Organometallic Ruthenium Complexes: Application in the Olefination of Carbonyl Compounds

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Ruthenium compounds of general formula $Cp'RuX(PR_2R')_2$ ($Cp' = \eta^5$-C_5H_5 (Cp), η^5-C_9H_7 (Ind), η^5-$C_5(CH_3)_5$ (Cp*); X = Cl, $CF_3C(O)O$; R = C_6H_5 (Ph), $C_6H_4(CH_3)$ (*m*-tolyl); R′ = C_6H_5, C_6H_{11} (Cy), $C_6H_4(CH_3)$ (*m*-tolyl, *o*-tolyl)) are examined as catalysts for the aldehyde olefination starting from diazo compounds, phosphanes, and aldehydes. $Cp^*RuCl(PPh_3)_2$ is highly active for the olefination of several aldehydes, displaying a very high *E*-selectivity, as well as for ketone olefination (with benzoic acid as cocatalyst). The reaction's mechanism is substantiated by the isolation of a catalytic active reaction species, namely, a mixed carbene/phosphane ruthenium complex, $Cp^*RuCl(=CHCO_2Et)(PPh_3)$ (**8**). Spectroscopic studies reveal that the latter compound reacts with PPh_3 to produce the phosphorus ylide $Ph_3P=CHCO_2$-Et, which further reacts with the aldehyde to produce the olefin.

Introduction

The olefination of carbonyl compounds, namely, the transformation of a carbonyl group into a carbon−carbon double bond, is one of the most convenient and universal methods for the preparation of alkenes.[1] The catalytic alternative to the classic Wittig reaction has proven to be quite promising, avoiding the need for stepwise generation of phosphorus ylides under basic conditions. Furthermore, the use of transition metal complexes as catalysts also opens the possibility of efficient asymmetric olefination.[2] Accordingly, several catalytic aldehyde and ketone olefination systems have been reported based on Ru,[3] Re,[4] Rh,[5] Fe,[6] and Co[7] complexes.

Compounds of the general formula $Cp'RuX(PR_3)_2$ have found widespread applications in catalysis. The ease of synthesis, the wide array of ligands available to coordinate with the metal center, and their general high stabilities make them a versatile and promising class of catalysts. Baratta et al.[8] studied the decomposition of ethyl diazoacetate (EDA) with this type of catalysts, presenting evidence for $PPh_3=CHCO_2Et$ formation in the presence of triphenylphosphane (PPh_3). This prompted us to study these compounds in the aldehyde olefination reaction as catalysts for phosphorus ylide generation. In a preliminary communication, we were able to confirm the activity of organometallic ruthenium complexes, by using $Cp'RuX(PR_2R')_2$ as efficient catalysts for the olefination of activated aldehydes.[9]

In the present study we explore the activity of these complexes more broadly, including the olefination reaction of nonactivated aldehydes and ketones. Investigations on the influence of changing the nature of the reaction components and conditions on catalytic activity are performed, in order to attempt establishing a better understanding of the olefination reaction catalyzed by $Cp'RuX(PR_2R')_2$ complexes. A comprehensive study of the reaction mechanism confirms the presence of a catalytically active mixed phosphane/carbene Ru species, $Cp^*RuCl(=CHCO_2Et)(PPh_3)$. Subsequent NMR spectrospic studies confirm the identity of the latter compound formed during the catalytic cycle and elucidate the way substrates and catalysts react to produce the desired olefin.

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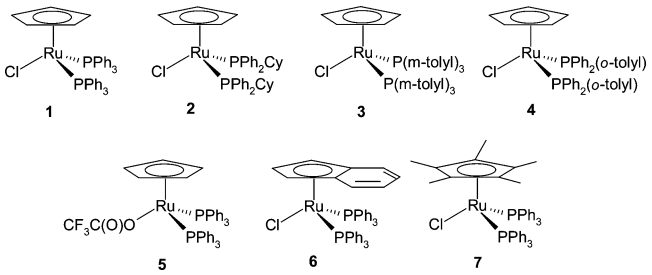
Chart 1



Experimental Section

General Information. All reactions were carried out under an inert gas atmosphere, using standard Schlenk techniques. Solvents were dried following standard procedures and kept under argon. THF was dried over Na/benzophenone and distilled before use. *n*-Hexane, *n*-pentane, *n*-heptane, ethanol, and toluene were dried over Na and stored over 4 Å molecular sieves.

