Ligand Effects on the Chemoselectivity of Ortho-Metalated Rhodium(II) Catalyzed α-Diazo Ketone Transformations

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$Rh_2(OOCR)_2(PC)_2$ complexes (PC = orthometalated phosphines, OOCR = carboxylates) with very polarizable ligands, such as aromatic rings directly joined to the rhodium atoms, control chemoselectivity in competitive metal carbene transformations of α-diazo ketones. These catalysts have a mixed set of ligands that allows choosing among a big selection of ligands to gradually affect the electronic and steric properties of the catalyst. Their selectivity depends on the electrophilicity of the ligands and the polarizability of the metalated aromatic rings. Thus, $Rh_2(OOCR)_2(PC)_2$ compounds [PC = $(C_6H_4)P(CH_3)(C_6H_5)$, $(p\text{-}CH_3C_6H_3)P(p\text{-}CH_3C_6H_4)_2$, $(C_6H_4)P(C_6H_5)_2$; R = C_3F_7 or CF_3] exhibit an exceptional selectivity for aliphatic C−H insertion over aromatic substitution in catalytic decomposition of 1-diazo-5-methyl-3-phenyl-2-hexanone. Results obtained from these complexes in competitive intramolecular cyclopropanation versus tertiary C−H insertion, cyclopropanation versus aromatic substitution, and C−H insertion versus aromatic substitution are compared with those obtained for other rhodium(II) compounds, such as rhodium(II) caprolactamate ($Rh_2(cap)_4$), rhodium(II) perfluorobutyrate, and rhodium(II) acetate.

Introduction

α-Diazocarbonyl compounds constitute a class of organics of quite exceptional flexibility in synthesis. Their most significant reactions are those that proceed with loss of nitrogen which can be brought about thermally, photochemically, or catalytically.[1] Their use in catalytic methods for the generation of metallocarbenes has attracted a great deal of attention in recent years. Early work in this area[2] made use of insoluble copper catalysts, but homogenous catalysts such as rhodium(II) complexes have become the premier catalysts.[2−4] These compounds catalyze a variety of important reactions, such as cyclopropanation, aliphatic carbon−hydrogen bond insertion, heteroatom−hydrogen bond insertion, aromatic substitution, and ylide formation. The success of these catalysts in intramolecular decomposition processes has maintained a high level of interest in diazocarbonyl compounds as synthetic intermediates.[3,4] While many recent reports deal with controlling the stereoselectivity and, in particular with chiral catalysts, the enantioselectivity of metal-catalyzed diazocarbonyl reactions,[5−13] there is a growing number of examples which also address the question of chemoselectivity.[14−17] This type of selectivity has been probed by the preparation of diazocarbonyl compounds containing two different reaction sites and the study of the competition between the two carbenoid processes. These studies have shown[15] that the chemoselectivity of the rhodium carbenoids, generated *in situ*, is greatly affected by the nature of the bridging ligand attached to the metal.

Pirrung et *al.*[18] analyzed the ligand effect on the selectivity of rhodium(II) carboxylate mediated transformations. Thus, two reactions of diazo compounds involving intramolecular competition of O-ylide versus secondary C−H insertion and tertiary C−H versus primary C−H insertion have been studied. They have found that the greatest selectivity is observed with ligands possessing low field effects and high polarizability raising the possibility that both electron-donating and electron-accepting abilities of the ligand might be important.

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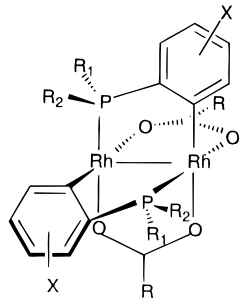

Figure 1.

It is accepted that the active site of the rhodium catalyst is one of the axial coordination positions of the dinuclear cage.[2,19] The decomposition of the diazo compound yields a carbene that can be stabilized forming a metal−carbenoid before undergoing further reaction. The ability of rhodium(II) compounds to form labile adducts by coordinating different donor ligands in these axial positions has been well investigated.[20] The stability of these Rh−L bonds roughly increases in the order O < N < P. Although the stability of the Rh−P bond has been interpreted as the result of a σ interaction augmented by the synergistic π-acceptor ability of the axial ligand, arguments based only on σ interaction have been proposed on the basis *ab-initio* calculations.[21] Cotton et *al.*[22] first prepared rhodium(II) compounds with metalated phosphines and have reported electrochemical studies on $Rh_2(OOCCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2 \cdot 2L$ with several donor ligands. As the oxidation potentials for the redox system Rh_2^{4+}/Rh_2^{5+} become more positive, the oxidation reaction becomes more difficult, in the order L = P < N < O, and consequently there is an increase of the electron density for the HOMO orbital in the order O < N < P. Drago and others[23,24] have reported coordination of CO to a limited set of rhodium carboxylates. They observed for the coordinated carbon monoxide a decrease in the ν_{C-O} stretching frequency compared to the free ligand. These results support the capability of these rhodium complexes to have a synergic π-Rh−L interaction in addition to the σ-L−Rh bond.

In contrast to the homoleptic $Rh_2(L\text{-}L)_4$ compounds used in previous catalytic studies,[14,26] we report in this paper the catalytic behavior of a series of ortho-metalated rhodium(II) compounds of the type $Rh_2(OOCR)_2(PC)_2$ [PC = ortho-metalated phosphine; R = CH_3, CF_3, C_3F_7] in the decomposition of three α-diazo ketones. The presence of two different ligands, the metalated phosphines with a highly polarizable phenyl group attached to the rhodium atom and the carboxylates, allows a better modulation of the electronic and steric properties of the catalyst that influence the activity and selectivity of the catalytic reactions.

