Electronic Effects in Dirhodium(II) Carboxylates. Linear Free Energy Relationships in Catalyzed Decompositions of Diazo Compounds and CO and Isonitrile Complexation

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Abstract: A linear free energy analysis of substituent effects in rhodium carboxylate complexes has been conducted. Two reactions of diazo compounds involving intramolecular competition between (1) *O*-ylide formation and secondary C–H insertion, and (2) tertiary C–H and primary C–H insertion were studied as well as complexation effects on the IR frequencies of CO and *tert*-butyl isocyanide. Aliphatic and aromatic carboxylate complexes were included. Regression equations that describe these processes include contributions from σ_α (polarizability) and σ_F (field effects) and, for the benzoates, σ_R (resonance). Complexes that deviate from the LFER include rhodium trifluoroacetate and rhodium triptycenecarboxylate, and their behavior was explained through (partial) release of the free carbene. The effect of ligand polarizability on selectivity in these reactions was interpreted as evidence for the importance of backbonding from rhodium to the carbene carbon in the product-determining step. The ability of these complexes to backbond was shown through the complexation study. Higher selectivity with increasing ability to backbond is analogous to other carbenes such as difluorocarbene. Increased selectivity engendered by backbonding could occur by facilitating the reversal of an intermediate complex between the carbenoid and the C–H bond undergoing insertion. Increased selectivity engendered by field effects and polarizability could be explained by increased selectivity for electron-rich sites.

The synthetic utility of highly catalytically-active rhodium (II) carboxylate salts in the reactions of diazo compounds, which can be conducted at or below room temperature, has become apparent over the last decade.[1] The range of transformations that can be mediated by rhodium carboxylates is impressive and includes cyclopropanation, C–H insertion, ylide formation, and dipolar cycloaddition. Likely one of the most practical carbenoid transformations in organic chemistry is the rhodium carboxylate-mediated intramolecular N–H insertion reaction that is the key ring-closure step in the Merck synthesis of thienamycin. Because the antibiotic is produced for sale by total synthesis,[2] this reaction is conducted on tens of thousands of kilograms annually.

The prototypical dirhodium carboxylate is rhodium acetate ($Rh_2(OAc)_4$), illustrated in Figure 1. This binuclear D_{4h}-symmetric compound with four bridging acetates has one vacant coordination site per metal atom, which weakly binds Lewis basic ligands. Of note is the extremely short Rh–Rh bond length (2.3855 Å for L = H_2O), which originally led to the assignment of a bond order of 3, but which is now accepted to be 1. The acetate ligands can be easily varied to other carboxylates, amidates, sulfates, or phosphates by ligand exchange or direct synthesis from rhodium trichloride and the acidic reagent.[3] The coordination chemistry of these complexes has been extensively studied.[4] One structural property of interest is the Rh–Rh bond length (Figure 2), which varies widely based both on the presence and identity of axial ligands and the bridging groups.

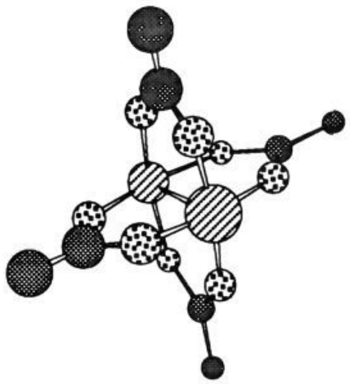

Figure 1. 3-Dimensional structure of rhodium acetate.

Rh_2L_4 ($r_{Rh\text{-}Rh}$)					
t-$BuCO_2$	HCO_2	AcO	CF_3CO_2	H_2PO_4	AcS
2.37	2.38	2.39	2.41	2.49	2.55

Figure 2. Variation of Rh–Rh bond length based on the bridging ligand. In all cases, the axial ligands are water.

Very little direct experimental data bears on the mechanisms of the reactions of diazo compounds mediated by rhodium complexes or the intermediates, such as metal carbenes, that may be generated. It is therefore difficult to know how these reactions can be rationally modified by conditions, including the incorporation of asymmetric catalysis.[5] In early studies on C–H insertions, Taber[6] proposed a mechanism involving cleavage of the rhodium–rhodium bond in a complex with the diazo compound to form a rhodium(I)–metal carbene and a spectator rhodium(III) bound to two bridging and two nonbridging acetates. This species could possess adjacent cis coordination sites that enable it to participate in C–H oxidative addition to generate a rhodium(III)–rhodium(III) complex that reductively eliminates. No evidence in favor of this mechanism has been reported. Alternatively, Doyle has proposed that the empty carbon p orbital of

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(2) Melillo, D. B.; Shinkai, I.; Liu, T.; Ryan, K.; Sletzinger, M. *Tetrahedron Lett.* **1980**, *21*, 2783.

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(5) Doyle, M. P. *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 305–316. Brunner, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1183–1185.

(6) See footnote 31 in: Taber, D. F.; Ruckle, R. E., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 7686–7693. Taber offered this speculation only at the request of referees and has not further supported it.

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the carbene approaches the C–H bond side-on in a three-centered transition state that leads directly to the insertion product plus the rhodium complex.[7] This model explains the decreased selectivity observed with increasing ligand electron-withdrawing power through an earlier transition state that is engendered by greater carbene electrophilicity. For cyclopropanations, Doyle and co-workers have found a correlation of the cis–trans ratios and relative reactivities between catalytic $Rh_2(OAc)_4/N_2CHPh$ and stoichiometric $(CO)_5WCHPh$, implying the intermediacy of a metal-bound carbene.[8] Hubert and Noels have determined that the cyclopropanation of styrene by ethyl diazoacetate catalyzed by rhodium acetate is first order in catalyst.[9] Kodadek and co-workers have observed by low temperature NMR the intermediate complex between ethyl diazoacetate and Rh(III) tetraphenylporphyrin iodide, which upon warming loses dinitrogen and cyclopropanates styrene, again implying a metal-bound carbene as the reactive intermediate.[10] The relation of this observation to the processes mediated by the binuclear complexes is unclear.

Recent studies of regioselectivity,[11] enantioselectivity,[12] and chemoselectivity[13] in rhodium-mediated reactions have shown that an impressive degree of control can be exerted by the ligands, but none have provided direct evidence concerning the molecular basis of the selectivity. For example, in the insertion reaction of ethyl diazoacetate with pentane, the triptycenecarboxylate salt of rhodium(II) provides in 86% yield a 60:30 mixture of C-2 and C-1 insertion products.[11g] For comparison, rhodium acetate gives 20% of a 4:66:33 (C-1:C-2:C-3) mixture. Another example that will be utilized and extended in this study is shown in Figure 3, wherein changing from an electron-poor perfluorobutyrate ligand to an electron-rich acetamide ligand causes a significant change in the product ratio, corresponding to a $\Delta\Delta G^{\ddagger}$ for the competing processes with the two catalysts of >3 kcal/mol.[11a] The ligand effects have often been attributed to their electronic influence, and it has been assumed that the electrophilicity of the putative metal-bound carbene increases as the ligands become more electron withdrawing. It has particularly been proposed by Doyle that little or no backbonding exists between the carbene and the metal,[1a,b,5a] and calculations at the *ab initio* level of dirhodium carboxylates complexed with *neutral donors* have supported this idea;[14] however, no theoretical studies with good π acid ligands have been reported.

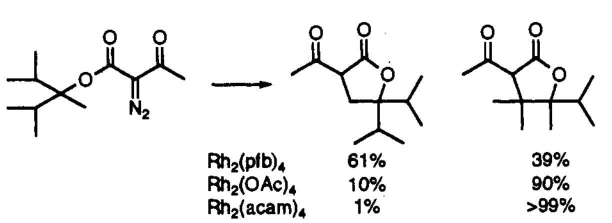

Figure 3. Catalyst dependence of selectivity in an intramolecular C–H insertion reaction.

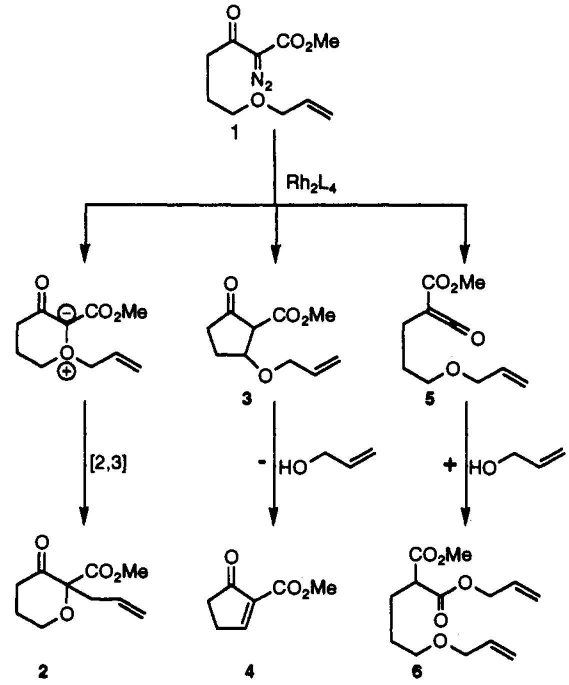

Figure 4. Reaction channels for and products of the rhodium-catalyzed decomposition of **1**.