Compounds **1**,[10] **2**,[8] **3**,[8] **4**,[8] **6**,[11] and **7**[12] (Chart 1) were synthesized following literature procedures.

NMR measurements were made with a 400 MHz Bruker Avance DPX-400 and a 400 MHz Jeol JNM-GX 400. Deuterated solvents were dried under molecular sieves and degassed prior to use.

Syntheses and Catalysis. CpRu(OC(O)CF$_3$)(PPh$_3$)$_2$ (5). CpRuCl(PPh$_3$)$_2$ (0.298 g, 0.41 mmol) and AgOC(O)CF$_3$ (0.1 g, 0.45 mol) were dissolved in 20 mL of THF. The mixture was stirred for 16 h under exclusion of light. The solution was slowly filtered followed by partial removal of the volatiles under vacuum. Addition of 15 mL of *n*-heptane and stirring afforded a yellow precipitate after a few minutes. The solution was filtered and the CpRu(OC(O)CF$_3$)(PPh$_3$)$_2$ (0.244 g, 74%) was washed twice with *n*-heptane. Anal. Calcd for $C_{43}H_{35}O_2F_3P_2Ru$: C, 64.26; H, 4.39. Found: C, 63.97; H, 4.39. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22−7.08 (30 H, m, C_6H_5), 4.30 (5 H, s, C_5H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1 (1 C, weak q, ^2J(F,C) 35.1 Hz, O*C*(O)CF$_3$), 137.3 (1 C, t, C_6H_5), 133.5 (2 C, t, C_6H_5), 129.0 (1 C, s, C_6H_5), 127.7 (2 C, m, C_6H_5), 113.2 (1 C, weak t, ^1J(F,C) 292.7 Hz, CF_3), 79.1 (5 C, s, C_5H_5). ^{31}P NMR (162 MHz, $CDCl_3$, standard 85% H_3PO_4): δ 41.1. ^{19}F NMR (376 MHz, $CDCl_3$, standard $CFCl_3$): δ −75.7.

Cp*RuCl(=CHCO$_2$Et)(PPh$_3$) (8). Cp*RuCl(PPh$_3$)$_2$ (0.305 g, 0.38 mmol) was dissolved in dry CH_2Cl_2 (30 cm^3) and cooled to −12 °C in a dry ice/isopropanol bath. Ethyldiazoacetate (0.217 g, 1.9 mmol) was added to the solution, and the mixture was stirred between −12 and −6 °C until the evolution of nitrogen ceased (which occurred usually within ca. 2 h). The solvent was concentrated in vacuum to approximately 5 cm^3, maintaining the temperature below −10 °C. The solution was cooled to −30 °C, and cold *n*-hexane (ca. 40 cm^3 at −30 °C) was added through a cannula to the solution. Stirring the solution produced a green precipitate, which was filtered and dried under vacuum. The product was dissolved in cold, dry toluene (2 cm^3 at −30 °C) and precipitated by adding cold, dry *n*-hexane (50 cm^3 at −30 °C). The precipitate (0.162 g, 68%) was dried in vacuum. For characterization the product was recrystallized from toluene/*n*-hexane (2/40 cm^3) and dried under vacuum for 2 h. Anal. Calcd for $C_{32}H_{36}O_2ClPRu$: C, 61.98; H, 5.85. Found: C, 62.74; H, 5.60. ^{1}H NMR (400 MHz, CD_2Cl_2, −20 °C): δ 14.90 (1 H, d, ^3J(H, P) 12.26 Hz, CH), 7.88−7.15 (15 H, br m, C_6H_5), 3.99 (2 H, q, ^3J(H,H) 7.35 Hz, CH_2), 1.30 (15 H, s, C_5Me_5), 1.26 (3 H, t, ^3J(H,H) 7.35 Hz, CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2, −20 °C): δ 264.5 (1 C, d, ^2J(C,P) 14.8 Hz, Ru=*C*HCO$_2$Et), 182.9 (1 C, s, *C*O), 135.7−127.7 (6 C, br m, C_6H_5), 104.0 (5 C, s, C_5Me_5), 59.1 (1 C, s, CH_2CH_3), 13.8 (1 C, s, CH_2CH_3), 8.8 (5 C, s, C_5Me_5). ^{31}P NMR (162 MHz, CD_2Cl_2, −20 °C, standard 85% H_3PO_4): δ 49.6.