Table 1. List of Catalysts

phosphine	X[a]	carboxylate	catalyst	ν_{CO} (cm^{-1})[b]
$(CH_3)_2(C_6H_5)P$	H	CH_3COO	**1a**	2028
$(CH_3)(C_6H_5)_2P$	H	CH_3COO	**1b**	2032
$(p\text{-}CH_3C_6H_4)_3P$	*m*-CH_3	CH_3COO	**1c**	2037
$(m\text{-}CH_3C_6H_4)_3P$	*p*-CH_3	CH_3COO	**1d**	2032
$(C_6H_5)_3P$	H	CH_3COO	**1e**	2041
$(p\text{-}FC_6H_4)_3P$	*m*-F	CH_3COO	**1f**	2043
$(m\text{-}FC_6H_4)_3P$	*p*-F	CH_3COO	**1g**	2044
$(p\text{-}CF_3C_6H_4)_3P$	*m*-CF_3	CH_3COO	**1h**	2042
$(C_6F_5)(C_6H_5)_2P$	H	CH_3COO	**1i**	2044
$(o\text{-}BrC_6F_5)(C_6H_5)_2P$	H	CH_3COO	**1j**	2042
$(CH_3)_2(C_6H_5)P$	H	C_3F_7COO	**1k**	2043
$(CH_3)(C_6H_5)_2P$	H	C_3F_7COO	**1l**	2042
$(p\text{-}CH_3C_6H_4)_3P$	*m*-CH_3	C_3F_7COO	**1m**	2042
$(C_6H_5)_3P$	H	C_3F_7COO	**1n**	2038
$(p\text{-}FC_6H_4)_3P$	*m*-F	C_3F_7COO	**1o**	2074
$(m\text{-}FC_6H_4)_3P$	*p*-F	C_3F_7COO	**1p**	2070
$(p\text{-}CF_3C_6H_4)_3P$	*m*-CF_3	C_3F_7COO	**1q**	2099
$(C_6H_5)_3P$	H	CF_3COO	**1r**	2040
	$Rh_2(OOCCF_3)_4$[c]			2128
	$Rh_2(OOCCH_3)_4$			2098
	$Rh_2(HNCOCH_3)_4$[d]			2046

[a] Substituent position relative to the metalated carbon atom. [b] Highest ν_{CO} carbonyl frequency for CH_2Cl_2 solution of the catalyst saturated with carbon monoxide (1 atm pressure). [c] From ref 22. [d] From ref 23.

Part of these results have been reported in a preliminary communication.[25]

Results

Catalysts. Different ortho-metalated dirhodium catalysts were synthesized with carboxylates of different electrophilicity and phosphines of different basicity, by changing the R_1 and R_2 groups and the substituent X on the metalated aromatic ring (see Table 1 and Figure 1).

To test the π-back-bonding ability of these dirhodium complexes, CO adducts were prepared by bubbling carbon monoxide (1 atm pressure) through CH_2Cl_2 solutions of the dimers. Since the stretching frequencies reported for CO bound to Rh(II) carboxylates were not clear to represent the 1:1 or the 1:2 CO adduct,[24] we looked only for the highest frequency band. These values could be related to the minimum capability for the catalyst to stabilize the carbene−Rh complex. Data for $Rh_2(OOCCF_3)_4$, $Rh_2(OOCCH_3)_4$, and $Rh_2(HNOCCH_3)_4$ were added for comparation. The C−O infrared stretching frequencies for all CO-bound ortho-metalated Rh(II) complexes occurred at lower energy than that of free CO (ν_{CO} = 2143 cm^{-1}), showing their π-back-bonding ability. The highest values were for those catalysts with perfluorobutyrate and fluorinated phosphine as ligands, such as **1o**−**q**. Furthermore, solution infrared spectroscopy of CO adducts of $Rh_2(OOCCH_3)_n(HNOCCH_3)_{4-n}$ species have shown that the CO stretching frequencies decrease as the number of acetamidate bridging ligands increases.[24] In our case, in catalysts which possess acetate, the lower ν_{CO} values were also found for those with more basic phosphines (catalysts **1a**−**d**; Table 1).

Crystal Structure of $Rh_2(OOCCH_3)_2((p\text{-}FC_6H_3)P(p\text{-}FC_6H_4)_2)_2 \cdot HOOCCH_3$ (1f). A view of the structure of **1f** is shown in Figure 2. Important bond distances and angles are listed in Table 6. In the molecular structure the two Rh atoms are bridged by two acetate groups and by two $P(p\text{-}FC_6H_4)_3$ metalated in one phenyl ring; two oxygen atoms of two acetic acid molecules,

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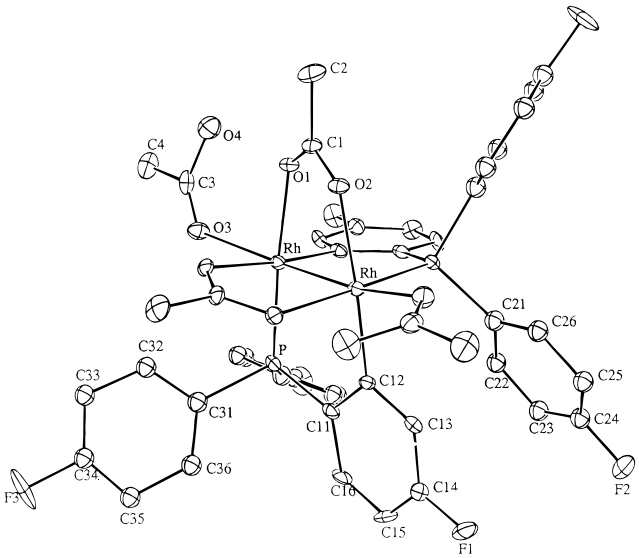
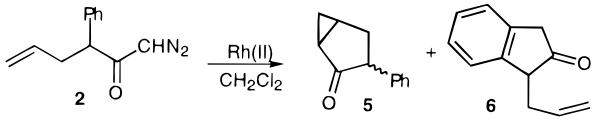


Figure 2. Structure of **1f**, showing the crystallographic labeling scheme.