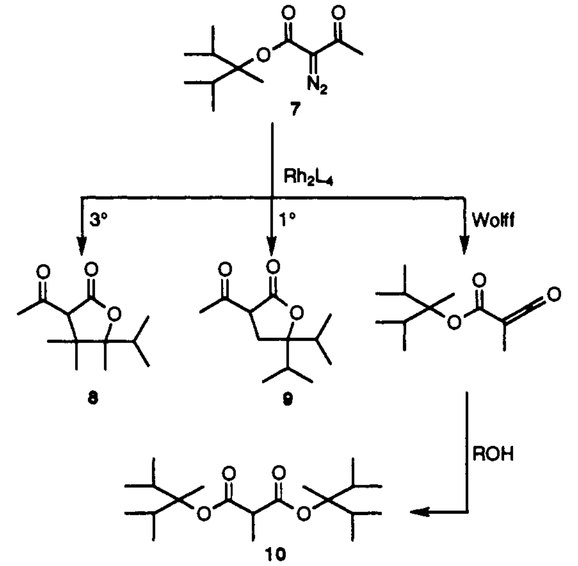

Figure 5. Products of the rhodium-catalyzed decomposition of **7**.

We have been interested in the development of two new strategies in oxygen heterocycle synthesis, dipolar cycloadditions,

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Table 1. Data for Reactions of Compound **1** Promoted by Rhodium Catalysts

$Rh_2(O_2CR)$: R =	pK_a[37] RCOOH	**2**:**4**:**6**,[a] %	σ_{α}[b]	σ_F[b]	σ_R[b]	$\Delta\Delta G^{\ddagger}$, kcal/mol
9-triptycene	5.20	21:35:44	–	–	–	–0.10
$(CH_3)_3C$	5.03	79:21:0	–0.75	0.00	–	1.21
$CH_3(CH_2)_3$	4.82	72:28:0	–0.57	0.00	–	0.97
$CH_3(CH_2)_2$	4.81	69:31:0	–0.54	0.00	–	0.88
CH_3CH_2	4.87	67:33:0	–0.49	0.00	–	0.83
CH_3	4.75	60:40:0	–0.35	0.00	–	0.65
CH_3OCH_2	3.53	49:34:17	–0.41	0.12	–	0.63
$ClCH_2$	2.85	58:42:0	–0.47[c]	0.22[c]	–	0.60
CH_3ClCH	2.83	65:35:0	–0.61[c]	0.22[c]	–	0.78
Cl_2CH	1.48	60:40:0	–0.58[c]	0.33[c]	–	0.65
Cl_3C	0.70	52:34:16	–0.70	0.44	–	0.70
F_3C	0.67	50:28:22	–0.25	0.44	–	0.75
$CH_3OC_6H_4$	4.47	80:20:0	–0.17	0.25	–0.42	1.23
$CH_3C_6H_4$	4.36	67:33:0	–0.35	0.00	–0.08	0.83
C_6H_5	4.19	63:37:0	0.00	0.00	0.00	0.73
4-ClC_6H_4	3.98	74:26:0	–0.43	0.45	–0.17	1.03
$CH_3O_2CC_6H_4$	3.51	59:41:0	–0.49	0.24	0.16	0.63
$O_2NC_6H_4$	3.41	55:45:0	–0.26	0.65	0.18	0.53
FC_6H_4	2.90	70:30:0	0.13	0.44	–0.25	0.91
$F_3CC_6H_4$	–	62:38:0	–0.25	0.44	0.07	0.70
Δ	–	14:0:86	–	–	–	–
3-ClC_6H_4	3.82	50:50:0	–	–	–	0.00

[a] Determined by NMR, average standard deviation is 2.0%. [b] See ref 16. [c] Estimated by analogy to FCH_2 and Cl_3C.

Table 2. Data for Reactions of Compound **7** Promoted by Rhodium Catalysts

$Rh_2(O_2CR)_4$: R =	product ratios[a] **8**:**9**	(**8** + **9**):**10**	σ_{α}[b]	σ_F[b]	$\Delta\Delta G^{\ddagger}$ kcal/mol
$(CH_3)_3C$	93:7	>99:1	–0.75	0.00	2.10
$CH_3(CH_2)_3$	92:8	>99:1	–0.57	0.00	2.00
$CH_3(CH_2)_2$	88:12	trace	–0.54	0.00	1.69
CH_3CH_2	87:13	trace	–0.49	0.00	1.62
CH_3	83:17	87:13	–0.35	0.00	1.40
CH_3OCH_2	72:28	trace	–0.41	0.12	0.95
CH_3CHCl	60:40	88:12	–0.61[c]	0.22[c]	0.57
$ClCH_2$	62:38	83:17	–0.47[c]	0.22[c]	0.63
Cl_2CH	47:53	72:28	–0.58[c]	0.33[c]	0.21
Cl_3C	42:58	60:40	–0.70	0.44	0.06
F_3C	40:60	40:60	–0.25	0.44	0.00
Δ	40:60	17:83	–	–	–

[a] Determined by NMR, average standard deviation is 1.4%. [b] See ref 16. [c] Estimated by analogy to FCH_2 and Cl_3C.

Table 3. IR Data for Complexes of Rhodium Catalysts with Carbon Monoxide

$Rh_2(O_2CR)_4$: R =	ν_{CO} (cm^{-1})[a]	$Rh_2(O_2CR)_4$: R =	ν_{CO} (cm^{-1})[a]
$(CH_3)_3C$	2094.5	CH_3CHCl	2114.1
$CH_3(CH_2)_3$	2097.4	$ClCH_2$	2114.1
$CH_3(CH_2)_2$	2097.6	Cl_2CH	2126.1
CH_3CH_2	ND	Cl_3C	2136.1
CH_3	ND	F_3C	2138.2

[a] Rhodium carboxylates are known to form 1:1 adducts with CO (ref 23). There is considerable variation in literature values for dirhodium–CO complexes that has been traced to the presence of small quantities of alcohol in the solvent. This hydrogen bonding influence, which can lower the ν_{CO} by as much as 10 cm^{-1}, was carefully excluded from these samples.

and oxonium ylide sigmatropic rearrangements, based on the rhodium-catalyzed decomposition of diazo compounds.[15] Other reaction manifolds, such as C–H insertion, can compete with the desired transformations, prompting this study of the influence of catalysts on the competing processes. We particularly aimed to correlate catalyst properties with product ratios using linear free energy relationships (LFER).[16] This analysis provides a better understanding of the interactions between the ligand, metal, and carbenoid, which should be useful in rational catalyst design, and could lead to more effective catalysts for enantioselective synthesis. A second LFER study with one of the previously-discussed systems was conducted to confirm the initial findings, and a spectroscopic analysis to directly address the ability of the dirhodium core to participate in backbonding with carbene-like ligands was performed. A significant parameter controlling these interactions is ligand polarizability, implying backbonding between the metal complex and the carbenoid. This work has provided the first experimental evidence concerning the molecular basis of the influence of ligands on the selectivity of a rhodium-mediated transformation.

Results

We previously reported that the rhodium acetate-catalyzed decomposition of methyl 2-diazo-3-oxo-6-(2-propenyloxy)hexanoate (**1**) provides two products: the oxonium ylide rearrangement product **2** and the C–H insertion product **4**, produced by β-elimination of allyl alcohol from **3**. The ylide manifold is slightly favored with rhodium acetate. This precedent provided a useful system to study the intramolecular competition between ylide formation and C–H insertion as a function of catalyst ligands. The catalysts listed in Table 1 were prepared by the conventional route, exchange with rhodium acetate. Reactions were conducted at room temperature until the starting material was consumed as indicated by TLC (0.25–1.0 h), and the reaction mixture was directly concentrated, analyzed by ^1H NMR, and chromatographed. The previously unobserved product **6**, which presumably arises *via* Wolff rearrangement to give ketene **5** followed by trapping with allyl alcohol, was observed in several cases. The results of the catalyst study are collected in Table 1. Uncatalyzed thermolysis in refluxing xylene (139–140 °C) gives **6** (the Wolff rearrangement product) and **2** in an 86:14 ratio (81% combined yield).