Ph$_3$P=N−N=CHCO$_2$Et (Phosphazine XIII).[13] PPh$_3$ (1.311 g, 5 mmol) was dissolved in 20 cm^3 of *n*-pentane. Ethyl diazoacetate (0.571 g, 0.5 mmol) was added to the mixture, and the solution was stirred for 8 h. The resulting solid was filtered and washed three times with cold pentane, producing a white powder (1.675 g, 89%). Anal. Calcd for $C_{22}H_{21}N_2O_2P$: C, 70.20; H, 5.62; N, 7.44. Found: C, 69.43; H, 5.74; N, 7.12. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (1 H, d, ^3J(H,P) 2.0 Hz, N=CH), 7.68−7.46 (15 H, m, C_6H_5), 4.19 (2 H, q, ^3J(H,H) 7.20 Hz, CH_2), 1.26 (3 H, t, ^3J(H,H) 7.20 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4 (1 C, s, C(O)), 138.1 (1 C, d, J(C,P) 47.6 Hz, N=CH), 133.5 (6 C, d, *o*-C_6H_5), 132.5 (3 C, s, *p*-C_6H_5), 128.7 (6 C, t, *m*-C_6H_5), 127.7 (3 C, d, J(C,P) 93.8 Hz, C−P), 59.7 (1 C, t, CH_2), 14.4 (1 C, q, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$, standard 85% H_3PO_4): δ 22.7.

General Procedure for Aldehyde Olefination. Aldehyde (2 mmol), PPh$_3$ (0.577 g, 2.2 mmol), and Cp′RuCl(PR$_2$R′)$_2$ (0.040 to 0.012 mmol) were dissolved in the appropriate solvent (10 cm^3) and heated (details concerning solvent and the reaction temperature of each run are described in Table 1). Ethyl diazoacetate (0.274 g, 2.4 mmol) was added in one portion and allowed to react while monitoring the reaction progress by GC-MS. Afterward the solution was cooled to room temperature and the solvent removed under reduced pressure. The residue was taken into a small amount of toluene and chromatographed over a silica gel column with *n*-hexane/ethyl acetate (20:1), affording the olefin(s). For 4-dimethylaminobenzaldehyde the yield was determined by GC-MS using a previously recorded calibration curve ($R^2 > 0.999$).

General Procedure for Ketone Olefination. Ketone (2 mmol), PPh$_3$ (0.577 g, 2.2 mmol), the ruthenium complex Cp*RuCl(PPh$_3$)$_2$ (0.016 g, 0.020 mmol), and benzoic acid (0.122 g, 1 mmol) were dissolved in the appropriate solvent (10 cm^3) and heated (details concerning solvent and the reaction temperature of each run are described in Table 2). Ethyldiazoacetate (0.274 g, 2.4 mmol) was added in one portion and allowed to react while monitoring the reaction progress by GC-MS. Afterward the solution was cooled to room temperature and the solvent removed under reduced pressure. The residue was taken into a small amount of toluene and chromatographed over a silica gel column with *n*-hexane/ethyl acetate (20:1), affording the olefin(s).

Mechanistic Studies. Catalysis without Aldehyde. Complex **7** (2 mg, 2.5 μmol) and PPh$_3$ (36 mg, 0.138 mmol) were dissolved in 0.6 cm^3 of CD_2Cl_2. The resulting solution was transferred via cannula to the NMR tube and cooled to −70 °C. EDA (14.3 mg, 0.125 mmol) was added and the NMR tube was kept at −70 °C until the beginning of the measurements, which were performed at RT.

Catalysis with Aldehyde. Complex **7** (2 mg, 2.5 μmol), PPh$_3$ (36 mg, 0.138 mmol), and benzaldehyde (26.5 mg, 0.25 mmol) were dissolved in 0.6 cm^3 of CD_2Cl_2. The resulting solution was transferred via cannula to the NMR tube and cooled to −70 °C. EDA (14.3 mg, 0.125 mmol) was added, and the NMR tube was kept at −70 °C until the beginning of the measurements, which were performed at RT.

