Reactivity and Selectivity of Ortho-Metalated Rhodium(II) Complexes in C−H Insertion Reactions of α-Diazo Compounds

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Regioselective intramolecular C−H insertion reactions of α-diazo β-keto esters and α-diazo ketones are mediated by $Rh_2[OOCR]_{4-x}[PC]_x$ (x = 1, 2; PC = ortho-metalated phosphine; R = CH_3, C_3F_7). In particular, the intramolecular transformation of 1-diazo-5-methyl-3-propyl-2-hexanone catalyzed by $Rh_2[OOCCH_3]_2[PC]_2$ (PC = $(C_6H_4)P(C_6H_5)_2$, head-to-tail (H−T) configuration) afforded only the tertiary C−H insertion product. By comparison, no C−H insertion reaction was promoted by doubly metalated complexes with a head-to-head (H−H) configuration. $Rh_2[OOCR]_3[PC]$ compounds were found to be less suited for these type of reactions.

Introduction

Rhodium(II) acetate is known to generate transient electrophilic metal carbenes from α-diazo compounds, which are then able to insert into unactivated C−H bonds.[1] Previous work has shown that the formation of a five-membered ring is a favored process for diazo compounds with freely rotating aliphatic side chains.[2] There is general agreement that, for a fixed ring size, C−H insertion occurs faster as the carbon is more substituted.[3] Studies have also indicated that the nature of the bridging ligands on the dirhodium(II) metal, as well as the type of α-substituent on the carbenoid carbon, have a marked influence on the regio- and chemoselectivities of the reaction.[4]

We have recently reported[5] good chemoselectivity in the transformation of α-diazo ketones catalyzed by rhodium(II) compounds of general formula $Rh_2(OOCR)_2(PC)_2$ (**1**), containing two ortho-metalated phosphines (PC) in a head-to-tail (H−T) configuration. These compounds have some unique characteristics which differentiate them from rhodium tetracarboxylates or tetraamidates, which are more frequently used.[4] For instance, they contain polarizable aromatic ligands attached to rhodium, and it is possible to modulate electronic and steric properties of the metal by variation of the carboxylate groups and the phosphine substituents. Previous work has shown[5] that such ligand changes greatly influence the activity and selectivity of these rhodium(II) complexes. Herein, we report results from studies on competitive C−H insertion reactions mediated by this type of catalysts.

Although the monometalated compounds $Rh_2(OOCR)_3(PC)$ (**2**) and doubly metalated dirhodium compounds $Rh_2(OOCR)_2(PC)_2$ (head-to-head configuration) (**3**) (Figure 1) are known,[6,7] their reactivity and selectivity in diazo compound transformations are unknown. To perform these studies, we chose two types of diazo compounds: α-diazo β-keto esters and α-diazo ketones, which offer two competing sites for C−H insertion.

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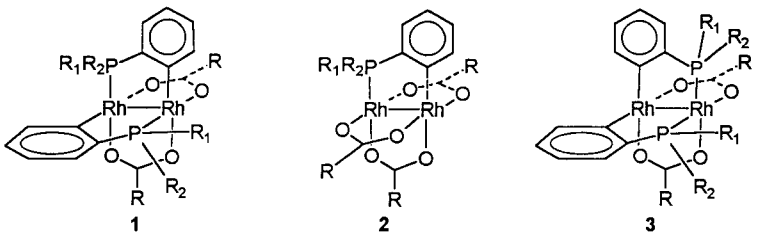


1 2 3

Catalysts	R_1	R_2	R	References
$\mathbf{1a_1}$	C_6H_5	C_6H_5	CH_3	6b, 7
$\mathbf{1a_2}$	C_6H_5	C_6H_5	C_3F_7	5b
$\mathbf{1b_1}$	C_6H_5	CH_3	CH_3	5b
$\mathbf{1c_1}$	CH_3	CH_3	CH_3	5b
$\mathbf{1d_1}$	C_6F_5	C_6H_5	CH_3	this work
$\mathbf{1d_2}$	C_6F_5	C_6H_5	C_3F_7	this work
$\mathbf{2a_1}$	C_6H_5	C_6H_5	CH_3	6b
$\mathbf{2a_2}$	C_6H_5	C_6H_5	C_3F_7	this work
$\mathbf{2b_1}$	C_6H_5	CH_3	CH_3	12
$\mathbf{2d_1}$	C_6F_5	C_6H_5	CH_3	this work
$\mathbf{2e_1}$	*o*-ClC_6H_4	C_6H_5	CH_3	13
$\mathbf{2f_1}$	*o*-BrC_6H_4	C_6H_5	CH_3	14
$\mathbf{3a_1}$	C_6H_5	C_6H_5	CH_3	6b

Figure 1.

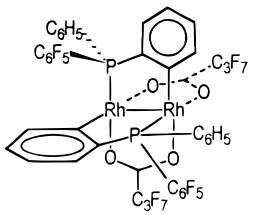


Figure 2.

