (Figure 1b,c). The decay rates were proportional to the concentrations of the (salen)metal complexes (Figure 2). The second-order rate constants were calculated from the pseudo-first-order decays of the ylide as shown in Figure 2. The magnitude of the rate constants depended on the nature of the metal complex and varied by a factor of about 10^4 (Table I). The greatest rate was obtained with oxo(salen)chromium(V) triflate. Fluorenone (83%) and (salen)chromium-

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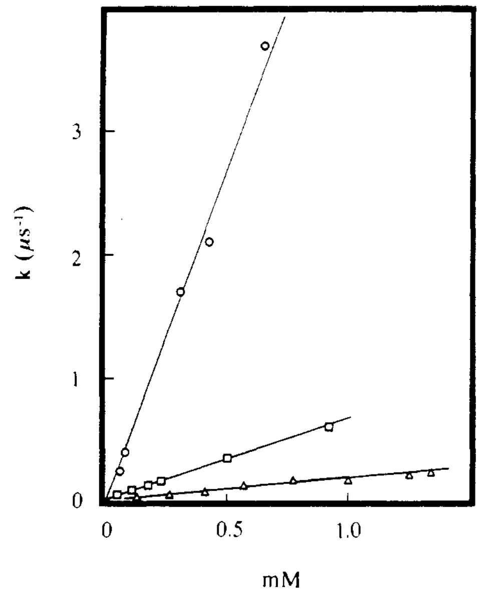
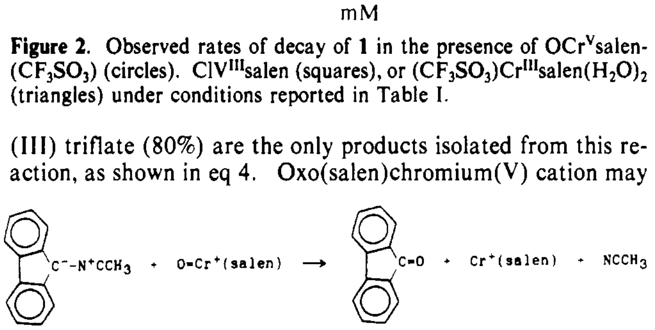


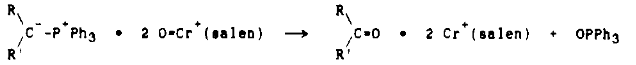
Figure 2. Observed rates of decay of **1** in the presence of OCr^{V}salen(CF$_3$SO$_3$) (circles). ClV^{III}salen (squares), or (CF$_3$SO$_3$)Cr^{III}salen(H$_2$O)$_2$ (triangles) under conditions reported in Table I.

(III) triflate (80%) are the only products isolated from this reaction, as shown in eq 4. Oxo(salen)chromium(V) cation may be regenerated in situ to the extent of ~90% by addition of iodosobenzene to the liberated (salen)chromium(III) triflate, and the regenerated complex is active toward subsequent oxidation.



(4)

The reaction of eq 4 is akin to the facile reaction observed for phosphorus ylides with the oxochromium complex to form ketones[5] (eq 5). The latter process also is catalytic with respect to chromium, with a turnover number of about 5 (~85% of the catalyst is regenerated each cycle). The rate constants for this reaction are too high to determine by conventional techniques.

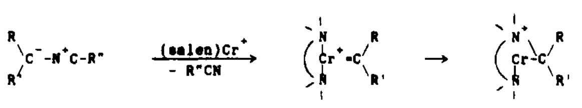


$$\overset{R}{\underset{R'}{\diagdown\!\!\diagup}}C^{-}\text{-}P^{+}Ph_3 + 2\ O{=}Cr^{+}(salen) \longrightarrow \overset{R}{\underset{R'}{\diagdown\!\!\diagup}}C{=}O + 2\ Cr^{+}(salen) + OPPh_3 \qquad (5)$$

(Salen)metal(III) salts were found to react with ylide **1**. The rate constant for the reaction of **1** with (salen)chromium(III) is smaller than that for reaction with oxo(salen)chromium(V) (eq 4). The same rate constant is observed with hexafluorophosphate, triflate, or chloride as counterion, indicating no participation of the counterion. However, the rate constants for reaction of **1** with various (salen)metal(III) cations depend on the identity of the metal as indicated in Table I. The decays were unaffected by the deliberate addition of water or of lithium trifluoromethanesulfonate. The failure of lithium salts to affect the ylide decay rules out a salt effect or action of the metals as simple Lewis acids.