Results and Discussion

Compounds **1**−**7**, CpRuCl(PPh$_3$)$_2$ (**1**), CpRuCl(PPh$_2$Cy)$_2$ (**2**), CpRuCl(P(*m*-tolyl)$_3$)$_2$ (**3**), CpRuCl(PPh$_2$(*o*-tolyl))$_2$ (**4**), CpRu(CF$_3$C(O)O)(PPh$_3$)$_2$ (**5**), IndRuCl(PPh$_3$)$_2$ (**6**), and Cp*RuCl(PPh$_3$)$_2$ (**7**) (see Chart 1), were tested for the aldehyde olefination reaction as catalysts for phosphorus ylide generation in nonbasic conditions (Scheme 1).

In the aldehyde olefination leading to α,β-unsaturated esters, both the reaction rate and *E*:*Z* selectivity have to be considered.

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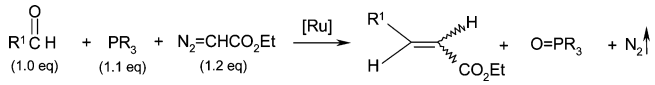
Table 1. Catalytic Aldehyde Olefination with Compounds 1−7 as Catalysts



entry	aldehyde	catalyst/phosphane	catalyst loading/% mol	yield[a]/%	time/h	*E*:*Z* ratio[b]
1	**I**	**1**/PPh_3	2	42	2	88:12
2	**I**	**2**/PPh_2Cy	2	46	2	94:6
3	**I**	**3**/P(*m*-tolyl)$_3$	2	63	2	98:2
4	**I**	**4**/PPh_2(*o*-tolyl)	2	92	2	96:4
5	**I**	**5**/PPh_3	2	29	2	87:13
6	**I**	**6**/PPh_3	1	96	1	92:8
7	**I**	**7**/PPh_3	1	98	5 min	99:1
8	**II**	**7**/PPh_3	1	97	0.5	94:6
9	**I**	Fe(TPP)Cl/PPh_3	1	97	2	92:8
10	**I**	$Cl_3ORe(PPh_3)_2$/PPh_3	1	95	2	98:2
11	**II**	**7**/PPh_3	0.6	96	2	96:4
12	**II**	Fe(TPP)Cl/PPh_3	0.6	96	2	91:9
13	**II**	$Cl_3ORe(PPh_3)_2$/PPh_3	0.6	42	2	93:7

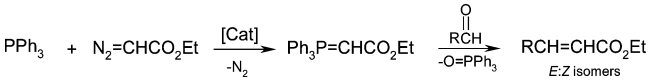
[a] Isolated yields. [b] *E*:*Z* ratios determined by GC-MS. Reaction temperature 50 °C, except entry 8, reaction conducted at 80 °C. Solvent THF, entry 8 toluene.

Table 2. Catalytic Aldehyde and Ketone Olefination with Compound 7 as Catalyst

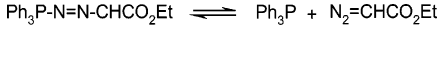
entry	aldehyde/ketone	catalyst	yield[a]/%	time/h	*E*:*Z* ratio[b]
1	**II**	7	95	3	95:5
2	**II**	7	96	0.25	84:16
3	**III**	7	61[c]	24	96:4
4	**VI**	7	92	1	97:3
5	**IV**	7	92	5	97:3
6	**V**	7	98	24	94:6
7	**III**	7[d]	98[c]	2	92:8
8	**VII**	7	85	4	88:12
9	**VIII**	7[d]	78	72	42:58
10	**IX**	7[d]	92	44	35:65
11	**X**	7[d]	57	7 days	41:59
12	**XI**	7[d]	84	24	
13	**XII**	7[d]	58	48	

[a] Isolated yields. [b] *E*:*Z* ratios determined by GC-MS. [c] Yield determined by GC-MS. [d] Benzoic acid (0.5 equiv) as cocatalyst. Solvent: toluene, except entry 2, ethanol. Temperature: 80 °C, except entry 1, RT, and entry 2, 78 °C. Catalyst loading: 1% mol of carbonyl compound.