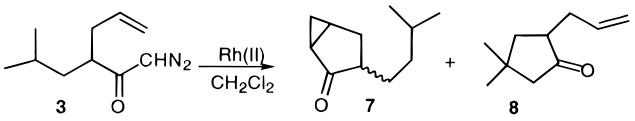
Table 2. Cyclopropanation versus Aromatic Substitution



run	catalyst	yield (%)	**5**	**6**
1	**1a**	90	100	0
2	**1b**	90	100	0
3	**1c**	92	100	0
4	**1d**	95	100	0
5	**1e**	90	100	0
6	**1f**	99	100	0
7	**1g**	94	100	0
8	**1h**	99	100	0
9	**1o**	94	100	0
10	**1p**	92	100	0
11	**1q**	98	100	0
ref 14	$Rh_2(OOCCH_3)_4$	99	63	26
ref 14	$Rh_2(OOCC_3F_7)_4$	95	0	100
ref 14	$Rh_2(cap)_4$	72	100	0

occupying the axial positions, complete the slightly distorted octahedral coordination [angles in the range 84.3(5)−96.7(3)°] around the metals. The value of the Rh−Rh bond distance, 2.488(3) Å, falls within the range reported for dirhodium compounds of similar structures. The bridge involving the metalated phosphine shows an "envelope" conformation that is normal in this type of dirhodium compounds. The Rh−P bond distance, 2.213-(4) Å, is comparable to those found in other doubly metalated compounds.[32] The Rh−O(2) bond trans to the carbon atom, 2.19(1) Å, is longer than that trans to the P atom, Rh−O(1) 2.12(1) Å, in agreement with the expected order of trans influence of M−C and M−P bonds.

Table 3. Cyclopropanation versus C−H Insertion



run	catalyst	yield (%)	**7**	**8**
1	**1a**	90	100	0
2	**1b**	87	100	0
3	**1c**	90	100	0
4	**1d**	92	100	0
5	**1e**	85	100	0
6	**1f**	99	100	0
7	**1g**	99	100	0
8	**1h**	99	100	0
9	**1i**	98	100	0
10	**1j**	98	80	20
11	**1n**	99	91	9
12	**1o**	88	80	20
13	**1p**	94	80	20
14	**1q**	93	80	20
ref 14	$Rh_2(OOCCH_3)_4$	97	44	56
ref 14	$Rh_2(OOCC_3F_7)_4$	56	0	100
ref 14	$Rh_2(cap)_4$	76	100	0

The longest Rh−O bond distance corresponds to the axial acetic acid molecules, Rh−O(3) 2.29(1) Å, and is indicative of the high trans influence of the metal−metal bond. The Rh−Rh−O_{axial} angle, 167.5(3)°, deviates from linearity most likely due to steric interactions between nonmetalated phenyl rings and the axial ligand.

Competitive Reactions. Intramolecular metal carbene reactions catalyzed by dirhodium(II) carboxylates generally exhibit an overwhelming preference for five-membered ring formation. We have synthesized diazocarbonyl compounds that possess two potentially reactive centers for five-membered ring formation. So, 1-diazo-3-phenyl-5-hexen-2-one (**2**), 1-diazo-5-methyl-3-(2-propenyl)-2-hexanone (**3**), and 1-diazo-5-methyl-3-phenyl-2-hexanone (**4**) were used for competitive reactions: cyclopropanation *vs* aromatic substitution, cyclopropanation *vs* C−H insertion, and C−H insertion *vs* aromatic substitution. The results for ortho-metalated dirhodium compounds were compared with those that have been obtained with other Rh(II) complexes.[14] Reactions were conducted in refluxing dichloromethane and were monitored by TLC until the starting material was consumed. The reaction mixture was directly concentrated and analyzed by ^{1}H-NMR. For some key experiments we confirmed that the catalyst can be recovered unchanged by column chromatography from the crude reaction mixture.

Cyclopropanation versus Aromatic Substitution. Addition of diazoketone **2** to a refluxing solution of $Rh_2(OOCR)_2(PC)_2$ catalysts (**1a**−**h** and **1o**−**q**) in dichloromethane resulted in the selective formation of the cyclopropanation product **5** (yield > 90%). No compound **6** resulting from aromatic substitution was observed in any case. Similar chemoselectivity was also reported for rhodium(II) caprolactamate,[14] but the yield was significantly lower (72%) (Table 2). In contrast, only the aromatic substitution product was obtained with rhodium(II) perfluorobutyrate.[14]

Cyclopropanation versus C−H Insertion. Competition between cyclopropanation and C−H insertion into a tertiary C−H bond provides another example of $Rh_2(OOCR)_2(PC)_2$ effectiveness in controlling chemoselectivity in carbene transfer reactions. The cyclopro-

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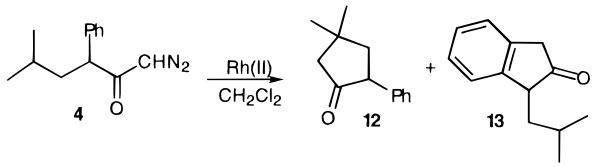
Table 4. C−H Insertion versus Aromatic Substitution



run	catalyst	yield (%)	**12**	**13**
1	**1a**	71	47	53
2	**1b**	69	54	46
3	**1c**	56	58	42
4	**1d**	60	59	41
5	**1e**	67	50	50
6	**1f**	86	56	44
7	**1g**	70	46	54
8	**1h**	99	62	38
9	**1i**	82	80	20
10	**1j**	95	30	70
11	**1l**	92	100	0
12	**1m**	93	100	0
13	**1n**	95	100	0
14	**1o**	93	70	30
15	**1p**	91	80	20
16	**1q**	89	60	40
17	**1r**	88	100	0
ref 14	$Rh_2(OOCCH_3)_4$	96	65	35
ref 14	$Rh_2(OOCC_3F_7)_4$	96	0	100
ref 14	$Rh_2(cap)_4$	64	70	30
ref 26	$Rh_2(tpa)_4$[a]	84	0	100