Results

Catalysts. Compound $\mathbf{2d_1}$ was prepared in moderate yield, by following the general literature method used for other monometalated compounds.[6] The doubly metalated compound $\mathbf{1d_1}$ was prepared by a synthetic method different from that previously described.[5] A $CHCl_3$ solution containing an equimolar amount of $\mathbf{2d_1}$ (see Experimental Section) and $P(C_6H_5)_2(C_6F_5)$ was irradiated for 2−3 h. $\mathbf{1d_1}$ was obtained as a mixture of the three possible diastereoisomers. $Rh_2(OOCC_3F_7)_2[(C_6H_4)P(C_6H_5)(C_6F_5)]_2$ was obtained from $\mathbf{1d_1}$ by a carboxylate exchange reaction using C_3F_7COOH. The more abundant isomer $\mathbf{1d_2}$ was isolated as a crystalline material from this sample. We assigned the structure shown in Figure 2 to this isomer on the basis of its ^{31}P NMR spectrum and prelimminary X-ray data.

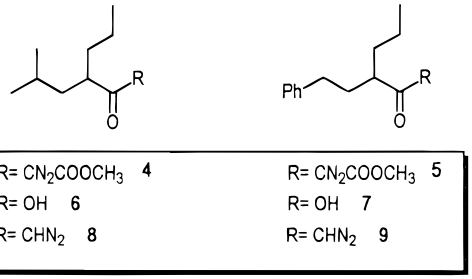
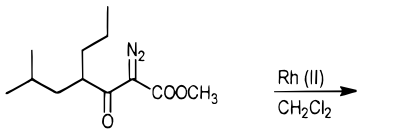


Figure 3.

Diazo Compounds. We have prepared a series of α-diazo *β*-keto esters (methyl 2-diazo-6-methyl-3-oxo-4-propylheptanoate (**4**), methyl 2-diazo-3-oxo-6-phenyl-4-propylhexanoate (**5**)) and α-diazo ketones (1-diazo-5-methyl-3-propyl-2-hexanone (**8**) and 1-diazo-5-phenyl-3-propyl-2-pentanone (**9**)) (Figure 3), which have two competing sites, in an attempt to study the regioselectivity of C−H insertion reactions catalyzed by ortho-metalated Rh(II) complexes. Treatment of α-diazo *β*-keto esters **4** and **5** with aqueous sodium hydroxide produced the cleavage of the $-COOCH_3$ group, leading to the corresponding diazo ketones **8** and **9**, respectively. This result is in contrast with a previous report on hydrolysis of other α-diazo *β*-keto esters, in which the keto group was cleaved under similar reaction condi-

Table 1. Tertiary Aliphatic C−H Insertion *vs* Secondary Aliphatic C−H Insertion



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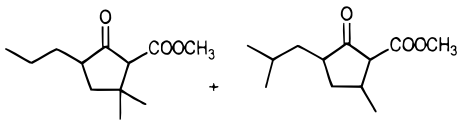


10 11

catalyst	C−H insertion yield (%)	reacn time (h)	relative ratio: tertiary C−H (**10**)	relative ratio: secondary C−H (**11**)
$Rh_2(OOCCH_3)_4$[a]	84	1	70	30
$Rh_2(OOCC_3F_7)_4$	70	1	63	37
$Rh_2(HNOCCH_3)_4$	91	2	70	30
1a$_1$	no reacn	100		
1b$_1$	79[b]	100	71	29
1c$_1$	91[c]	100	73	27
1a$_2$	no reacn	100		
2a$_1$	99	1	69	31
2b$_1$	99	1	71	29
2d$_1$	99	1	71	29
2e$_1$	95	1	70	30
2f$_1$	99	1	65	35
3a$_1$	no reacn	8		

[a] See ref 3a. [b] 21% of diazo compound recovered. [c] 9% of diazocompound recovered.

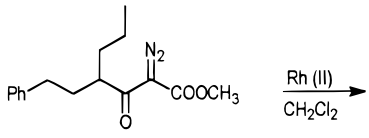
tions.[8] We suggest that steric crowding near the keto group in diazo compounds **4** and **5** protected this group from attack by a nucleophile. Alternatively, diazo ketones **8** and **9** could be obtained from the corresponding acid (**6** and **7**, respectively) by reaction with ethyl chloroformate, followed by treatment with freshly prepared diazomethane.[9]

Competitive Reactions. Catalytic reactions were performed by addition of the rhodium(II) complex (1.0 mol %) to a dichloromethane solution containing the diazo compound. The mixture was refluxed for 1 h (unless indicated otherwise). The solvent was removed, and the crude product was analyzed by ^1H and ^{13}C NMR.