Doyle and co-workers have previously shown that rhodium acetate-catalyzed decomposition of 2,3,4-trimethyl-3-pentyl diazoacetoacetate (**7**) gives a 90:10 ratio of **8** to **9**. Rhodium caprolactam gives >99:1, while rhodium perfluorobutyrate shows no selectivity beyond statistical (40:60).[11a] A subset of the nonbenzoate catalysts was used to study the intramolecular competition between tertiary C–H insertion to give **8** and primary C–H insertion to give **9**. These reactions were conducted under reaction conditions identical to those reported by Doyle, 12 h at reflux in benzene. Isolated yields were 76–90%. The previously unreported compound **10** was isolated from several reaction mixtures. It presumably arises from trapping of the ketene produced in a Wolff rearrangement by alcohol liberated via decomposition of the starting material. These results are summarized in Table 2. Uncatalyzed thermolysis in refluxing xylene (139–140 °C) gives **10** in an 83:17 ratio to **8**/**9** (84% combined yield). No selectivity is shown in the C–H insertion (**8**:**9** = 40:60).

Analysis of the results of these studies suggested that a significant backbonding interaction from the dirhodium core to the carbenoid directs the reaction pathway (*vide infra*). To address the capability of these complexes to backbond, both *tert*-butyl isocyanide and carbon monoxide complexes were formed from a selection of aliphatic catalysts and the IR frequencies of their CX bonds were measured. The results are summarized in Tables 3 and 4. Unfortunately, because the *tert*-butyl isocyanide and carbon monoxide complexes with benzoate ligands are completely insoluble, their spectral data could not be obtained.

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Table 4. IR Data for Complexes of Rhodium Catalysts with *tert*-Butyl Isocyanide

$Rh_2(O_2CR)_4$: R =	ν_{CN}, cm^{-1} [a]	$Rh_2(O_2CR)_4$: R =	ν_{CN}, cm^{-1} [a]
$(CH_3)_3C$	2151.6	CH_3OCH_2	2162.1
$CH_3(CH_2)_3$	2155.9	CH_3CHCl	2166.3
$CH_3(CH_2)_2$	2156.4	$ClCH_2$	2166.3
CH_3CH_2	2156.6	Cl_2CH	2174.8
CH_3	2158.3	Cl_3C	2180.4
H	2166.8	F_3C	2186.8

[a] 1:2 adduct by NMR.

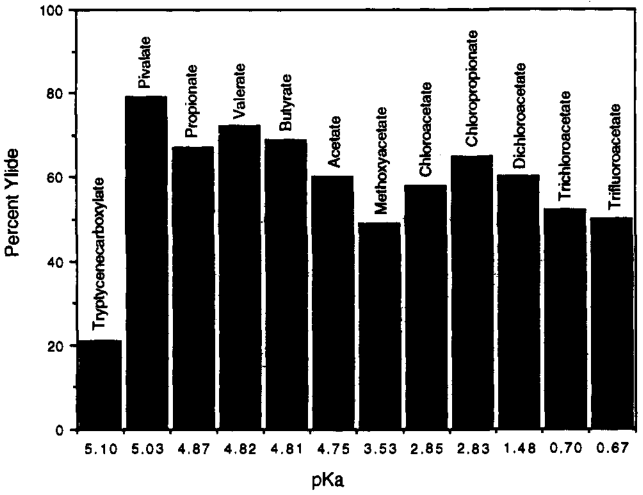

Figure 6. Percent ylide product **2** *versus* pK_a of simple alkyl carboxylate ligands.

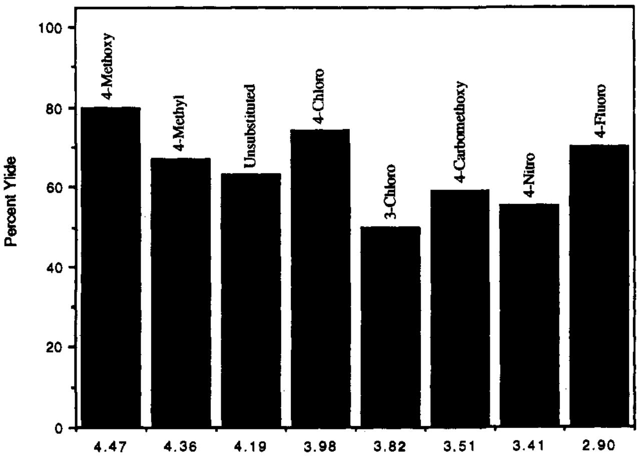

Figure 7. Percent ylide product **2** *versus* pK_a of benzoate ligands.

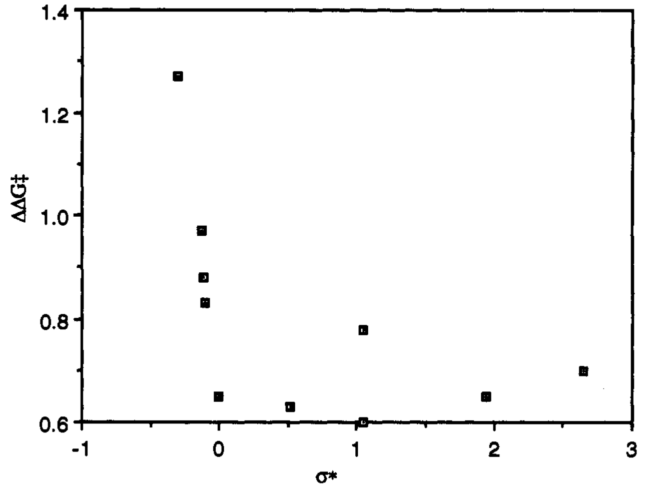

Figure 8. Experimental $\Delta\Delta G^{\ddagger}$ *versus* σ^* for simple alkyl carboxylate ligands in the rhodium-catalyzed decomposition of **1**.

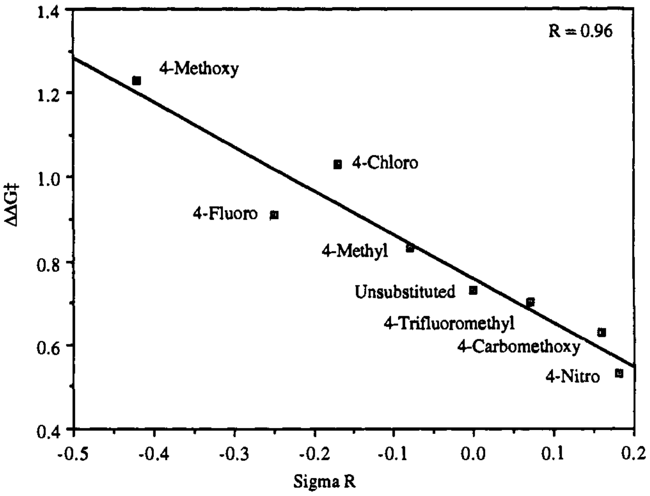

Figure 9. Experimental $\Delta\Delta G^{\ddagger}$ *versus* σ_R for benzoate ligands in the rhodium-catalyzed decomposition of **1**.

Discussion

It has been earlier proposed that the electron-withdrawing properties of ligands directly affect the electrophilicity of the rhodium carbenoid.[1b,f,11-13] Following this line of reasoning, we postulated that more electrophilic carbenoids would favor ylide formation with the Lewis basic oxygen of the allylic ether over insertion into a weakly nucleophilic C–H bond. If true, their ratios should correlate with the pK_a of the conjugate acid of the ligand, one measure of relative electron-withdrawing ability. For the purposes of these analyses, the ligands were split into two groups, aliphatic acids and *p*-substituted benzoic acids. Figures 6 and 7 show that no correlations exist between the product ratio and the pK_a of the rhodium carboxylate ligand in the decomposition of **1**. The pivalate complex gives much greater selectivity than acetate with only a small change in pK_a, while the 2-chloropropionate complex is more selective than acetate despite a much lower pK_a. In the substituted benzoates, the 4-chloro and 4-fluoro substituents give much higher selectivity than expected based on their pK_as.

A simple frontier MO analysis suggests that the interaction between the LUMO of a carbene and the HOMO of the rhodium complex could be important in controlling carbenoid electrophilicity. A parameter that therefore might be used to mirror the electrophilicity of the rhodium carbenoid is the ligand σ^*, since Bear, Kadish, and co-workers have found that it correlates with the electrochemical oxidation potentials of rhodium carboxylate complexes.[17] For the reactions of **1**, plotting σ^* for the aliphatic ligands against $\Delta\Delta G^{\ddagger}$ for the ylide and C–H insertion pathways does not produce a correlation (Figure 8), also indicating that simple models based upon the electron-withdrawing properties of aliphatic ligands cannot accommodate the data. However, plotting σ_R against $\Delta\Delta G^{\ddagger}$ for the substituted benzoates does give a good correlation (Figure 9).