[a] tpa = triphenylacetate.

panation compound **7** was selectively isolated from the reaction of **3** in the presence of catalysts **1a**−**h** (yields 85−99%). Similar chemoselectivity was reported[14] for rhodium(II) caprolactamate but again the yield was lower (76%), but rhodium(II) tetraacetate catalyzes decomposition of diazoketone **3** with high yield but no selectivity (**7**:**8** ratio 44:56). By contrast, rhodium(II) perfluorobutyrate decomposition of diazoketone **3** resulted in the exclusive formation of the insertion product with moderate yield (56%).[14]

These results demonstrated that ortho-metalated rhodium(II) compounds with acetate groups led to intramolecular cyclopropanation process with very high effectiveness. However, minor amounts of the C−H insertion product **8** (9−20%) were obtained when catalysts **1n**−**q**, which contain perfluorobutyrate groups, were used (Table 3). It was interesting to observe that while only the cyclopropanation product was formed with catalyst **1i**, containing the phosphine (C_6F_5)-$(C_6H_5)_2P$ and acetate ligands, complex **1j**, with the bulkier $(o\text{-}BrC_6F_4)(C_6H_5)_2P$ ligand, gave rise also to the C−H insertion product **8** (20%). Steric crowding caused by the bromine atom near the reactive center of the carbenoid may influence its chemoselectivity. Thus, in general changing the acetate by the perfluorobutyrate ligand slightly reduced the chemoselectivity, but this effect was more important when electron-withdrawing substituents, such as F and CF_3, were introduced on the aromatic ring of triarylphosphine ligands (see catalysts **1o**−**q** on Table 3).

Aromatic Substitution versus C−H Insertion. We investigated the competition between aromatic substitution and C−H insertion using the diazoketone **4**. The reactivity and selectivity of these catalysts in this competitive transformation greatly depends on the nature of the bridging ligands and the substituents on the metalated aromatic ring. So, compounds **1a**−**e** (with basic phosphines and acetate ligands) exhibit poor selectivities and reactivities (Table 4). These values compare well with those reported for rhodium(II) caprolactamate that in this particular reaction exhibit slighly higher selectivity (**12**:**13** ratio 70:30) but lower yield.

The introduction of electron-withdrawing substituents on the three phenyl rings of the metalated phosphine, catalysts **1f**−**h**, increased the yields but still gave poor selectivites. The use of catalysts **1o**−**q** with electron-withdrawing substituents both in the phosphine and the carboxylate group increased the yields and selectivities to a limited extent (compare results for catalyst **1f**−**h** *vs* **1o**−**q** in Table 4). The selectivities were also increased if the electron-withdrawing substituents were introduced only in one nonmetalated phenyl ring, R_1 or R_2, catalysts **1i,j** (see Table 4). The change of selectivity with the later catalyst could be attributed to steric crowding created by the bromine atom near the reactive center of the carbenoid.

The most effective way to increase both reactivities and selectivities was found to be the use of perfluorobutyrate as carboxylate and triphenyl-, tris(*p*-tolyl)-, or methyldiphenylphosphine as metalated phosphine (catalysts **1l**−**n**). Trifluoroacetate groups produced similar desirable effects as perfluorobutyrate (catalysts **1n**,**r**). For these four catalysts we selectively obtained product **12**, with yields higher than 90%, while the aromatic substitution product **13** was not obtained.

Table 5. Summary of Crystallographic Data for the Complex $Rh_2(O_2CCH_3)_2((p\text{-}FC_6H_3)P(p\text{-}FC_6H_4)_2)_2\cdot 2HO_2CCH_3$

molecular formula	$Rh_2P_2F_6O_8C_{44}H_{34}$
M_r	1072.505
cryst system	monoclinic
space group	*P*2/*n*
cell dimens (16 °C)	
a, Å	20.659(4)
b, Å	9.996(6)
c, Å	23.125(5)
β, deg	113.77(4)
V, Å^3	4370.11
Z	4
d_{calc}, g/cm^3	1.630 (16 °C)
cryst dimens, mm	0.26 × 0.24 × 0.15
diffractometer	CAD4
radiation; λ, Å	Mo Kα; 0.710 73
data collcn method	$\theta-2\theta$
scan speed, deg/min	variable
reflcns measd	8406
range/indices (*h*,*k*,*l*)	0 to 24, 0 to 11, −27 to 27
2θ limit, deg	2.00−50.00
no. of reflcns between stds	98
tot. no. of unique data	8167
no. of obsd data, $I > 3\sigma(I)$	2697
abs coeff, cm^{-1}	8.897
min transm, %	87.6748
max transm, %	93.9948
no. of variables	455
goodness of fit	1.9278
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0593
$R_w = \sum\|\|F_o\| - \|F_c\|\|w^{1/2}/\sum\|F_o\|w^{1/2}$	0.0702
Δ/σ(max)	0.001
$\Delta\rho$(max), e/Å^3	1.217

Discussion

The rhodium(II)-catalyzed α-diazoketone decompositions are accepted to occur *via* a carbenoid species schematically represented in Figure 3. One canonical

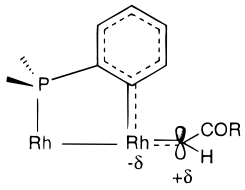


Figure 3.

form of the resulting complex has a polar $Rh^{-\delta}-C^{+\delta}$ bond. In studies of intramolecular selectivity the substrates contain two nucleophilic groups as carbon−carbon double bonds, aromatic C−H bonds, or aliphatic C−H bonds competing for the electrophilic carbon atom. The aim was to study the influence of the ligands attached to the Rh_2^{4+} core on the selectivity of the two possible intramolecular transformations. According to Pirrung[18] stable carbenoids, with relatively strong σ and π bonds, are required to achieve selective transformations. Ligand field effects strengthen σ-bonds and make the carbene more electrophilic and therefore more selective for electron-rich sites of reactions. Ligand polarizability stabilizes the carbene through back-bonding but can also withdraw electron density from the metal to stabilize the σ bond and make the carbene more electrophilic.