Catalytic Reactions of α-Diazo *β*-Keto Esters. It has been reported[3a] that addition of $Rh_2(OOCCH_3)_4$ to α-diazo *β*-keto ester **4** results in the formation of the cyclization products **10** and **11** (overall yield 84%). The ratio of tertiary to secondary C−H insertion has been found to be 70/30 (Table 1).

We found that when (H−T) doubly metalated rhodium complexes **1a$_1$**, **1b$_1$**, **1c$_1$**, and **1a$_2$** were used, no diazo compound decomposition was observed after 1 h. Longer reaction time (100 h) resulted in 79% C−H insertion for catalyst **1b$_1$** and 91% for **1c$_1$**, with no detectable byproducts. However, compounds **1a$_1$** and **1a$_2$** did not decompose **4** after 4 days in boiling dichloromethane.

Scheme 1



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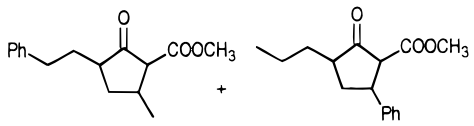

12 13

High yields of C−H insertion (>95%) were also obtained when using monometalated rhodium compounds **2**, whose ligands are carboxylates and phosphines of different basicities. The head-to-head dimetalated rhodium compound **3** was also evaluated in catalytic reactions with diazo compound **4**; no reaction progress was observed after 8 h in refluxing dichloromethane.

Interestingly, $Rh_2(OOCCH_3)_4$,[3a] $Rh_2(OOCC_3F_7)_4$, $Rh_2(HNOCCH_3)_4$,[10] and catalysts **1** and **2** showed very similar regioselectivities in the decomposition of diazo compound **4**, indicating no differential ligand effects in this case. Likewise, the same behavior was found in the transformation of diazo **5**. This substrate, which offered the possibility of secondary aliphatic and benzylic C−H bonds, gave a similar ratio for products **12** and **13** (close to 70:30) (Scheme 1) when $Rh_2(OOCCH_3)_4$ and **2d$_1$** were used.

Catalytic Reactions of α-Diazo Ketones. Competition between tertiary C−H and secondary C−H bonds was studied in α-diazo ketone **8**. Thus, addition of $Rh_2(OOCCH_3)_4$ to a solution containing **8** resulted in the formation of 4,4-dimethyl-2-propylcyclopentanone (**14**) and 4-methyl-2-(2-methylpropyl)cyclopentanone (**15**)[11] in high yield (99%). The ratio of tertiary to secondary C−H insertion products was 79/21 (Table 2).

The doubly metalated complex **1a$_1$** was both reactive and very selective, yielding ketone **14** as the only product. Catalyst **1d$_1$**, having a less basic phosphine, $P(C_6H_5)_2(C_6F_5)$, showed slightly decreased reactivity and selectivity. Analogous catalysts with perfluorobutyrate ligands, **1a$_2$** and **1d$_2$**, showed a considerable reduction in regioselectivity. High ligand dependence was observed for mono metalated compounds. While compound **2a$_1$** was not effective, **2a$_2$**, with more electrophilic carboxylates (perfluorobutyrates), showed good efficiency but low selectivity (**14**/**15**; 65/35). The best catalytic behavior for monometalated compounds was observed for catalysts **2d$_1$**, which led to 79% yield in cyclization products with very good regioselectivity (**14**/**15**, 92/8). On the other hand, the doubly metalated rhodium compound **3a$_1$** reacted with **8** but no C−H insertion products were observed. $Rh_2(HNOCCH_3)_4$ has also shown a selectivity similar to that of **1a$_1$**.[10]

Competition between secondary aliphatic and secondary benzylic C−H insertion was studied with α-diazo ketone **9**. $Rh_2(OOCCH_3)_4$ led to an 85% yield of C−H insertion products with low selectivity (Table 3). When the doubly metalated **1a$_1$** was used, the yield was low (55% yield) without a significant increase in selectivity. The highest yields of C−H insertion products were

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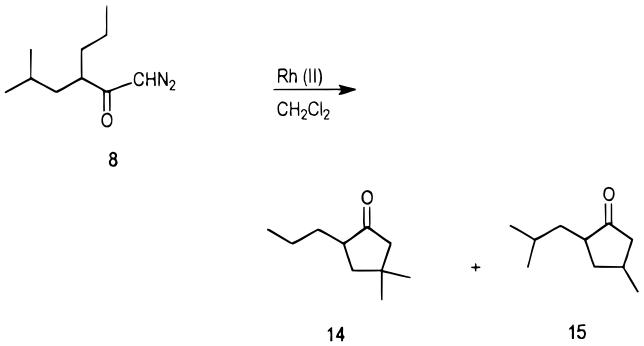
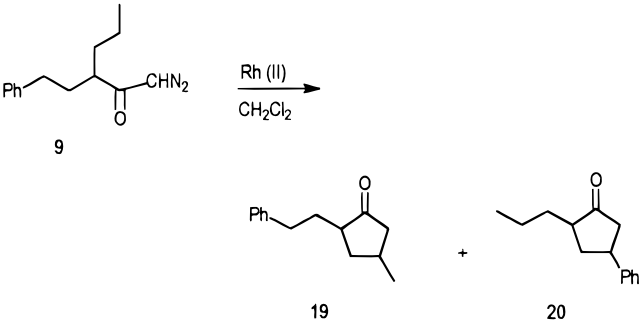
(9) For an overview of diazo transfer chemistry, see: Regitz, M.; Mass, G. *Diazo Compounds: Properties and Synthesis*; Academic Press: Orlando, FL, 1986.
(10) This experiment was suggested by a reviewer.
(11) The preparation of compound **15** was reported by: Ruecker, G.; Baslas, R. K. *Planta Med*. **1974**, *25*, 361−365.