It was apparent from these relatively unsuccessful attempts to explain the selectivity in this reaction based on preconceived chemical models of the process that a multiparameter regression analysis would be required. The system of Taft and Topsom[16] uses four parameters: σ_F or field effect, based on charge–charge or dipole–dipole interactions; σ_R or resonance effect, based on π-electron bonding and delocalization; σ_α or polarizability, based on charge-induced dipoles; and σ_χ or electronegativity, based on partial ionic character of the sigma bond between the substituent and a bonded atom. Following the example of Taft and Topsom,

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(17) Das, K.; Kadish, K. M.; Bear, J. L. *Inorg. Chem.* **1978**, *17*, 930–934.

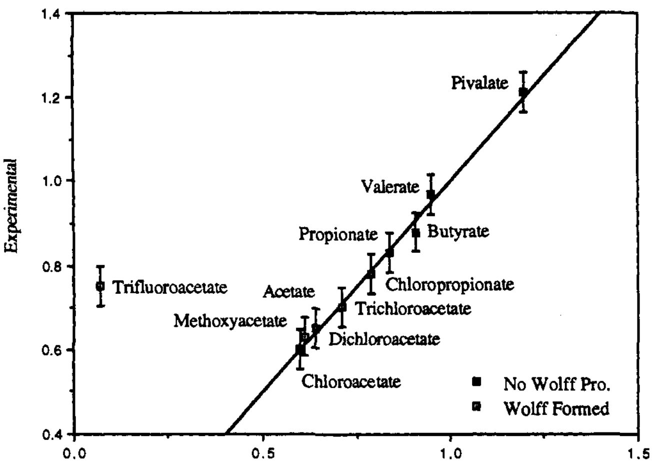

Figure 10. Calculated *versus* experimental $\Delta\Delta G^{\ddagger}$ in kcal/mol for simple alkyl carboxylate ligands in the rhodium-catalyzed decomposition of **1**. $\Delta\Delta G^{\ddagger}(\text{calc}) = 0.150 - 1.403\sigma_{\alpha} - 0.968\sigma_{F}$. $R = 0.997$.

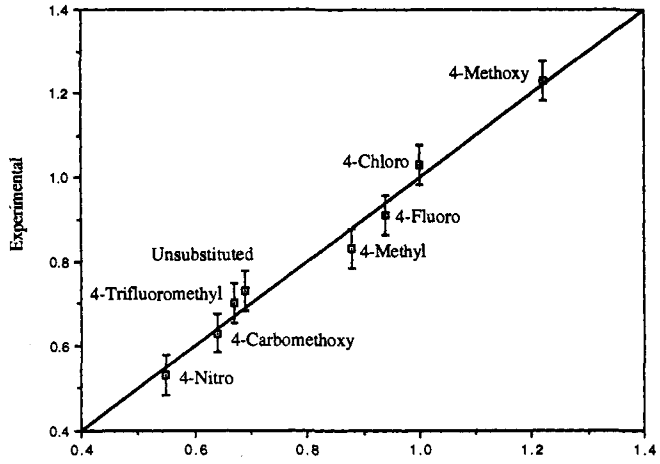

Figure 11. Calculated *versus* experimental $\Delta\Delta G^{\ddagger}$ in kcal/mol for benzoate ligands in the rhodium-catalyzed decomposition of **1**. $\Delta\Delta G^{\ddagger}(\text{calc}) = 0.691 - 0.270\sigma_{\alpha} - 0.008\sigma_{F} - 1.156\sigma_{R}$. $R = 0.991$.

the electronegativity parameter was ignored as it has been found important only in systems bearing an electronegative atom directly at the reactive center. The application of this method to the data in Table 1 gave the correlations shown in Figures 10 and 11, which will be analyzed in detail below. The range of $\Delta\Delta G$s observed was sufficient to provide strong but not overwhelming validation to the weights of the different parameters and therefore the molecular basis of selectivity. While there is always concern when data are fit using multiparametric methods, the results show that these reactions are dominated by only two parameters. Addition of further parameters (steric for aliphatic carboxylate, field effect for benzoates) makes no significant improvement in the quality of the fit.

The results with aliphatic carboxylate ligands on rhodium are presented in Figure 10. The best fit line and equation are based only on the catalysts that did not produce the Wolff rearrangement product **6**. The important contributors to determining the competition between C–H insertion and ylide formation are polarizability and field effects. Two of the four catalysts that produce the Wolff product deviate only slightly from the correlation. Rhodium trifluoroacetate differs considerably, and rhodium triptycenecarboxylate is not shown because its σ parameters are unavailable. It is presumably an electron-rich and polarizable catalyst, like pivalate, but it shows the least selectivity and produces more **6** than even rhodium trifluoroacetate. Deviations from linearity generally imply a change in mechanism or rate-determining step (*vide infra*). The results with substituted rhodium benzoates are shown in Figure 11. The strong dependence on σ_R observed previously is again seen, but contributions from substituent polarizability are also present, although with a smaller contribution easily ascribed to their distance from the metal. The field effect is evidently not important because of its more rapid decrease with distance.

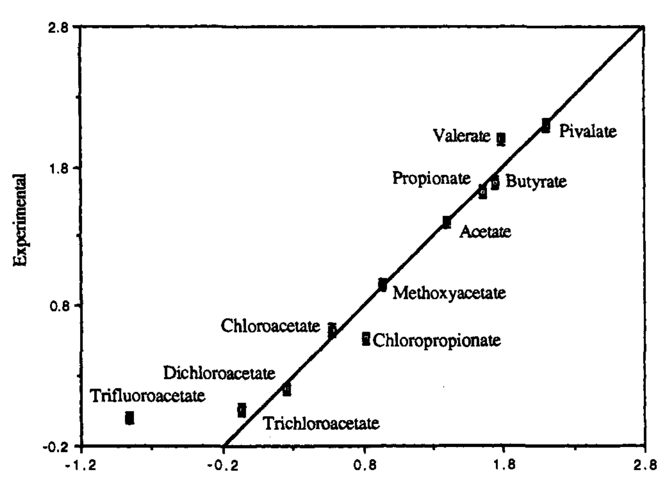

Figure 12. Calculated *versus* experimental $\Delta\Delta G^{\ddagger}$ in kcal/mol for simple alkyl carboxylate ligands in the rhodium-catalyzed decomposition of **7**. $\Delta\Delta G^{\ddagger}(\text{calc}) = 0.779 - 1.784\sigma_{\alpha} - 4.749\sigma_{F}$. $R = 0.987$.

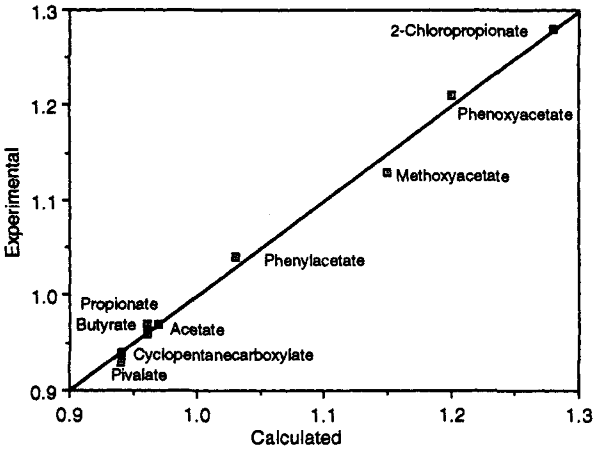

Figure 13. Calculated *versus* experimental $E_{1/2}$ (*versus* SCE) for simple alkyl carboxylate ligands in dirhodium complexes. $E_{1/2}(\text{calc}) = 0.996 + 0.070\sigma_{\alpha} + 1.496\sigma_{F}$. $R = 0.996$. Oxidation potentials from ref 17.

With these favorable results for correlating the competition between ylide formation and secondary C–H insertion, multiparameter regression analysis was applied to the competition between tertiary C–H and primary C–H insertion in the decomposition of **7** using the data from Table 2. The results are presented in Figure 12. The important factors determining the partitioning in this reaction are again polarizability and field effects, although the latter receives relatively more weight. As before, rhodium trifluoroacetate gives the least selectivity and the highest proportion of the Wolff rearrangement product **10** and differs from theoretical by the largest amount.