In the ortho-metalated rhodium(II) catalysts reported in this paper, the polarizability should be dominated by the highly polarizable π-system of the metalated aromatic ring, so the electron-donating or electron-withdrawing properties of the substituents on the metalated ring could modulate the changes on their selectivity through resonance.

In the competition between cyclopropanation and aromatic substitution of diazo **2**, Rh(II) catalysts having ligands with very high field effects, such as $Rh_2(OOCC_3F_7)_4$, could strengthen the σ-bond and make the carbene highly electrophilic and therefore charge control could lead to selective aromatic substitution. In contrast, HOMO/LUMO control may be operating when catalysts with more π-back-bonding ability, such as $Rh_2(cap)_4$ or $Rh_2(OOCR)_2(PC)_2$, were used.

The high selectivity observed in the ortho-metalated dirhodium catalyzed decomposition of diazo **3**, where there is competition between cyclopropanation and C−H insertion, agreed with the order of functional group nucleophilicity, which places a double bond at a higher level of reactivity than a C−H bond. However, increasing the electrophilicity of the carbenoid intermediate but decreasing the ability of the metalated aromatic ring to donate back electron density to the carbene reduced its selectivity. So, catalysts **1o**−**q**, with perfluorobutyrate and fluorine-substituted metalated aromatic rings, were less selective, though always with clear predominance of the cyclopropanation process.

On the other hand, it also appeared that there were similarities in factors that promoted aromatic substitution and C−H insertion as shown by the low selectivity in the decomposition of diazo compound **4** by rhodium(II) acetate, caprolactamate, and ortho-metalated catalysts **1a**−**h**,**q**. However, catalysts **1l**−**n**,**r**, with ligands able to strengthen both σ- and π-bonding, gave unique results, since they selectively produced the C−H insertion product in the α-diazocarbonyl compound in high yield (>90%). No other rhodium(II) catalyst has provided similar result.

In the decomposition of diazo **4**, the dependence of the chemoselectivity on the π-back-bonding ability of catalysts $Rh_2(OOCC_3F_7)_2(PC)_2$ was probed by introducing in the aromatic ring of the phosphine electron-withdrawing groups such as CF_3 or F in *meta* and *para* positions relative to the rhodium atom (catalysts **1o**−**q**). The chemoselectivity decreased as the electronic or polar effect of the substituent increased, that is as the ability of the metalated aromatic ring to retrodonate density to the carbene decreased. Selectivity decreased in the order **1p** > **1o** > **1q** (Hammett σ constants for *p*-F, *m*-F, and *m*-CF_3 being 0.06, 0.34, and 0.43, respectively).[27]

Thus, results here reported show that the activity of these catalysts increased when less basic phosphines and/or high electron-withdrawing carboxylates were used. However, chemoselectivity required electrophilic catalysts with a high density metalated aromatic ring. Thus, electron-withdrawing groups on the ring reduced the chemoselectivity (compare catalysts **1l**−**n**,**r** with **1o**−**q**). No differences were found for catalysts **1n**,**r**, having respectively perfluorobutyrate and trifluoroacetate as carboxylate groups.

The selectivity of the rhodium tetrakis(triphenylacetate)-mediated transformation of diazo **4** has been suggested as due to the bulkiness of the triphenylacetate ligand.[26] So, it seems that steric shielding of the active center of the carbenoid retards the tertiary C−H insertion to favor the aromatic C−H insertion. Thus, differences in selectivity observed for catalysts **1i**,**j** could also be mainly attributed to the steric effect caused by the bromine atom in **1j**.

Conclusion

It has been confirmed that activity and selectivity of competitive α-diazoketone decomposition reactions catalyzed by $Rh_2(OOCR)_2(PC)_2$ compounds can be modulated to a great extent by changing R groups and substituents on the metalated phenyl ring. Several catalysts containing electron-rich metalated rings and electrophilic carboxylate groups give rise to selective C−H insertion in a α-diazocarbonyl compound in which the aromatic substitution process could be competitive. Such selectivity was not previously reported for any other rhodium(II) catalysts. Furthermore, these data agree with Pirrung's finding for rhodium(II) carboxylates that increasing electrophilicity of the bridging ligand plus stability of the Rh(II)−carbene complex through back-donation can increase the selectivity of the catalyst.

Moreover, steric effects may play a dominant role in the product distribution when the catalysts used have big substituents near the reactive center.