Table 2. Tertiary Aliphatic C−H Insertion vs Secondary Aliphatic C−H Insertion



catalyst	C−H insertion yield (%)	rel ratio tertiary C−H (**14**)	rel ratio secondary C−H (**15**)
$Rh_2(OCOCH_3)_4$	99	79	21
$Rh_2(HNOCCH_3)_4$	99	100	0
1a$_1$	99	100	0
1d$_1$	91	93	7
1a$_2$	99	70	30
1d$_2$	94	64	31
2a$_1$	0		
2d$_1$	79	92	8
2a$_2$	89	65	35
3a$_1$	0		

Table 3. Secondary Aliphatic C−H Insertion *vs* Secondary Benzylic C−H Insertion



catalyst	C−H insertion yield (%)	rel ratio aliphatic secondary C−H (**19**)	rel ratio benzylic secondary C−H (**20**)
$Rh_2(OOCCH_3)_4$	85	56	44
1a$_1$	55	62	38
1a$_2$	99	60	40
1d$_2$	99	66	34
2a$_1$	52	50	50
2d$_1$	71	58	42

obtained with the more electrophilic catalysts such as **1a$_2$**, with perfluorobutyrate as carboxylate ligand, or **1d$_2$**, with $P(C_6H_5)_2(C_6F_5)$ and perfluorobutyrate as ligands. Compounds of type **2** did not show improved reactivity or selectivity in this reaction (Table 3).

Discussion

The results described above suggest that steric effects play a significant role in the reactivity of the doubly metalated compounds **1**. For example, compound **4** did not react with **1a$_1$** or **1a$_2$** but did react with the less hindered analogues **1b$_1$** and **1c$_1$**. Significantly, **1a$_1$** can transform the less sterically demanding α-diazo ketone **8**.

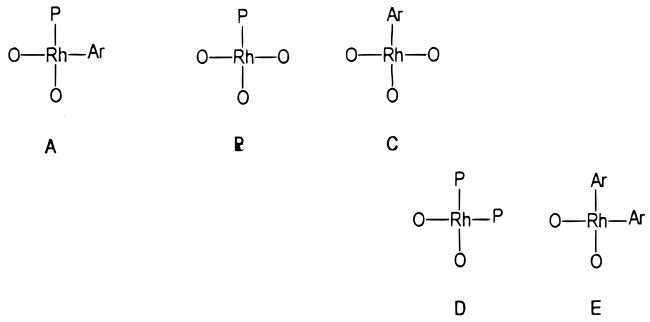


Figure 4.

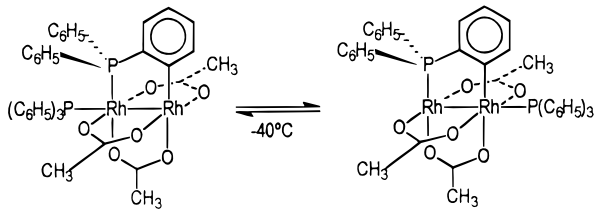


Figure 5.

While complexes of type **1** have a symmetric structure, offering two equivalent axial positions (**A**) for interaction with a diazo compound, those of types **2** and **3** have two different ligand environments at each axial position (**B**, **C** and **D**, **E**, respectively) (Figure 4). Previous variable-temperature ^{31}P NMR studies[12] on the **2a$_1$**/$P(C_6H_5)_3$ system gave information about the relative coordinating ability in monometalated compounds. These studies confirmed[12] that both axial sites are suitable for coordination, and two monoadducts in equilibrium have been spectroscopically detected. At room temperature, coordination of the phosphine at the less hindered site **C** is more favorable. However, at low temperature (−40 °C), site **B** is favored (Figure 5). The question of which of the two axial sites of the catalysts **2** is operating in diazo compound transformation is unknown. That the product distribution in the reaction of **8** depends on the substitution on the phosphorus atom is the only evidence supporting that coordination site **B**, more influenced by the nature of the phosphine, could be the reactive center.

In the case of the doubly metalated compound **3a$_1$**, prelimminary results show that this compound is not a promising catalyst with this type of substrate. This may be due to steric hindrance of site **D** (RhP_2O_2) or to low reactivity of site **E** (RhO_2C_2).