The strong dependence of reaction selectivity on the polarizability ($\rho_{\alpha} = -1.403$ in Figure 10 and $\rho_{\alpha} = -1.784$ in Figure 12) for the aliphatic carboxylate catalysts was unexpected based on previous models of rhodium-mediated processes popularized by Doyle. Since the oxidation potential of rhodium carboxylates demonstrates little dependence on polarizability (Figure 13), their HOMO energy is not affected by this property of the substituents. Therefore, the ligand effects observed in these two reactions are related to the metal LUMO and/or are expressed after generation

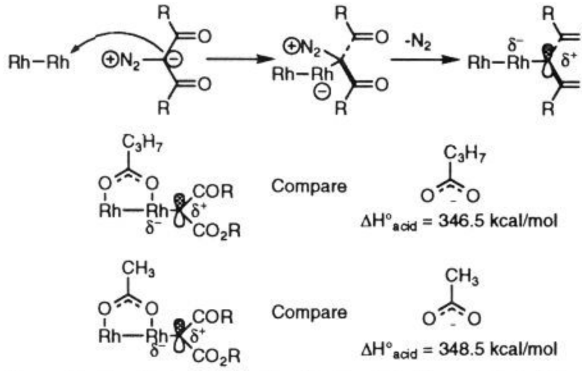

Figure 14. Postulated mechanism for the dirhodium-mediated decomposition of a diazocarbonyl compound and the ability of polarizable substituents to stabilize a negative charge.

of an intermediate. The latter is our preferred explanation, as shown in Figure 14. Carbene generation has been envisioned to occur via σ-bond formation between the metal and the diazo compound followed by loss of nitrogen to give the carbenoid.[1b,f,11–13] One canonical form of the resulting complex possesses a formal negative charge on rhodium and a formal positive charge on carbon. The ability of the ligand to polarize away from the negative charge would thus stabilize the carbenoid–catalyst complex, analogous to the stabilization of negative charge that makes butyric acid more acidic than acetic acid in the gas phase,[18] but polarizability may also permit stabilization of the carbenoid via backbonding (*vide infra*). This mechanism is distinct from the field effect that has generally been used to explain selectivity based on affinity for electron-rich sites. The field effect also acts to stabilize the negative charge on the metal, which in turn should increase the σ-bond strength, with more electron-withdrawing ligands affording the most stabilization. If the carbenoid is in fact a metal-bound carbocation (*i.e.*, no backbonding) as has been previously postulated by Doyle,[1a,b] the strongest stabilization of the carbene should arise when the σ-bond is strongest. The lengthening of the metal–metal bond in rhodium carboxylates bearing electron-withdrawing ligands[3] should also reduce the *trans* effect. For example, rhodium perfluoroalkanoates are strong Lewis acids, binding olefins in solution, as opposed to rhodium acetate, which does not.[19] However, the catalysts bearing ligands with strong field effects show the least selectivity in these intramolecular competition studies, showing that a model dependent only on the ability to stabilize a negative charge and thereby affecting the strength of the σ-bond cannot be correct. That the greatest selectivity is observed with ligands possessing low field effects and high polarizability raises the possibility that their ability to donate electron density is as important as acceptance. One way that donation from the ligand could affect the reactivity of the carbenoid is backbonding.

The question of backbonding between rhodium carboxylates and axial ligands has been long debated.[1b,f,11–13] Computations using *ab initio* methods suggest that there is no backbonding with neutral donors,[20] and extended Huckel studies of methylene-(dirhodium tetraacetamide) have suggested that there is a very low barrier to rotation of the carbene ligand.[21] Drago and others have used backbonding to explain the thermodynamics of ligand binding to dirhodium complexes, and have also reported a small decrease in C-O stretching frequency upon coordination of CO to a limited set of rhodium carboxylates.[22] Backbonding has also been used to explain other results, including EPR parameters, X-ray photoelectron spectra, and the electrochemistry of rhodium carboxylates and amidates and their adducts with σ-donating and π-accepting bases.[23] The orbitals involved in backbonding with different ligands and the electronic configurations (derived from theoretical studies) are illustrated in Figure 15. While none of these calculations found significant backbonding interactions between phosphines or water and rhodium carboxylates, the filled rhodium π^* orbitals could overlap with the low-lying empty p orbital (LUMO) of a bound carbene. The analogy between carbon monoxide, which does appear to have a π-component in bonding, and the carbene is closer than that between the carbene and phosphine or water.

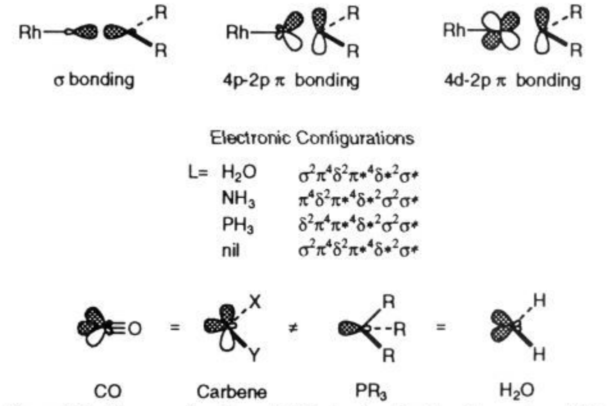

Figure 15. Three molecular orbitals involved in the interaction of the dirhodium core with axial ligands and the electronic configuration with different ligands bound.

Spectroscopic data for complexes between the aliphatic rhodium carboxylates and the carbene-like axial ligands *tert*-butyl isocyanide and CO are found in Tables 3 and 4 and linear regression analyses of the data are presented in Figures 16 and 17. Because the isonitrile is a relatively poor π-acceptor, the σ-interaction dominates its interaction with the rhodium complex and the IR stretching frequency is in all cases greater than that of the free isonitrile. With CO, an excellent π-acceptor, the stretching frequency is decreased compared to the free ligand, an effect *opposite* to that predicted for a σ-only bonding scheme, demonstrating the capability of these rhodium complexes to backbond. Regression analysis shows that the field parameter dominates both complexation effects on IR frequency, as expected, but that polarizability still plays a significant role: more polarizable ligands increase backbonding. It is therefore reasonable to propose that backbonding exists in rhodium carbenoids, since the "carbocation" center and the carbonyl substituents usually found in substrates for rhodium-mediated diazo compound decomposition should facilitate excellent π-acceptance.

These results, supporting the idea that backbonding in the intermediate metal–carbenoid can be important to its properties, permit an analysis of the behavior of a number of the catalysts.

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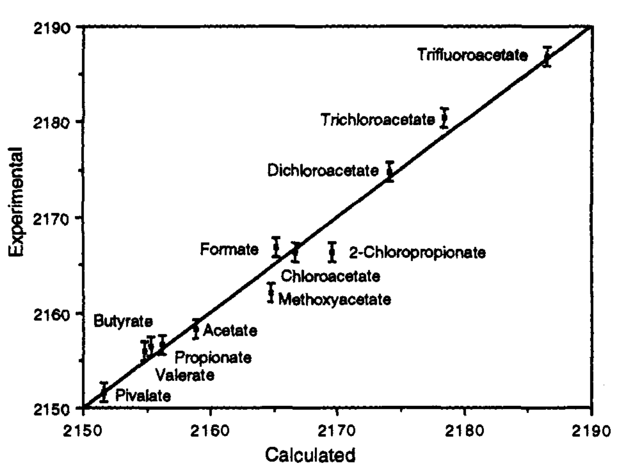

Figure 16. Calculated *versus* experimental ν_{CN} in cm^{-1} for *tert*-butyl isocyanide complexes of dirhodium bearing simple alkyl carboxylate ligands. $\nu_{CN}(\text{calc}) = 2165.10 + 18.08\sigma_\alpha + 59.03\sigma_F$. $R = 0.989$.

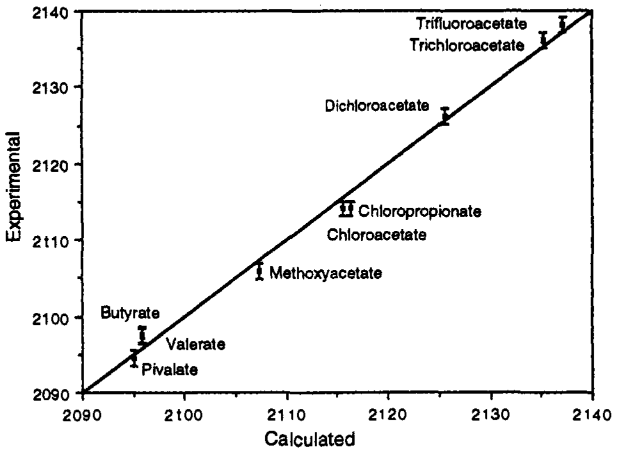

Figure 17. Calculated *versus* experimental ν_{CO} in cm^{-1} for carbon monoxide complexes of dirhodium bearing simple alkyl carboxylate ligands. $\nu_{CO}(\text{calc}) = 2098.14 + 4.14\sigma_\alpha + 90.92\sigma_F$. $R = 0.996$.

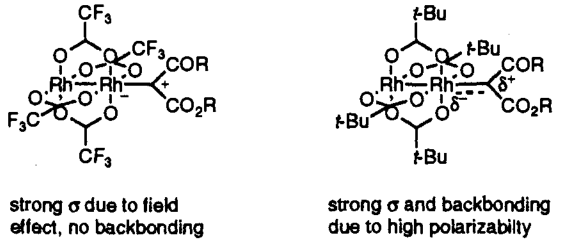

Figure 18. Polarizability controls the amount of backbonding in dirhodium carboxylate–carbene complexes.