Experimental Section

General Comments. All manipulations were performed under an argon atmosphere. All solvents were of analytical grade. Toluene and chloroform were dried and degassed, and methylene chloride was distilled from CaH_2 under argon atmosphere. Tetrahydrofuran (THF) and ethyl ether were distilled from sodium/benzophenone under an argon atmosphere. Acetic acid was only degassed. ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were measured in $CDCl_3$ on Bruker AC-200 FT and 250 FT spectrometers, operating at 300 K. Tetramethylsilane (TMS) was used as a reference for ^{1}H and ^{13}C spectra, while H_3PO_4 (85% in D_2O) was the external reference for ^{31}P NMR spectra. All compounds show ^{31}P NMR spectra corresponding to an AA′XX′ system. Elemental analyses were performed by

C.A.I. Microanalysis, Complutense de Madrid. α-Diazoketones **2**−**4** were prepared as reported previously.[14] $Rh_2(OOCCH_3)_4(MeOH)_2$[28] and $Rh_2(OOCCF_3)_4$[29] were prepared by a literature procedure. Phosphines $(CH_3)P(C_6H_5)_2$, $(CH_3)_2P(C_6H_5)$, $P(p\text{-}CH_3C_6H_4)_3$, $P(m\text{-}CH_3C_6H_4)_3$, $P(C_6H_5)_3$, $P(p\text{-}FC_6H_4)_3$, $P(m\text{-}FC_6H_4)_3$, and $P(p\text{-}CF_3C_6H_4)_3$ are commercially available, and they were used as received. The phosphines $P(o\text{-}BrC_6F_4)(C_6H_5)_2$[30] and $P(C_6F_5)(C_6H_5)_2$[31] were prepared by literature procedures. Catalysts **1c**,[32] **1d**,[33] **1e**,[22] **1j**,[34] and **1r**[35] were prepared according to literature methods. The remaining catalysts containing acetate groups were prepared according to the following synthetic method.

Synthesis of $Rh_2(OOCCH_3)_2(PC)_2\cdot 2HOOCCH_3$: General Procedure. $Rh_2(OOCCH_3)_4(MeOH)_2$ (150 mg; 0.296 mmol) and 0.592 mmol of the corresponding phosphine were refluxed in 30 mL of a mixture (3:1) of toluene/acetic acid in an argon atmosphere for 90 min. After evaporation to dryness under vacuum, the crude product was chromatographed (2 × 30 cm, silica gel (70−230 mesh)/hexane). The column was first washed with CH_2Cl_2/hexane (1:1) and was later eluted with mixtures of CH_2Cl_2/hexane/acetic acid of increasing polarity (from 40:40:1 to 10:10:3). A major purple band was collected in each case and was concentrated under reduced pressure to produce purple crystalline materials. The samples were recrystallized by slow diffusion of hexane into a CH_2Cl_2 solution of the compound in the presence of small amounts (1−2 drops) of acetic acid.

Compound 1a. Yield: 48.96 mg (23%) of $Rh_2(OOCCH_3)_2((C_6H_4)P(CH_3)_2)_2\cdot 2HOOCCH_3$. ^1H NMR ($CDCl_3$): δ 0.89 (d, J = 10.36 Hz, 6H, CH_3, phosphine), 1.40 (d, J = 10.32 Hz, 6H, CH_3, phosphine), 1.97 (s, 6H, bridging acetate), 2.10 (s, 6H, axial acetic acid), 6.75−7.19 (m, 8H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −0.5 ($^1J_{Rh-P}$ = 163.15 Hz, $^2J_{Rh-P}$ = 18.70). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.91 (d, J_{PC} = 35.85 Hz, CH_3, phosphine), 16.19 (d, J_{PC} = 29.11 Hz, CH_3, phosphine), 21.92 (s, CH_3, axial acetic acid), 24.03 (s, CH_3, bridging acetate), 121.58−150 (m, aromatics), 163.5 (m), 178 (s, COO), 182 (s, COO).

Compound 1b. Yield: 126 mg (51%) of $Rh_2(OOCCH_3)_2((C_6H_4)P(C_6H_5)(CH_3))_2\cdot 2HOOCCH_3$. ^1H NMR ($CDCl_3$): δ 1.39 (d, J = 10.18 Hz, 6H, CH_3, phosphine), 1.50 (s, 6H, bridging acetate), 2.17 (s, 6H, axial acetic acid), 6.7−8.2 (m, 18H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 8.4 ($^1J_{Rh-P}$ = 163 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.16 (d, J_{PC} = 35.46 Hz, CH_3, phosphine), 22.13 (s, CH_3, axial acetic acid), 23.41 (s, CH_3, bridging acetate), 121−146.63 (m, aromatics), 164.2 (m), 180 (s, COO), 182 (s, COO). Anal. Calcd (found) for $C_{34}H_{38}O_8P_2Rh_2$: C, 48.48 (48.12); H, 4.82 (4.67).

Compound 1f. Yield: 238.9 mg (75%) of $Rh_2(OOCCH_3)_2((p\text{-}FC_6H_3)P(p\text{-}FC_6H_4)_2)_2\cdot 2HOOCCH_3$. ^1H NMR ($CDCl_3$): δ 1.3 (s, 6H, CH_3, bridging acetate), 2.2 (s, 6H, CH_3, axial acetic acid), 6.4−7.6 (m, 22H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.5 (d, $^1J_{Rh-P}$ = 163.33 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21 (s, CH_3, bridging acetate), 22.3 (s, CH_3, axial acetic acid), 114−140 (m, aromatics), 165 (m), 181 (s, COO), 182 (s, COO). Anal. Calcd (found) for $C_{44}H_{36}F_6O_8P_2Rh_2$: C, 49.18 (48.66); H, 3.38 (3.39).

Compound 1g. Yield: 249.3 mg (85%) of $Rh_2(OOCCH_3)_2((m\text{-}FC_6H_3)P(m\text{-}FC_6H_4)_2)_2\cdot 2H_2O$. ^1H NMR ($CDCl_3$): δ 1.7 (s, 6H, bridging acetate), 6.7−7.6 (m, 22H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.5 (d, $^1J_{Rh-P}$ = 172.52 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21 (s, CH_3, bridging acetate), 116−144 (m, aromatics), 163 (m), 180 (s, COO), 182 (s, COO). Anal. Calcd (found) for $C_{40}H_{32}F_6O_6P_2Rh_2$: C, 48.51 (48.82); H, 3.26 (3.28).