The tertiary/secondary C−H insertion ratios found with **4** reacting with catalysts **1** and **2** were different from the statistical 1/2 ratio based on the number of available carbon−hydrogen bonds of each type. This suggests that C−H insertion occurs from an intermediate metal carbene rather than from a free carbene. The very low effect of the ancillary ligand on the product ratio suggests an early transition state for these insertion reactions, as the presence of two electron-withdrawing groups (OOCR and COR) leads to a very reactive carbenoid. This behavior has been observed with other α-diazo β-keto esters.[4c] In the decomposition of the α-diazo ketone **8**, the ligand effect on the selectivity was evident, and compounds with acetates were more selective than those with perfluorobutyrate groups.

(12) Borrachero, M. V.; Estevan, F.; Lahuerta, P.; Payá, J.; Peris, E. *Polyhedron* **1993**, *13*, 1715.

As expected, diazo ketone **9**, with only secondary C−H bonds available for insertion, was less reactive than diazo ketone **8**, which possess a tertiary C−H bond (compare results for $Rh_2(OOCCH_3)_4$ and doubly metalated **1a$_1$** in Tables 2 and 3). However, excellent yields of ca. 99% were obtained when more electrophilic rhodium complexes such as **1a$_2$** and **1d$_2$** were used. With respect to regioselectivity, only a slight improvement over the use of $Rh_2(OOCCH_3)_4$ was obtained with dimetalated catalysts **1**.

Conclusions

A series of ortho-metalated rhodium(II) complexes with structures **1**−**3** were tested in C−H insertion reactions for two different types of α-diazo compounds. The best results were obtained with doubly metalated Rh(II) complexes **1** having a head-to-tail configuration. Their reactivity and selectivity can be modulated to a great extent by changing either the carboxylates or the substituents on the phosphine. In our experiments monometalated complexes **2** proved to be less selective. Doubly metalated **3a$_1$**, with a head-to-head configuration, is unreactive.

Experimental Section

General Procedures. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC-200 FT spectrometer as solutions in $CDCl_3$ unless specified otherwise. ^{19}F NMR spectra were determined on a Bruker AC-250 FT spectrometer. Chemical shifts are reported in ppm. The coupling constants (*J*) are in hertz (Hz). All compounds of type **1** show ^{31}P NMR spectra corresponding to AA'XX' systems. The infrared (IR) spectra were determined on a Perkin-Elmer spectrometer and are reported in reciprocal centimeters (cm^{-1}) in CH_2Cl_2. Elemental analysis was provided by the Centro Microanalisis Elemental Universidad Complutense de Madrid. Column chromatography was performed on silica gel (70−230 mesh). Solvents mixtures are volume/volume mixtures. Organic chemicals were purchased from Aldrich Chemical Co. α-Diazo *β*-keto esters **4** and **5** were prepared as reported previously.[3a] $Rh_2(OOCCH_3)_3(MeOH)_2$ and complexes **1a$_1$**,[6b,7] **1b$_1$**,[5b] **1c$_1$**,[5b] **1a$_2$**,[5b] **2a$_1$**,[6b] **2b$_1$**,[12] **2e$_1$**,[13] **2f$_1$**,[14] and **3a$_1$**[6b] were prepared according to literature methods. THF was distilled from sodium/benzophenone under argon prior to use. CH_2Cl_2 was distilled from CaH_2 under argon immediately before use. All reactions were carried out in flame-dried glassware under an argon atmosphere.