Scheme 1

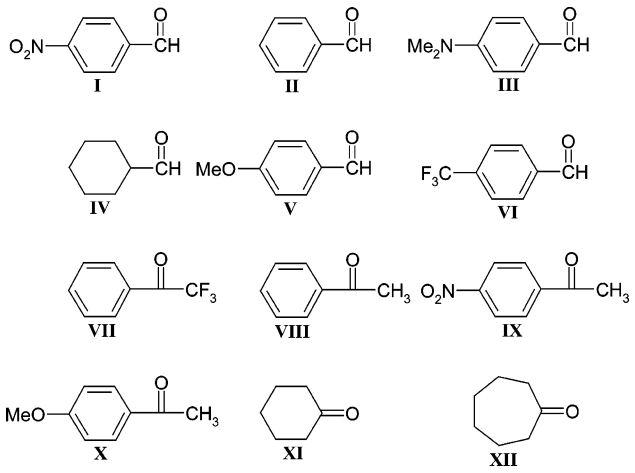


Scheme 2



Frequently, the most active catalysts present relatively low selectivities.[14] The aldehydes and ketones used as substrates are depicted in Chart 2.

Chart 2



Catalyst Optimization. Compound **1** shows a comparatively low activity in the olefination of 4-nitrobenzaldehyde (4-nba), reaching an olefin yield of 42% (Table 1, entry 1) after 2 h reaction time. Simultaneously the selectivity is rather poor, with a final *E*:*Z* ratio of 88:12.

It has been observed for several other processes that the phosphane structure has a paramount effect on the catalysts performance,[15] since it allows the fine-tuning of the metal's reactivity and selectivity. According to previous studies, for example, complexes **2**−**4**, bearing bulky phosphanes, decompose EDA at lower temperatures compared to compound **1** ligated by PPh_3.[8b] On the basis of this observation compounds **1**−**4** were tested in the aldehyde olefination reaction in this study. The use of phosphanes with high Tolman cone angles[15c] has a positive influence on the reaction outcome, since these catalysts improve both the olefin yield and the *E*-isomer selectivity. The best yield among the compounds **1**−**4** is obtained with complex **4** (entry 4), affording 92% olefin yield after 2 h reaction time, and the best selectivity with complex **3**, with a final *E*:*Z* ratio of 98:2 (entry 3). For all of these catalytic runs it is essential to use the same phosphane both as ligand and as oxygen abstractor during the reaction, since the use of PPh_3 as oxygen abstractor in combination with another phosphane as ligand rapidly ensues the replacement of (at least one of) the bulkier phosphanes and would therefore change the activity of the catalyst, turning it increasingly similar to that of compound **1** (in a control experiment with compound **4** and 4-nba, using PPh_3 as oxygen abstractor, only 63% of olefin yield was observed).

Changing the phosphane ligand of the studied complexes has a twofold influence on the catalytic reaction: (1) It changes the catalyst activity as a result of combined effects of the steric

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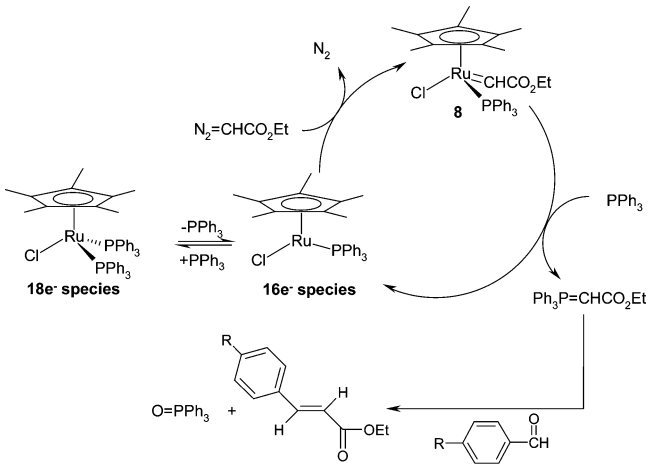
Scheme 3



bulk of the phosphanes (main factor) and their electron donation abilities; (2) the generated phosphorus ylides show different reactivity toward the aldehyde, once again, depending on both electron donor ability and bulkiness.