Electron-rich complexes should show a stronger backbonding interaction, a shorter Rh–Rh bond, and a consequently weaker σ-bond due to the *trans* effect than electron-poor catalysts. Rhodium pivalate or rhodium acetate would therefore have a stronger π-bond and a weaker σ-bond than rhodium trifluoroacetate (Figure 18). Ligands with higher polarizability and field effects will have a stronger σ-bond between the metal and the carbenoid via stabilization of the negative charge on the metal. In general, the shorter the σ-bond, the stronger the backbonding interaction because orbital overlap increases. However, those ligands that are strongly electron withdrawing due to their field effects will decrease the ability of the metal to donate electrons back to the bound carbene. Polarizability of the ligand allows stabilization of the negative charge on the metal without reducing the ability of the metal to donate back to the carbene, and can thus strengthen both σ- and π-bonding. Because the empty p orbital of the carbenoid is proposed as the site of reactivity (*vide infra*), it follows that backbonding, which donates directly into this orbital, would strongly influence the reactivity of the carbenoid. In general, since backbonding should strengthen the Rh–C bond and reduce the electrophilicity of the bound carbene, selectivity should change with increasing electron density at the metal. However, assuming the first step in the formation of the catalytically-active complex involves nucleophilic attack on the metal by the carbon of the diazo compound (Figure 14), reducing the Lewis acidity of the complex will slow formation of the intermediate, and with an extremely electron-rich catalyst reaction may not occur. Because metal–axial ligand bonding in these complexes is extremely weak,[3] even small contributions to stability can have a large effect on the course of the reaction.

The complexes that violate the LFER correlations can also be accommodated by this model. Rhodium trifluoroacetate is the least polarizable ($\sigma_\alpha = -0.25$) catalyst and has a strong field effect ($\sigma_F = 0.44$) and should therefore have a relatively strong σ-bond but a weak to nonexistent π–bond. Its deviation from the correlations in Figures 10 and 12 can be explained by the existence of two parallel mechanisms, one rhodium-mediated and one involving release of the free carbene. Demonceau and co-workers have earlier reported that very electron-deficient catalysts give selectivity similar to that of free carbenes in C–H insertions with diazomalonates and explained this observation by release of the free carbene.[24] In the decomposition of **7**, no selectivity in C–H insertion beyond the statistical ratio of 60:40 was observed with rhodium trifluoroacetate, and the greatest proportion of the Wolff rearrangement product was seen. These results are similar to the thermolysis of **7**, producing all three products with the same selectivity and nearly the same amount of Wolff rearrangement.[25] It therefore seems reasonable to postulate that both these processes proceed via the free carbene. In the decomposition of **1**, rhodium trifluoroacetate gives no selectivity between **2** and **4** and an appreciable amount of Wolff product **6**. The thermolysis of **1**, which produces **2** and **6** but not **4**, suggests that almost all of the Wolff rearrangement product (and some of **2**) in the catalyzed reaction arises from the free carbene. If this is so, the selectivity in the catalyzed reaction (slightly favoring **4**) reflects the intrinsic selectivity of a very electron-poor carbenoid. Since rhodium trichloroacetate and rhodium trifluoroacetate show approximately the same selectivity in the C–H insertion process but different amounts of Wolff product, their derived carbenes likely have similar charge densities at carbon and differ only in the proportion of the reaction pathway carried by the free carbene. While the Wolff rearrangement to give ketene could occur from either bound or free carbene, the deviation from the LFER in the decompositions promoted by rhodium trifluoroacetate suggests the latter explanation. Rhodium trifluoroacetate likely reflects the limit among carboxylate catalysts for the strength of its carbene–Rh σ-bond and the absence of a π–bond. It is reasonable that the tendency of rhodium trifluoroacetate to release a free carbene will be dependent on the particular diazo compound carbene precursor. Recently, high control and selectivity has been reported in a number of carbenoid reactions (tertiary C–H insertion ≫ cyclopropanation, aromatic cycloaddition ≫ benzylic C–H insertion, aromatic substitution ≫ cyclopropanation, aromatic substitution ≫ tertiary C–H insertion) catalyzed by rhodium perfluorobutyrate.[13a] While we have not studied this complex and therefore cannot comment on the basis of its action, one would predict that it is more polarizable than rhodium trifluo-

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(24) Demonceau, A.; Noels, A. F.; Costa, J. L. *J. Mol. Catal.* **1990**, *58*, 21–26.

(25) It is somewhat difficult to compare these results because of the different temperatures (thermolysis at 140 °C, catalyzed decomposition at 80 °C) at which the reactions were conducted. Wolff rearrangements are reported to be favored by increasing temperature (Meier, H.; Zeller, K. P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32–43), suggesting that lower temperature would produce a lower ratio, though in general greater selectivity is expected at lower temperature. The termperature dependence of the free energies of activation for all of the catalyzed and uncatalyzed reaction pathways would be required to answer this question with certainty.

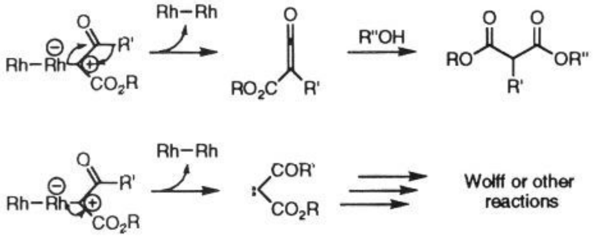

Figure 19. Direct Wolff rearrangement of a rhodium-bound carbene *versus* release of free carbene.

roacetate, less likely to release free carbene, and therefore still able to demonstrate selectivity.

Another exception to the LFER correlation is rhodium 9-triptycenecarboxylate. It produces more **6** than rhodium trifluoroacetate in the decomposition of **1**, though its ligand is expected to be polarizable and show only a weak field effect. However, the great bulk of the ligands may sterically push the bound carbene away from the metal. This weakening of both σ- and π- (which falls off faster with distance) bonds would make the bound carbenoid far less stable, and thus more analogous to rhodium trifluoroacetate than rhodium pivalate. These data contrast with the high selectivity reported by Ikegami in aromatic substitution using the sterically-encumbered triphenyl acetate ligand.[26]

The instances of the Wolff rearrangement with other catalysts show that it is favored by strong field effects and disfavored by highly polarizable ligands. Rhodium methoxyacetate, despite its relatively small field effect, likely promotes the production of as much of the Wolff product **6** as rhodium trichloroacetate because it is also less polarizable. Rhodium chloroacetate and rhodium chloropropionate have the same field effect, but the more polarizable catalyst produces slightly less Wolff product **10**. This dependence on polarizability suggests that the stability of the complex determines the ratio of free carbene to bound carbene and thus the amount of Wolff rearrangement. If the Wolff rearrangement arose from the bound carbene (Figure 19), the ratio of products **2** and **4** should be catalyst-specific and there would be no deviation from linearity.

In the decomposition of **1**, the substituted benzoate catalysts show little dependence on polarizability ($\rho_\alpha = -0.264$) and no dependence on field effects of the *p*-substituent. This is not surprising, as the field effect is reduced by distance and the polarizability is dominated by the highly polarizable π-system of the benzoate. Therefore, the electron-donating or -withdrawing properties of the substituent through resonance determines the selectivity ($\rho_R = 1.159$). The benzoate catalysts differ radically from the aliphatic carboxylate catalysts due to the overlap of the π-system of the benzoate with the π-system of the dirhodium carboxylate core (see Figure 20).[27] In this bonding scheme, the σ-bond between the metals and the metal-metal σ^* orbital involved in the σ-bond with the carbene are unaffected by the ability of substituents to donate or withdraw electrons because overlap is minimal, while the metal–metal π and π^* orbitals involved in backbonding to the carbene are greatly affected. The σ-bond between rhodium and carbon is expected to be fairly strong for rhodium benzoates, stabilized by the polarizability (σ_α ca. $= -0.80$) and field effect of the benzoate (σ_F ca. $= 0.10$), while the π-bond strength would depend on the ability of the substituent to donate or withdraw electrons from the π-system. Thus rhodium *p*-anisate, with the electron-donating OCH_3 group, shows high selectivity, while the rhodium *p*-nitrobenzoate shows little selectivity. However, because the complexes are stabilized by the strong σ-bond, no more than a trace of the Wolff rearrangement product appears even in the case of the rhodium nitrobenzoate. Rhodium *m*-chlorobenzoate, which cannot increase backbonding through resonance donation from chlorine, shows less selectivity than rhodium nitrobenzoate (**2**:**4** = 50:50) and forms only trace amounts of **6**, illustrating the importance of this stabilization on selectivity but not on the propensity of these benzoate complexes to release the free carbene.