Synthesis of $Rh_2(OOCCH_3)_2[(C_6H_4)P(C_6H_5)(C_6F_5)]_2\cdot 2H_2O$ (1d$_1$). $Rh_2(OOCCH_3)_3[(C_6H_4)P(C_6H_5)(C_6F_5)]\cdot 2H_2O$ (**2d$_1$**; 300 mg; 0.389 mmol) and $P(C_6H_5)_2(C_6F_5)$ (164 mg, 0.467 mmol) were dissolved in 30 mL of degassed $CHCl_3$. After the mixture was stirred for 10 min, 10 mL of acetic acid was added and the mixture was irradiated for 3 h. The resulting solution was evaporated to dryness under vacuum, and the residue was transferred to a column chromatograph (2 × 15 cm, silica gel (70−230 mesh)/hexane); the column was washed with acetone, eluting a single band that was concentrated and transferred to a new column (2 × 30 cm, silica gel (70−230 mesh)/hexane). The column was washed with hexane/acetone (5:1) and afterwards was eluted with hexane/ethyl acetate (4:3), giving a pink band that was collected and was concentrated to dryness. Crystallization from ethyl acetate/hexane/CH_2Cl_2 mixtures gave 202 mg (49% yield) of $Rh_2(OOCCH_3)_2[(C_6H_4)P(C_6H_5)(C_6F_5)]_2\cdot 2H_2O$ (**1d$_1$**). NMR spectra ($CDCl_3$): $^{31}P\{^1H\}$ δ 14.5 (dd, $^1J_{Rh-P}$ = 173.3 Hz, $^2J_{Rh-P}$ = 9.5 Hz), 17.4 (dd, $^1J_{Rh-P}$ = 175.3 Hz, $^2J_{Rh-P}$ = 7.4 Hz); $^{13}C\{^1H\}$ δ 22.8 (s, CH_3, bridging acetate), 23.3 (s, CH_3, bridging acetate), 123.2 (s, aromatic), 128.1 (d, *J* = 10 Hz, aromatic), 128.4 (d, *J* = 10 Hz, aromatic), 129.0 (s, aromatic), 129.6 (s, aromatic), 130.5 (s, aromatic), 130.8 (s, aromatic), 131.0 (s, aromatic), 133.0 (s, aromatic), 133.9 (d, *J* = 10 Hz, aromatic), 134.4 (s, aromatic), 135.5 (d, *J* = 12 Hz, aromatic), 136.9 (s, aromatic), 138.0 (d, *J* = 250 Hz, aromatic), 138.2 (s, aromatic), 139.4 (s, aromatic), 147.5 (d, *J* = 248 Hz, aromatic), 161.6 (m, Rh−C), 162.4 (m, Rh−C), 182.4 (s, COO), 182.9 (s, COO); $^{19}F\{^1H\}$ δ −162.4 (m, 2F meta), −160.9 (m, 2F meta), −151.2 (t, 1F para), −150.5 (t, 1F para), −126.6 (b, 2F ortho), −120.5 (b, 2F ortho). Anal. Calcd (found) for $C_{40}H_{28}F_{10}O_6P_2Rh_2$: C, 45.22 (45.08); H, 2.66 (2.83).

Synthesis of $Rh_2(OOCC_3F_7)_2[(C_6H_4)P(C_6H_5)(C_6F_5)]_2\cdot 2H_2O$ (1d$_2$). To 100 mg of $Rh_2(OOCCH_3)_2[(C_6H_4)P(C_6H_5)(C_6F_5)]_2\cdot 2H_2O$ (**1d$_1$**) in 20 mL of $CHCl_3$ was added 2 mL of heptafluorobutyric acid with vigorous stirring. The solution was stirred for 48 h at room temperature and was monitored until the substitution of bridging acetate ligands was completed. The solution was evaporated under reduced pressure, and the residue was dissolved in CH_2Cl_2/hexane and was chromatographed on silica gel. Elution with hexane/acetone (20:1) separated a blue band that was collected. The solvent was evaporated, and the product was crystallized from CH_2Cl_2/hexane. Yield: 104 mg (81%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of this solution. NMR spectra ($CDCl_3$): ^1H δ 2.2 (br, H_2O), 6.2−8.0 (m, 18H, aromatics); $^{31}P\{^1H\}$ δ 13.5 (d, $^1J_{Rh-P}$ = 176.9 Hz, $^2J_{Rh-P}$ = 27.2 Hz); $^{13}C\{^1H\}$ δ 137.7 (d, *J* = 8 Hz, aromatic), 142.4 (s, aromatic), 142.6 (s, aromatic), 142.8 (s, aromatic), 143.9 (d, *J* = 24 Hz, aromatic), 145.4 (d, *J* = 22 Hz, aromatic), 147.7 (s, aromatic), 148.2 (s, aromatic), 148.6 (s, aromatic), 148.8 (s, aromatic), 150.0 (d, *J* = 13 Hz, aromatic), 152.2 (s, aromatic), 161.3 (d, *J* = 256 Hz, aromatic), 172.0 (m), 182.0 (s, COO), 183.0 (s, COO); $^{19}F\{^1H\}$ δ −161.0 (s, 2F), −160.3 (s, 2F), −149.7 (m, 2F), −126.9 (m, 6F), −123.2 (s, 2F), −117.5 (m, 4F), −81.1 (b, 6F). Anal. Calcd (found) for $C_{44}H_{22}F_{24}O_6P_2Rh_2$: C, 38.56 (38.85); H, 1.61 (1.96).