Bulkier phosphanes than PPh_3 are less strongly bonded to the Ru center due to their increased steric requirements,[16] and thus removal of one phosphane ligand becomes easier in complexes **2**−**4**, a key factor for triggering the catalytic cycle (see Scheme 3). On the basis of this rationalization complexes **2**−**4** should also show higher catalytic activity than PPh_3—as they in fact do.

Ylides of the type $(p\text{-R-}C_6H_4)_3P{=}CHCO_2Et$ bearing electron-donating groups R react faster with aldehydes than $Ph_3P{=}CHCO_2Et$ does.[17,18] However, bulkier ylides than $Ph_3P{=}CHCO_2Et$ such as $Ph_2(o\text{-tolyl})P{=}CHCO_2Et$ react slower with aldehydes.[18] When the electron donation of the ligands is not significantly different (both $PPh_2(o\text{-tolyl})$ and $P(m\text{-tolyl})_3$ display only slightly higher electron donation abilities than PPh_3),[19] bulkiness seems to exert a stronger effect over the ylide reactivity than the electron donation. Therefore, when it concerns the ylides' reactivity, PPh_2Cy should be the most effective ligand, followed by $PPh_2(o\text{-tolyl})$ and $P(m\text{-tolyl})_3$.

Bulkier phosphanes enable an easier formation of the phosphorus ylide, by facilitating the release of a phosphane ligand, but also produce less reactive ylides, which slow the second step. These observations emphasize the importance of the ease of phosphane release in the ylide generation, since it overcompensates, at least to a certain degree, the more sluggish second step. The results presented here show that the optimal result is found in a compromise between the ease of phosphane release from the catalyst and the reactivity of the ylide, which is accomplished in this case with $PPh_2(o\text{-tolyl})$ and complex **4**.

The increase of selectivity toward the *E*-isomer follows the trend also observed in the Wittig reaction,[18] where an increase of the ligand bulkiness leads to higher *E*:*Z* ratios. Although an eventual influence of the catalyst in the second step cannot be entirely discarded, the *E*:*Z* ratios improve directly with the bulkiness of the phosphane:[14c] $PPh_3 < PPh_2Cy < PPh_2(o\text{-tolyl}) < P(m\text{-tolyl})_3$.

The substitution of the −Cl ligand by a more electron-withdrawing group, namely, $-OC(O)CF_3$ (compound **5**), has a negative effect on the outcome of the catalytic reaction, producing only 29% yield. This is not surprising, since a more electron-poor metal withdraws more electron density from the attached phosphanes and coordinates them more strongly. The *E*:*Z* ratio is within the measurement error equal to that obtained with compound **1**.

The most striking results were obtained when instead of the cyclopentadienyl ligand bulkier ligands such as indenyl (Ind) **6** or pentamethylcyclopentadienyl (Cp*) **7** were applied. These catalysts show an enhanced activity that allows 100% conversion of 4-nba into olefin after 60 min (entry 6) and 5 min (entry 7) of reaction time, for **6** and **7**, respectively. For these catalysts it was possible to decrease the catalyst loading to 1 mol % without any activity decrease or additional side product formation. The *E*:*Z* ratios, 92:8 for **6** and 99:1 for **7**, show a substantial selectivity improvement in comparison to **1**.

On going from Cp to Ind and Cp* ligands, the catalyst activities rise in accord with the increasing bulkiness and better electron donation abilities of the ligands.[19] The increased bulkiness weakens the P−Ru bond,[16b] enabling a faster dissociation of the phosphine[21] (see Scheme 3). The increased electron donation is likely to stabilize the 16e⁻ active species and thus favor the P−Ru bond cleavage as well.

The promising results obtained with compound **7** regarding both activity and selectivity tempted us to compare its performance to other known aldehyde olefination catalysts. Fe(TPP)Cl[6c] (TPP = tetra(*p*-tolyl)porphyrin) and $Cl_3ORe(PPh_3)_2$[4h] have been tested successfully in the olefination of several aldehydes and presented the highest activities yet reported.