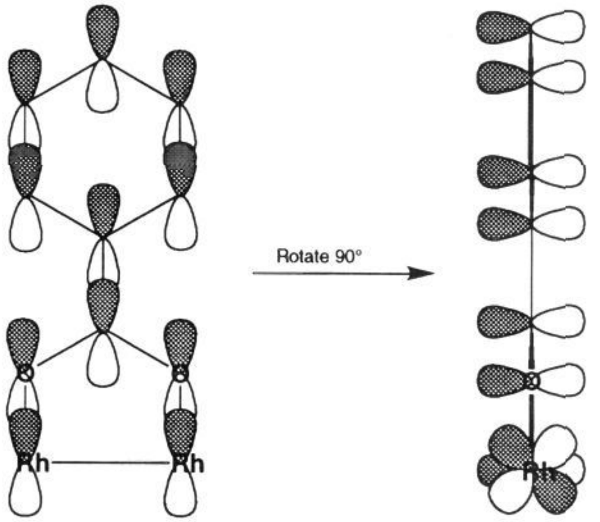

Figure 20. Two views of the bonding between benzoate ligands and dirhodium.

A molecular-level explanation must be provided for the influence of backbonding on the course of these reactions. An assumption implicit in this analysis is that both ylide formation and C–H insertion are electrophilic processes and that the order of nucleophilicity of the functional groups involved is ROR′ > tertiary C–H > secondary C–H > primary C–H. Interesting parallels can be drawn between rhodium carbenoids and the behavior of free carbenes. In the latter, selectivity in C–H insertion generally follows the order tertiary > secondary ≫ primary. Halocarbenes are more selective for electron-rich C–H bonds than methylene, with difluorocarbene showing the greatest preference.[28] Data on the selectivity of simple carbenes in ylide formation are meager; singlet methylene shows a 5:3:2 ratio of C–H insertion, cyclopropanation, and ylide formation–rearrangement products, respectively, with 3-methoxycyclohexene.[29] Methylene is widely regarded as reacting at a diffusion-controlled rate and therefore nondiscriminating. Some useful comparisons of the electron demands of various carbenes come from the Moss description of selectivity (the *selectivity index* m_{CXY}) in cyclopropanation reactions.[30] Dichlorocarbene has $m_{CXY} = 1.00$ (by definition), while difluorocarbene is more selective for electron-rich alkenes with $m_{CXY} = 1.48$, and bromo(ethoxycarbonyl)carbene is less selective with $m_{CXY} = 0.29$. These data can be correlated using $\sigma_R{}^+$ and σ_I for the substituents on the carbene carbon, with both π-electron donation (resonance) and σ-electron withdrawal (inductive effect) increasing selectivity for electron-rich alkenes. Since fluorine is a strong π-donating substituent, difluorocarbene is more selective for electron-rich alkenes than dichlorocarbene. The ability of fluorine to "backbond" to the carbene center is implicit in the dipolar resonance structures that can be written (Figure 21) and is superior to that of the other halogens because of better overlap of the fluorine 2p lone pair

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(26) Hashimoto, S.-I.; Watanabe, N.; Ikegami, S. *J. Chem. Soc., Chem. Commun.* **1992**, 1508.

(27) The benzene ring must be parallel to the carboxylate and Rh–Rh bond for this overlap to occur. The crystal structure of rhodium benzoate with pyridine axial ligands has this structure. See Li, G.; Sun, Y. *Huaxue Xuebao* **1981**, *39*, 945–950.

(28) *Carbene Chemistry*, 2nd ed.; Kirmse, W., Academic Press: New York, 1971; pp 222–225. *Carbenes*; Moss, R. A., Jones, M. Jr., Eds.; Wiley: New York, 1973 and 1975; Vols. 1 and 2.

(29) Young, T. A.; O'Rourke, C.; Gray, N. B.; Lewis, B. D.; Dvorak, C. A.; Kuen, K. S.; DeLuca, J. P. *J. Org. Chem.* **1993**, *58*, 6224–6228.

(30) Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58–64. Moss, R. A. *Acc. Chem. Res.* **1989**, *22*, 15–20.

Figure 21. Backbonding in difluorocarbene.

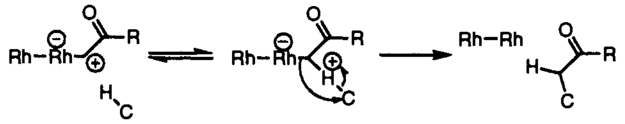

Figure 22. A possible mechanism for the C–H insertion of a dirhodium carbenoid.

orbital with the empty carbon 2p orbital. A second factor that has been used by Moss to explain selectivity in cyclopropanations is reaction exothermicity. Stabilization of the carbene (relative to methylene) by substituents increases its selectivity, which can be explained by application of the Hammond postulate.

The connection between the foregoing, where "backbonding" and σ-acceptance confer on carbenes high selectivity for electron-rich sites, and rhodium carbenoids is striking. All carbenoids are σ-donors to rhodium, and those bound to electron-rich, backbonding catalysts are more selective for electron-rich C–H bonds and the nucleophilic oxygen atom than those bound to electron-deficient catalysts. A difference between difluorocarbene and rhodium carbenoids is that the backbonding substituents remain attached to carbon throughout the reaction in the former, while the backbonding group is lost at some point in the mechanism in the latter. That similar factors influence the selectivities of rhodium carbenoids and carbenes suggests that an early reaction step, when the backbonding rhodium is still present on the carbene carbon, is product-determining. On this basis, we suggest our data support a mechanism for the rhodium-mediated C–H insertion (Figure 22) that was earlier proposed by Taber to account for the selectivity in intramolecular C–H insertion processes.[6,31] The electrophilic p orbital of the carbene attacks at the hydrogen atom, producing a σ-complex that carries positive charge at hydrogen and carbon and, *if formed reversibly*, would account for the selectivity for tertiary over primary sites. The migration of carbon to the site of negative charge accounts for the overall C–H insertion process. The factors controlling selectivity can include both the basicity of the C–H bond, affecting the rate of formation of the σ-complex, and the ability of the carbon to accommodate positive charge, affecting the stability of the σ-complex. This picture also explains the effective insertion of rhodium carbenoids into Si–H bonds, since the hydrogens of silanes should be among the most basic in organic compounds.

A similar pathway involving a σ-complex can be written for ylide formation. We have earlier suggested that the rhodium pivalate-catalyzed formation of oxonium ylides can be reversible,[32] but exactly *how* reversible ylide formation might be and how this factor would be affected by the catalyst was not addressed in that study. For any rhodium-mediated reaction, it is reasonable that catalysts with poor backbonding and therefore low stability of their carbenoids are less likely to reverse, explaining the low, near statistical selectivity in the C–H insertions with electron-deficient catalysts even though the metal is clearly involved in the reaction (no Wolff product to imply release of the free carbene). The key influence of backbonding in this model would be to facilitate reversal of the intermediate.

The greatest selectivity is shown by carbenoids that should be most stable because they have both strong σ- and π-bonding. Ligand field effects strengthen the σ-bond and make the carbene more electrophilic and therefore more selective for electron-rich sites of reaction. Ligand polarizability stabilizes the carbene through backbonding but can also withdraw electron density from the metal to stabilize the σ bond and make the carbene more electrophilic. Catalysts that can release the free carbene obviously provide little stabilization to the bound carbene, and the increasing proportion of products derived from the free carbene observed as the catalyst becomes more electron deficient supports the importance of backbonding to carbenoid stability. Exothermicities in reactions with such catalysts must be large and the selectivities small even in pathways that involve the metal-bound carbene. Conversely, selectivity increases as exothermicity decreases with increased stabilization provided to the carbene by the catalyst. Ligand polarizability and field effects make the carbene more electrophilic, but stabilization of the carbene by ligand polarizability is necessary for its electrophilicity to be fully expressed (electrophilicity + stability = selectivity).

The so-called ambiphilic carbenes are an interesting outgrowth of Moss' selectivity studies. They exhibit nucleophilic character with electron-deficient alkenes and electrophilic character with electron-rich alkenes because they bear a π-donor and a σ-acceptor. Even though the metal-bound carbenoids studied here bear both a π-donor and σ-acceptor (the Rh), all show electrophilic behavior they because they also bear a strong π-acceptor (the dicarbonyl). Studies of rhodium carbenoids without such substituents and those bearing other π- or σ-donors or acceptors would be of interest.

Conclusion

This study has shown a correlation between reaction selectivity and the polarizability of the rhodium carboxylate (carboxamide) bridging ligand in two carbenoid transformations. It draws on spectroscopic observations of stable rhodium complexes with good π-acid axial ligands for analogies, suggesting the importance of backbonding. It provides a framework within which to evaluate selectivity in other reactions promoted by these catalysts that can also be used to analyze structural properties of the complexes and guide efforts to develop complexes that induce asymmetry during catalyzed reactions.