Synthesis of $Rh_2(OOCC_3F_7)_3[(C_6H_4)P(C_6H_5)_2]\cdot 2CH_3COCH_3$ (2a$_2$). To 200 mg (0.261 mmol) of $Rh_2(OOCCH_3)_3[(C_6H_4)P(C_6H_5)_2]\cdot 2HOOCCH_3$ in 15 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 the reaction was monitored 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; 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 blue solid, which was filtered off and dried under vacuum. Yield: 254 mg (85%) of $Rh_2(OOCC_3F_7)_3[(C_6H_4)P(C_6H_5)_2]\cdot 2CH_3COCH_3$. NMR spectra ($CDCl_3$): ^1H δ 2.4 (s, CH_3, acetone), 6.8−8.2 (m, 18H, aromatics); $^{31}P\{^1H\}$ δ 15.8 (d, $^1J_{Rh-P}$ = 131.8 Hz); $^{13}C\{^1H\}$ δ 31.1 (s, acetone), 123.8 (d, *J* = 8 Hz, aromatic), 128.5 (d, *J* = 10 Hz, aromatic), 129.2 (d, *J* = 17 Hz, aromatic), 129.9 (s, aromatic), 131.0 (s, aromatic), 132.2 (s, aromatic), 133.4 (s, aromatic), 133.6 (s, aromatic), 137.7 (d, *J* = 6 Hz, aromatic), 141.9 (s, aromatic), 143.0 (s, aromatic), 156.5 (m, R−C), 174.0 (s, OOC), 174.5 (s, OOC) 213.9 (s, OC); $^{19}F\{^1H\}$ δ −127.5 (t, CF_3, trans heptafluorobutyrate bridging), −127.4 (t, CF_3, cis heptafluorobutyrate bridging), −118.3 to −118.1 (m, CF_2, trans heptaflurobutyrate bridging), −117.9 to −118 (m, CF_2, *trans* heptafluorobutyrate bridging), −81.3 to −81.2 (t, CF_2, cis heptafluorobutyrate bridging), −81.1 to −81 (t, CF_2, heptafluorobutyrate bridging). Anal. Calcd (found) for $C_{36}H_{26}O_8F_{21}PRh_2$: C, 35.37 (34.97); H, 2.14 (2.20).

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Synthesis of $Rh_2(OOCCH_3)_3[(C_6H_4)P(C_6H_5)(C_6F_5)]\cdot 2H_2O$ ($2d_1$). $Rh_2(OOCCH_3)_4\cdot 2MeOH$ (250 mg; 0.494 mmol) and $P(C_6H_5)_2(C_6F_5)$ (208.8 mg; 0.593 mmol) were stirred for 10 min in 30 mL of degassed toluene. After addition of 10 mL of acetic acid the mixture was refluxed for 2.5 h, resulting in a blue solution. After evaporation to dryness under vacuum, the crude product was chromatographed (2 × 30 cm, silica gel (70−230 mesh)/hexane). The column was first eluted with CH_2Cl_2/hexane/acetone (20:20:1), and a minor purple band was collected corresponding to the doubly metalated compound $\mathbf{1d_1}$. Further elution with CH_2Cl_2/hexane/acetone (20:20:4) gave a green band due to unreacted $Rh_2(OOCCH_3)_4$ followed by a major blue-gray band that was collected and was concentrated under reduced pressure to produce 249 mg (65%) of $Rh_2(OOCCH_3)_3[(C_6H_4)P(C_6H_5)(C_6F_5)]\cdot 2H_2O$ ($\mathbf{2d_1}$). NMR spectra (CD_3COCD_3): ^1H δ 1.21 (s, 3H, cis acetate), 1.44 (s, 3H, cis acetate), 2.1 (s, 3H, trans acetate), 2.86 (s, H_2O), 6.80 (m, 1H), 7.01 (m, 2H), 7.47 (m, 3H), 7.96 (m, 2H), 8.10 (m, 1H); $^{31}P\{^1H\}$ 18.2 (d, $^1J_{Rh-P} = 159.8$ Hz); $^{13}C\{^1H\}$ 23.2 (s, CH_3, *trans*-bridging acetate), 23.8 (m, CH_3, *cis*-bridging acetate), 122.8 (d, $J = 9$ Hz, aromatic), 128.3 (d, $J = 2$ Hz, aromatic), 129.5 (d, $J = 11$ Hz, aromatic), 131.9 (s, aromatic), 132.9 (d, $J = 49$ Hz, aromatic), 134.9 (d, $J = 12$ Hz, aromatic), 139.9 (d, $J = 16$ Hz, aromatic), 147.7 (d, $J = 260$ Hz, aromatic), 167.8 (m, Rh−C), 182.0 (s, COO), 189.2 (s, COO), 189.3 (s, COO); $^{19}F\{^1H\}$ −160.7 (m, 2F meta), −149.1 (t, 1F para), −126.6 (b, 2F ortho). Anal. Calcd (found) for $C_{24}H_{22}F_5O_8PRh_2$: C, 37.43 (37.35); H, 2.88 (2.65).