The differential baseline does not completely return to zero for the reaction of **1** with the (salen)metal(III) complexes. The observation of residual absorptions following the decay of the ylide is indicative of the formation of long-lived species by reaction of the ylide with the metal complexes. For example, a small residual absorption following reaction of **1** in the presence of (salen)chromium(III) salts is apparent (Figure 1c). Product studies concerning reaction of (salen)chromium(III) triflate with stoichiometric amounts of diazofluorene indicate that the metal complex is altered permanently by alkylation of the ligand at nitrogen (indicated schematically in eq 6).

Reactions in benzonitrile solvent also were examined. Photolysis of diazofluorene in benzonitrile affords the benzonitrile ylide **2** (eq 3), with optical absorptions similar to the acetonitrile ylide **1**.[7] The half-life of **2** in the absence of additives was more than 1 order of magnitude longer than that of **1**. The decay of **2** in the presence of (salen)metal complexes also followed excellent pseudo-first-order kinetics (Table I).[12]



(6)

Discussion

The reaction of ylide **1** with oxo(salen)chromium(V) cation affords fluorenone and the (salen)chromium(III) cation (eq 4). The rate constant observed for this process is close to that for diffusional encounter in acetonitrile.[13] Reaction of **1** with the isoelectronic oxo(salen)vanadium(IV) is slower by a factor of 6 × 10^3 and represents one of the slowest reactions observed. Fluorenone was not a product of reaction with the oxovanadium complex and most of the oxo(salen)vanadium(IV) may be recovered unchanged. Therefore, the rate of oxygen transfer from oxovanadium(IV) must be slower than that from oxochromium(V) by a factor of greater than ~10^5. This dramatic rate difference does not seem to be due to differences in the oxygen–metal bond strengths. Thus, a force constant $k_{M=O}$ of 7.26 mdyn/Å is estimated for oxovanadium(IV)[14] whereas the value for oxochromium(V) is about 7.30 mdyn/Å (calculated for a diatomic oscillator by using an IR stretching frequency of 1006 cm^{-1}).[9a] At least two effects may be responsible for the difference in rates: (1) the presence of charge, which makes the oxochromium(V) species a better electrophile, and (2) a thermodynamic contribution, concerning the less favorable formation of V(II) from oxovanadium(IV) as opposed to that of Cr(III) from oxochromium(V) following oxygen transfer.

The rate constant for the reaction of **1** with the (salen)chromium(III) cation is 100-fold lower than that for the reaction with the oxo(salen)chromium(V) cation. Rate constants for reactions of the ylide would be expected to depend upon a number of additional considerations, including the charge, oxidation state, and coordination and solvation of the metal. For example, chemical trapping studies indicate that the carbene ylide **1** behaves as a nucleophile.[7,15] Reaction should be promoted with electrophilic complexes. Thus, the 5,5′-dichlorosalen and 5,5′-dinitrosalen complexes of chromium(III) react with **1** faster than the corresponding unsubstituted salen complex (Table I). The high rate of reaction of oxo(salen)chromium(V) cation is in line with this interpretation.

Nevertheless, electrophilicity does not seem to be the only important factor in deciding the relative reactivities of (salen)metal(III) complexes when the metal itself is changed. The (salen)metal(III) salts react with **1** with rate constants k (Table I), which decrease monotonically in order of increasing atomic number, V > Cr > Mn > Fe. The strong dependence of the rates on the identity of the metal suggests an association of the ylide with the metal atom, such as shown in eq 7 (Scheme I).[16] The

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(12) Photolysis of diazofluorene in THF afforded a transient with absorption near 310 nm believed to be the THF ylide of fluorenylidene. Further studies are in progress to address this possibility.

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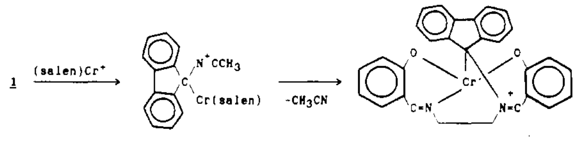
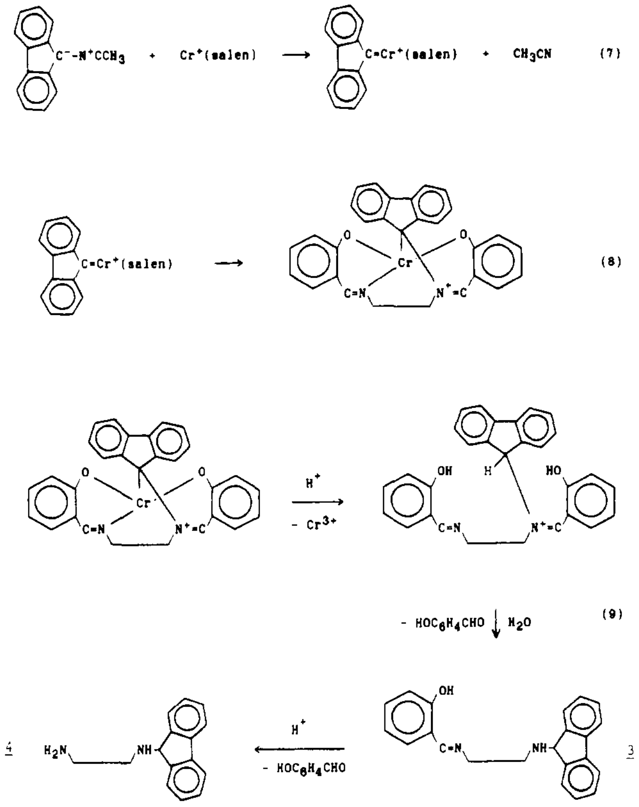
(16) Insertion occurring by an alternative process that does not involve a metallocarbene is not ruled out; viz.:



Scheme I



single-electron-reduction potentials of metal complexes[17] decrease in the same order as the reactivities decrease, indicating that electron donation to the metals from the ylide is not responsible for the observed trend. Instead, the trend in reactivities follows the ease of oxidation of the metals, which is consistent with promotion of the metals from the +3 to the +5 formal oxidation state according to eq 7.

The dependence of the reactivities on the oxidation state and charge of the metals in the complexes are amenable to a similar interpretation. Thus, the rate constant for reaction of the (salen)vanadium(IV) dication with **1** is lower than that for reaction of the (salen)vanadium(III) cation. Vanadium(IV) is a d^1 system and, despite its greater positive charge density, should back-bond to a coordinated carbene ligand less efficiently than a d^2 system such as vanadium(III).[18]

A product study also supports the formation of organometallic species. The observed products of the reaction of **1** with (salen)chromium(III) triflate contain an *N*-aminofluorenyl group. The alkylation products formally arise by insertion of fluorenylidene into a chromium–nitrogen bond, as shown in Scheme I and in skeletal eq 6.[16] This process is related to carbene insertions that involve the metal–nitrogen bonds of carbene complexes of iron porphyrin derivatives.[3]

Reaction of the oxo(salen)chromium(V) cation in benzonitrile with **2** occurs 1 order of magnitude more slowly than the reaction in acetonitrile with **1**. This can be ascribed principally to the higher viscosity of benzonitrile (1.24 cP at 25 °C[19]) compared to acetonitrile (0.345 cP at 25 °C[19]), which results in lower rates for diffusion-limited processes in benzonitrile. Reactions of (salen)metal(III) triflate, tetrafluoroborate, and hexafluorophosphate salts occur at rates that are much less than the rate of diffusion, and nearly the same rate constants are observed for ylides **1** and **2** (Table I). However, the rate constants for reaction of the (salen)metal chlorides are markedly lower in benzonitrile than in acetonitrile. Benzonitrile is significantly less polar than acetonitrile,[20] and the chlorides are notably less soluble in benzonitrile. Therefore, the anomalous behavior of the chlorides may be ascribed to a change in coordination for the chloride counterion, e.g., from outer sphere in acetonitrile (in which solvent the counterions do not affect the rates) to inner sphere in benzonitrile. Such a change in coordination would affect both the electrophilicity and unsaturation of the metal and would be expected to decrease the favorability of the reaction (eq 7).

Only estimates or upper limits for the rate constants involving the neutral (salen)metal(II) complexes could be obtained due to their relatively low solubilities (Table I). It is apparent nevertheless that the (salen)metal(II) complexes are less reactive than the cationic (salen)metal(III) complexes studied. (Salen)copper(II) is the only metal(II) complex to give any indication of reaction with **1**, in accord with the known facility with which copper salts promote carbene transfer.[21]

Conclusion

These results demonstrate the suitability of transient absorption spectroscopy for direct observation of reactions between nitrile ylides and (salen)metal complexes. The reactivities of such complexes with the nucleophilic fluorenylidene ylides **1** and **2** can be interpreted in terms of (1) the electrophilicity of the metals and (2) the favorability of two-electron change in the oxidation states of the metals. The oxo(salen)chromium(V) cation reacts with **1** and **2** to produce fluorenone and the (salen)chromium(III) cation with nearly diffusion-limited rates; the analogous reaction of oxo(salen)vanadium(IV) was not observed. The rate constants obtained for reactions of **1** and **2** with (salen)metal(III) complexes are lower and decrease monotonically with increasing atomic number of the metal. The transient absorption spectra, decay rates, and product studies indicate the formation of metallocarbenes or related species in the rate-limiting step of the reactions.

Ylides serve as one-center, two-electron donors. On the other hand, alkenes are two-center, two-electron donors. Formation of products derived from ligand alkylation may provide a common mechanism for deactivation of the (salen)metal(III) complexes as oxidation catalysts.[3] The relationship between the reactions of ylides, alkenes, and alkynes will be pursued in a subsequent study.

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