Compound 1h. Yield: 286 mg (70%) of $Rh_2(OOCCH_3)_2((p\text{-}CF_3C_6H_3)P(p\text{-}CF_3C_6H_4)_2)_2\cdot 2HOOCCH_3$. ^1H NMR ($CDCl_3$): δ 1.5 (s, 6H, CH_3, bridging acetate), 2.4 (s, 6H, CH_3, axial acetic acid), 6.5−7.8 (m, 22H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22 ($^1J_{Rh-P}$ = 170.11 Hz, $^2J_{Rh-P}$ = 7.26 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21 (s, CH_3, bridging acetate), 22.6 (s, CH_3, axial acetic acid), 120−140 (m, aromatics), 165 (m), 180 (s, COO), 182 (s, COO). Anal. Calcd (found) for $C_{50}H_{36}F_{18}O_8P_2Rh_2$: C, 43.69 (43.31); H, 2.64 (2.80).

Compound 1i: Mixture of Two Isomers. Yield: 142.70 mg (42%) of $Rh_2(OOCCH_3)((C_6H_4)P(C_6F_5)(C_6H_5))_2\cdot 2HOOCCH_3$. ^1H NMR ($CDCl_3$): δ 1.2 (s, 6H, CH3, bridging acetate), 1.8 (s, 6H, CH_3, axial acetic acid), 6.5−7.4 (m, 18H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 15.2 (d, $^1J_{Rh-P}$ = 179.12 Hz), 18 (d, $^1J_{Rh-P}$ = 183.4 Hz, $^2J_{Rh-P}$ = 8.11 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.81 (s, CH_3), 23.14 (s, CH_3), 122−149 (m, aromatics), 160.5 (m), 182 (s, COO), 183 (s, COO).

The rhodium compounds with perfluorobutyrate groups, catalysts **1k**−**q**, were synthesized from the acetate analog by the following synthetic procedure.

Synthesis of $Rh_2(OOCC_3F_7)_2(PC)_2\cdot 2H_2O$. To 300 mg of $Rh_2(OOCCH_3)_2(PC)_2\cdot(HOOCCH_3)_2$ in 20 mL of $CHCl_3$ was added 3 mL of heptafluorobutyric acid with vigorous stirring under an atmosphere of argon. The color of the solution immediately changed from purple to dark blue. The solution was stirred for 24 h at room temperature and was monitered by ^{31}P NMR until total substitution of bridging acetate ligands was achieved. The solvent was evaporated under reduced pressure. The resulting dark crude product was redissolved in CH_2Cl_2/hexane and was chromatographed on silica gel. After the column was washed with hexane/CH_2Cl_2, elution with hexane/acetone (10:2) separated a dark blue band which was collected. The solvent was evaporated, and the dark blue crude product was redissolved in CH_2Cl_2; addition of hexane precipitated a dark green solid, which was filtered off and dried in vacuum. Catalyst **1o** was only crystallized in the form of the adduct with $HOOC_3F_7$.

Compound 1k. Yield: 59.1 mg (15%) of $Rh_2(OOCC_3F_7)_2((C_6H_4)P(CH_3)_2)_2\cdot 2H_2O$. ^1H NMR ($CDCl_3$): δ 0.89 (d, J = 6.13 Hz, 6H, CH_3), 1.5 (d, J = 6.09 Hz, 6H, CH_3), 6.8−8 (m, 8H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −2.6 (d, $^1J_{Rh-P}$ = 163.17 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 15.2 (d, J_{PC} = 24.88 Hz, CH_3), 16.57 (d, J_{PC} = 31.35 Hz, CH_3), 121−153 (m, aromatics), 167.3 (m), 181 (s, COO), 187 (s, COO).

Compound 1l. Yield: 37.97 mg (10%) of $Rh_2(OOCC_3F_7)_2((C_6H_4)P(C_6H_5)(CH_3))_2\cdot 2H_2O$. ^1H NMR ($CDCl_3$): δ (d, J = 8.30 Hz, 6H, CH_3), 6.6−7.4 (m, 18H, aromatics). $^{31}P\{^1H\}$ ($CDCl_3$): δ 5.75 (d, $^1J_{Rh-P}$ = 165.77 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.26 (d, J_{PC} = 33.58 Hz, CH_3), 120−143.5 (m, aromatics), 167 (m), 183 (s, COO), 187 (s, COO).

Compound 1m. Yield: 262.02 mg (72%) of $Rh_2(OOCC_3F_7)_2((p\text{-}CH_3C_6H_3)P(p\text{-}CH_3C_6H_4)_2)_2\cdot 2H_2O$. ^1H NMR ($CDCl_3$): δ 1.8 (s, 6H, CH_3), 2.25 (s, 6H, CH_3), 2.3 (s, 6H, CH_3), 6.3−7.6 (m, 22H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 13.8 (d, $^1J_{Rh-P}$ = 161.19 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.17 (s, CH_3), 21.17 (s, CH_3), 21.59 (s, CH_3), 123.8−143.6 (m, aromatics), 167 (m), 176 (s, COO), 186 (s, COO).

Compound 1n. Yield: 200.68 mg (56%) of $Rh_2(OOCC_3F_7)_2((C_6H_4)P(C_6H_5)_2)_2\cdot 2H_2O$. ^1H NMR ($CDCl_3$): δ 6.4−7.6 (m, 28H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 16 (d, $^1J_{Rh-P}$ = 175.47 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 121.5−142 (m, aromatics), 162 (m), 176 (s, COO), 182 (s, COO). Anal. Calcd (found) for $C_{44}H_{32}F_{14}O_6P_2Rh_2$: C, 44.39 (43.20); H, 2.71 (2.81).