1-Diazo-5-methyl-3-propyl-2-hexanone (8). A flame-dried, one-necked flask equipped with an argon bulb was charged with methyl 6-methyl-3-oxo-4-propylheptanoate (1.35 g, 6.3 mmol), methanesulfonyl azide (0.84 g, 6.9 mmol, 1.1 equiv), and CH_3CN (14 mL). To this solution was added triethylamine (1.74 mL, 12.5 mmol). The reaction took about 3 h at room temperature. The mixture was diluted with 10% aqueous NaOH, stirred overnight, and extracted with ether. The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo. The residual oil was chromatographed on 50 g of silica gel with hexane/ethyl acetate (20:1) to give α-diazo ketone **8** as a yellow oil: 0.98 g (85%). R_f (10% ethyl acetate/hexane): 0.49. ^1H NMR ($CDCl_3$): δ 0.9 (m, 9H), 1.1−1.7 (m, 7H), 2.4 (bb, 1H), 5.2 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 14.1 (q), 20.6 (t), 22.2 (q), 23.1 (q), 25.9 (d), 35.4 (t), 41.9 (t), 48.9 (d), 54.1 (d), 199.1 (s). IR (neat): 2861 (CHN_2), 2100 ($C{=}N_2$), 1635 ($C{=}O$) cm^{-1}. HRMS (CI): calcd for $C_{10}H_{19}N_2O$ 183.1497, found 183.1494. Anal. Calcd (found) for $C_{10}H_{18}N_2$: C, 65.88 (65.93); H, 9.96 (9.70).

1-Diazo-5-phenyl-3-propyl-2-pentanone (9). α-Diazo ketone **9** was prepared using the same procedure as indicated above for compound **8**; diazo transfer was performed on methyl 3-oxo-6-phenyl-4-propylhexanoate (0.895 g, 3.4 mmol). The residual oil was chromatographed to give **9** as a yellow oil: 0.698 mg (89%). R_f (10% ethyl acetate/hexane): 0.55. ^1H NMR ($CDCl_3$): δ 0.9 (t, $J = 7.2$ Hz), 1.3−2.0 (m, 6H), 2.3 (bb, 1H), 2.5 (m, 2H), 5.1 (s, 1H), 7.1−7.3 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 14.1 (q), 20.5 (t), 33.5 (t), 34.1 (t), 34.9 (t), 50.2 (d), 54.4 (d), 125.9 (d), 128.3 (d), 141.7 (s), 198.4 (s). IR (neat): 2861 (CHN_2), 2100 ($C{=}N_2$), 1635 ($C{=}O$) cm^{-1}. HRMS (CI): calcd for $C_{14}H_{19}N_2O$ 231.1497, found 231.1491.

Dirhodium Complex Catalyzed Reactions of Diazo Compounds. The appropiate diazo compound (0.5 mmol) was disolved in dry CH_2Cl_2 under an argon atmosphere. The rhodium compound (0.005 mmol) was added to the solution, and the mixture was heated at reflux temperature for 1 h. The material was directly concentrated in vacuo, and the residue was analyzed by ^1H and ^{13}C NMR. In some experiments the products were purified by column chromatography (hexane/ethyl acetate 20/1). Data for compounds **14**, **19** and **20** are as follows.

4,4-Dimethyl-2-propylcyclopentanone (14): R_f (10% ethyl acetate/hexane) 0.55; ^1H NMR ($CDCl_3$) δ 0.9 (m, 3H), 1.0 (s, 3H), 1.2 (s, 3H), 1.2−1.9 (m, 6H), 1.9−2.2 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 13.9 (q), 20.7 (t), 27.8 (q), 29.7 (q), 32.7 (t), 34.0 (s), 43.9 (t), 47.9 (d), 53.2 (t), 221.8 (s); IR (neat) 1730 ($C{=}O$) cm^{-1}. HRMS (CI) calcd for $C_{10}H_{18}O$ 154.1430, found 154.1436. Anal. Calcd (found) for $C_{10}H_{18}O$: C, 77.85 (77.80); H, 11.77 (11.70).

2-(Phenylethyl)-4-methylcyclopentanone (19): R_f (10% ethyl acetate/hexane) 0.50; ^1H NMR ($CDCl_3$) δ 1.2 (d, $J = 6$ Hz, 3H), 1.4−2.8 (m, 10H), 7.1−7.4 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 20.3 (q), 29.7 (d), 31.4 (t), 33.6 (t), 38.6 (t), 46.8 (t), 50.1 (d), 126.1 (d), 128.6 (d), 141.6 (s), 220.8 (s); IR (neat) 1730 ($C{=}O$) cm^{-1}; HRMS (CI) calcd for $C_{14}H_{18}O$ 202.1358, found 202.1414.

4-Phenyl-2-propylcyclopentanone (20): R_f (10% ethyl acetate/hexane) 0.43; ^1H NMR ($CDCl_3$) δ 0.9 (t, $J = 7$ Hz, 3H), 1.2−2.8 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 14.0 (q), 20.7 (t), 31.7 (t), 37.9 (t), 40.1 (d), 45.9 (t), 50.6 (d), 126.7 (d), 128.4 (d), 129.7 (d), 143.1 (s), 219.6 (s); IR (neat) 1730 ($C{=}O$) cm^{-1}; HRMS (CI) calcd for $C_{14}H_{18}O$ 202.1358, found 202.1414.

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