Experimental Section

General. ^1H NMR were recorded at 300 MHz. ^{13}C NMR were recorded at 75 MHz. Infrared spectra were obtained on CCl_4 solutions on a BOMEM FTIR instrument with resolution of 4 cm^{-1}. Microanalyses were performed by Atlantic Microlabs, Inc. Methylene chloride and benzene were distilled from CaH_2 under inert atmosphere. All dirhodium catalysts were synthesized from commercially available carboxylic acids (except triptycenecarboxylic acid, synthesized by literature methods[33]) by exchange with rhodium acetate[34] or reduction of $RhCl_3$ hydrate in ethanol.[35] All the alkyl substituted catalysts and the unsubstituted benzoate were previously reported and were purified and characterized by literature methods.[4,17,36] All reactions were performed under inert atmosphere.

General Procedure for Decomposition of 1. To a solution of methyl 2-diazo-3-oxo-6-(2-propenyloxy)hexanoate (**1**) (0.01 M in dichloromethane) was added 0.02 molar equiv of the rhodium catalyst at room temperature. The reaction was followed to completion by TLC (1:1 ether:hexane). Product ratios were determined by NMR spectroscopy on crude reaction mixtures obtained after removal of the solvent *in vacuo*. The resulting oil was subjected to flash chromatography on silica gel with 1:1 ether:hexane. Previously observed products **2** and **4** were obtained, and occasionally **6** as well. The isolated yields of **2** in these reactions ranged from 22 to 77%, but these primarily reflect isolation difficulties due to streaking of the cyclopentenone and decomposition on silica gel; the crude mass balances were essentially quantitative and showed only **2**, **4**, and, occasionally, **6** by NMR. The **2**:**4**:**6** ratio was calculated by

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comparison of the following peaks: δ 5.11 and 5.12 (allylic protons of **2**), 8.45 (vinyl proton of **4**), 3.78 (methyl proton of **2**), 3.84 (methyl proton of **4**), and 3.70 (methyl proton of **6**). The average standard deviation for 15 sets of decompositions of **1** was 2.0%. Chromatography on alumina also increased the isolated yields of **2** by 10–20%. 2′-Propenyl 2-carbomethoxy-5-(2-propenyloxy)pentanoate (**6**). ^{1}H NMR (acetone-d_6): δ 1.60 (m, 2H), 1.95 (m, 2H), 3.44 (t, J = 6.3 Hz, 2H), 3.52 (t, J = 7.5 Hz, 1H), 3.70 (s, 3H), 3.94 (dt, J = 5.1, 1.5 Hz, 2H), 4.64 (dt, J = 5.7, 1.5 Hz, 2H), 5.10–5.40 (m, 4H), 5.85–6.05 (m, 2H). ^{13}C NMR (acetone-d_6): δ 26.6, 28.0, 52.0, 52.5, 66.0, 70.1, 72.0, 116.1, 118.1, 133.1, 136.3, 169.5, 170.31. IR (thin film): 2947, 2863, 1742 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_5$: C, 60.90; H, 7.87. Found: C, 60.93; H, 7.92.

General Procedure for Decomposition of 7. A solution of 2,3,4-trimethyl-3-pentyl diazoacetoacetate and 0.01 molar equiv of the rhodium catalyst were refluxed for 12 h in benzene. The resulting solution was passed through a short plug of neutral alumina and further eluted with dichloromethane. Product ratios were determined by NMR spectroscopy on crude reaction mixtures obtained after removal of the solvent *in vacuo*. Flash chromatography on silica gel with 7:1 hexane:ethyl acetate resulted in isolation of the previously reported **8** and **9** and the unreported **10**. The **8**:**9**:**10** ratio was calculated by comparison of the following peaks: δ 3.43 and ca. 11.7 (**8**), 3.73 and ca. 11.05 (**9**), and 3.31 (**10**). The average standard deviation for 10 sets of decompositions was 1.4%. The isolated yields for these reactions ranged from 76 to 90%. Bis(2,3,4-trimethyl-3-pentyl) methylmalonate (**10**). ^{1}H NMR (CDCl$_3$): δ 0.93 (t, J = 6.6 Hz, 12H), 0.93 (t, J = 6.6 Hz, 12H), 1.35 (d, J = 7.3 Hz, 3H), 1.41 (s, 6H), 2.26 (septet, J = 6.6 Hz, 2H), 2.27 (septet, J = 6.6 Hz, 2H), 3.31 (q, J = 7.3 Hz, 1H). ^{13}C NMR (CDCl$_3$): δ 14.4, 17.8, 17.9, 18.1, 34.3, 48.8, 92.0, 169.7. IR (thin film): 1735 cm^{-1}. Anal. Calcd for $C_{20}H_{38}O_4$: C, 70.13; H, 11.18. Found C, 70.25; H, 11.13.

General Procedure for Synthesis of Substituted Benzoate Complexes. Rhodium acetate and 16 equiv of the substituted benzoic acid in chlorobenzene solution were refluxed for 48 h in a Soxhlet extraction apparatus whose thimble was charged with sodium carbonate. After cooling, the solvent was removed under vacuum and the resulting solid dissolved in methanol and dichloromethane. Removal of the dichloromethane and dropwise addition of water followed by cooling resulted in crystallization. Vacuum drying (24–48 h) of the resulting blue crystals resulted in a color change to green due to loss of axial water or methanol ligands. If necessary, the recrystallization procedure was repeated.

Tetrakis(4-Methoxybenzato)dirhodium. ^{1}H NMR (acetone-d_6): δ 3.74 (s, 12H), 6.80 (d, J = 8.7 Hz, 8H), 7.83 (d, J = 8.7 Hz, 8H). Anal. Calcd for $C_{32}H_{28}O_{12}\cdot H_2O$: C, 46.40; H, 3.65. Found: C, 46.42; H, 3.54.

Tetrakis(4-chlorobenzato)dirhodium. ^{1}H NMR (acetone-d_6/DMSO-d_6): δ 7.34 (d, J = 9.0 Hz, 8H), 7.88 (d, J = 9.0 Hz, 8H). Anal. Calcd for $C_{28}H_{16}Cl_4O_8$: C, 40.61; H, 1.95; Cl, 17.13. Found: C, 40.54; H, 2.02; Cl, 17.06.

Tetrakis(3-chlorobenzato)dirhodium. ^{1}H NMR (CDCl$_3$/CD$_3$OD): δ 7.25 (t, J = 7.5 Hz, 4H), 7.37 (d, J = 7.2 Hz, 4H), 7.75 (d, J = 7.8 Hz, 4H), 7.83 (s, 4H). Anal. Calcd for $C_{28}H_{16}Cl_4O_8\cdot 2H_2O$: C, 38.92; H, 2.33; Cl, 16.41. Found: C, 39.16; H, 2.44; Cl, 16.59.

Tetrakis(4-fluorobenzato)dirhodium. ^{1}H NMR (acetone-d_6/DMSO-d_6): δ 7.04 (t, J = 8.7 Hz, 8H), 7.91 (dd, J = 9.0, 5.6 Hz, 8H). Anal. Calcd for $C_{28}H_{16}F_4O_8$: C, 44.12; H, 2.12. Found: C, 44.10; H, 2.19.

Tetrakis(4-methylbenzato)dirhodium. ^{1}H NMR (acetone-d_6/DMSO-d_6): δ 2.25 (s, 12H), 7.10 (d, J = 8.1 Hz, 8H), 7.76 (d, J = 8.1 Hz, 8H). Anal. Calcd for $C_{32}H_{28}O_8\cdot H_2O$: C, 50.28; H, 3.96. Found: C, 50.39; H, 3.90.

Tetrakis[4-(trifluoromethyl)benzato]dirhodium. ^{1}H NMR (CDCl$_3$/DMSO-d_6): δ 7.52 (d, J = 8.4 Hz, 8H), 7.99 (d, J = 8.1 Hz, 8H). Anal. Calcd for $C_{32}H_{16}F_{12}O_8\cdot 2H_2O$: C, 38.50; H, 2.02. Found: C, 38.86; H, 1.76.

Tetrakis[4-(methoxycarbonyl)benzato]dirhodium. ^{1}H NMR (CDCl$_3$/DMSO-d_6): δ 7.89 (d, J = 9.0 Hz, 8H), 7.93 (d, J = 9.0 Hz, 8H). Anal. Calcd for $C_{36}H_{28}O_{16}\cdot H_2O$: C, 45.98; H, 3.22. Found: C, 45.68; H, 3.28.

Tetrakis(4-nitrobenzato)dirhodium. ^{1}H NMR (CDCl$_3$/DMSO-d_6): δ 8.06 (d, J = 9.0 Hz, 8H), 8.10 (d, J = 9.0 Hz, 8H). Anal. Calcd for $C_{28}H_{16}N_4O_{16}\cdot H_2O$: C, 37.86; H, 2.04. Found: C, 37.78; H, 1.96.

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