Compound 1o. Yield: 330.8 mg (70%) of $Rh_2(OOCC_3F_7)_2((p\text{-}FC_6H_3)P(p\text{-}FC_6H_4)_2)_2\cdot 2HOOC_3F_7\cdot(CH_2Cl_2)$. ^1H NMR ($CDCl_3$): δ 5.4 (s, 2H, CH_2Cl_2), 6.6−7.8 (m, 22H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19 (d, $^1J_{Rh-P}$ = 165.69 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 56.8 (s, CH_2), 118−148 (m, aromatics), 163 (m), 180 (s, COO), 182 (s, COO). Anal. Calcd (found) for $C_{54}H_{28}F_{34}O_8P_2Rh_2$: C, 34.88 (34.69); H, 1.52 (2.31).

Compound 1p. Yield: 235.63 mg (65%) of $Rh_2(OOCC_3F_7)((m\text{-}FC_6H_3)P(m\text{-}FC_6H_4)_2)_2\cdot 2H_2O$. ^1H NMR ($CDCl_3$): δ 6.2−7.4 (m, 22H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 18.5 (d, $^1J_{Rh-P}$ = 171.26 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 122−151 (m, aromat-

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ics), 166 (m), 169 (s, COO), 172 (s, COO). Anal. Calcd (found) for $C_{44}H_{26}F_{20}O_6P_2Rh_2$: C, 40.7 (39.55); H, 2.02 (2.27).

Compound 1q. Yield: 258.2 mg (74%) of $Rh_2(OOCC_3F_7)_2$-$((p\text{-}CF_3C_6H_3)P(p\text{-}CF_3C_6H_4)_2)_2 \cdot 2H_2O$. ^{1}H NMR ($CDCl_3$): δ 6.4−7.8 (m, 22H, aromatics). $^{31}P\{^1H\}$ NMR (CDCl3): δ 20 (d, $^1J_{Rh-P}$ = 166.34 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 123−153 (m, aromatics), 167 (m), 171 (s, COO), 172 (s, COO). Anal. Calcd (found) for $C_{40}H_{26}F_{32}O_6P_2Rh_2$: C, 37.57 (37.05); H, 1.64 (1.93).

Infrared spectra of carbon monoxide adducts of $Rh_2(OOCR)_2$-$(PC)_2$ compounds in dichloromethane solution were recorded on a Perkin-Elmer 882 instrument. These adducts were prepared *in situ* by bubbling carbon monoxide through 5.0×10^{-3} M dichloromethane solutions of the $Rh_2(OOCR)_2(PC)_2$ compounds. The catalysts were used after drying in vacuum for 2 h. The rhodium compounds gave the same catalytic results independently of the adduct used, water or carboxylic acid.

Dirhodium Complex Catalyzed Reaction of Diazo Compounds. The appropriate α-diazo ketone (1 mmol) was dissolved in dry CH_2Cl_2 under an argon atmosphere. Rh_2-$(OOCR)_2(PC)_2$ (0.05 mol)[36] was added to the solutions, and the mixture was immersed in a water bath set at 45 °C. There was evolution of N_2 gas before the start of refluxing, and the color of the mixture changed from yellow to brown. The mixture was refluxed for 1−2 h, cooled to room temperature, filtered, and evaporated. The residue was directly analyzed by ^{1}H and ^{13}C NMR. In some key experiments the products were purified by column chromatography before identification.

Crystal Structure of $Rh_2(OOCCH_3)_2((p\text{-}FC_6H_3)P(p\text{-}FC_6H_4)_2)_2 \cdot 2HOOCCH_3$) (1f). X-ray data were collected on an Enraf Nonius Cad4 diffractometer by standard procedures. Data were collected as summarized in Table 5. Cell constants were obtained from 25 reflections ($20° < 2\theta < 50°$), and the space group was determined from systematic absences and subsequent least-squares refinement. Lorentz, polarization, and empirical absorption (ψ scans) corrections were applied. The structures were solved by standard heavy-atom techniques with the Molen/Vax package.[37] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogens were refined isotropically from their idealized geometrical positions. Scattering factors, $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[38]

(36) Following the suggestion of one reviewer, the decomposition of the α-diazo ketone **4** was also performed using only 1% catalyst **1n**. The yield and selectivity were the same reported when 5% catalyst was used.

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for the Complex $Rh_2(O_2CCH_3)_2((p\text{-}FC_6H_3)P(p\text{-}FC_6H_4)_2)_2 \cdot (HO_2CCH_3)_2$

Rh−Rh	2.488(3)	P−C(11)	1.77(2)
Rh−P	2.213(4)	P−C(21)	1.82(2)
Rh−O(1)	2.12(1)	P−C(31)	1.85(2)
Rh−O(2)	2.19(1)	F(1)−C(14)	1.34(2)
Rh−O(3)	2.29(1)	F(2)−C(24)	1.38(2)
Rh−C(12)	1.99(2)	F(3)−C(34)	1.42(2)
Rh−Rh−P	89.8(1)	O(1)−Rh−O(2)	85.6(4)
Rh−Rh−O(1)	86.0(3)	O(1)−Rh−O(3)	87.6(5)
Rh−Rh−O(2)	84.5(3)	O(1)−Rh−C(12)	89.7(5)
Rh−Rh−C(12)	96.2(6)	O(2)−Rh−O(3)	84.3(5)
P−Rh−O(1)	175.7(3)	O(3)−Rh−C(12)	94.5(6)
P−Rh−O(2)	95.0(3)	Rh−P−C(11)	111.5(6)
P−Rh−O(3)	96.7(3)	Rh−P−C(21)	114.3(5)
P−Rh−C1(2)	89.8(4)	Rh−P−C(31)	113.9(6)

Acknowledgment. We thank the DGICYT (Project PB94-988) for financial support.

Supporting Information Available: Tables of positional and thermal parameters and bond distances and angles (15 pages). Ordering information is given on any current masthead page.

OM9608162

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