Three catalysts, $Cp^*RuCl(PPh_3)_2$, Fe(TPP)Cl, and $Cl_3ORe(PPh_3)_2$, were tested in the olefination of 4-nba under the same reaction conditions, namely, at 50 °C in THF, using 1 mol % catalyst loading. All three compounds reach quantitative yield within 2 h of reaction time. The *E*:*Z* ratios are 99:1, 92:8, and 98:2, and the TOFs (determined after 5 min reaction time) 900, 890, and 1200 h^{-1}, respectively. With a catalyst loading of 0.1% mol none of the catalysts reach quantitative yield. The TOFs are 1600, 3680, and 1230 h^{-1}, respectively. The differences in initial activity between these catalysts at low concentrations are explained by the mechanism depicted in Scheme 3. The huge excess of free PPh_3 when low concentrations of catalyst **7** are applied (more than 1000 times excess for a 0.1 mol % loading) shifts the equilibrium strongly toward the inactive 18e⁻ species, reducing greatly the catalytic activity. This effect very likely also occurs for $Cl_3ORe(PPh_3)_2$, while Fe(TPP)Cl, having no PPh_3 ligands, is devoid of any PPh_3 inhibition, and so maintains high activity even at low concentrations. Also in the olefination of benzaldehyde $Cp^*RuCl(PPh_3)_2$ affords the highest *E*-isomer selectivity for this set of catalysts (entries 12 to 14).

None of the tested catalysts produce any olefin product when we attempted aldehyde olefination with diethyl diazomalonate in place of ethyl diazoacetate. By ^{31}P NMR spectroscopy the formation of the corresponding phosphorus ylide, $Ph_3P{=}C(CO_2Et)_2$, can be observed, but this ylide is unable to react further with 4-nba. This strongly suggests that this class of complexes catalyzes phosphorus ylide formation from phosphanes and

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diazo compounds, but not the further reaction of ylide to the desired olefin.

Through careful tuning of the ligands coordinating to the metal, it was possible to turn a medium-performance catalyst (compound **1**) into a good catalyst (compound **7**) combining fast reaction rates with high *E*-olefin selectivity. On the basis of these results, complex **7** was tested for the olefination of several other aldehydes and also ketones as described below.

Aldehyde and Ketone Olefination with Compound 7. Before testing its activity toward different aldehydes and ketones, studies were carried out on the optimization of the reaction conditions. Taking the olefination of benzaldehyde as the model reaction, it was shown that the best results are obtained at 80 °C in toluene (Table 1, entry 8); the reaction is—not surprisingly—much faster under these conditions than at 50 °C in THF (Table 1, entry 12). The same reaction in toluene at room temperature (Table 2, entry 1) reaches quantitative yield after 3 h, also with an *E*:*Z* ratio of 95:5. Using ethanol as solvent (Table 2, entry 2), the reaction is completed after 25 min, but the selectivity decreases notably to a final *E*:*Z* ratio of 84:16.

As it seems, the solvent influences both the reaction rate and selectivity. While in THF and toluene the selectivities are similar, the reaction time can be considerably shortened in toluene due to its higher boiling point. In ethanol the reaction is slightly faster than in toluene, but the loss in selectivity overcomes the gain in reaction speed. This decrease is also observed for the Wittig reaction in different solvents.[22] Therefore all further olefination reactions were performed in toluene at 80 °C. The obtained results are summarized in Table 2.

Regarding the aldehyde olefination, the results present the expected trends: activated aldehydes, i.e., compounds containing electron-withdrawing groups such as aldehyde **I** and **VI** (entry 4), reach quantitative yields in short reaction times, typically in less than 1 h. Deactivated aldehydes, containing electron-donating groups, react comparatively slowly. By extending the reaction time to 24 h high yields (98%) in the olefination of **V** (entry 6) are obtained, while with substrate **III** even with prolonged reaction times, only moderate yields are observed (entry 3). A nonaromatic aldehyde, **IV**, reacts fairly fast under the conditions applied, reaching 92% yield after 5 h reaction time (entry 5).

A common feature found among all the results presented in this work is the high *E*-isomer selectivity displayed by catalyst **7**, being the highest selectivity reported so far.

The Wittig reaction between aldehydes[17b] or ketones[6d,7,17b,23] and $Ph_3P{=}CHCO_2Et$ can be strongly accelerated by submolar quantities of benzoic acid. The acid activation is not limited to benzoic acid, as several other acids display similar properties,[23a] but it seems to have a broader efficiency regarding the ketones and ylides. The influence of benzoic acid was therefore also investigated in this work. The olefination of **III** proceeds smoothly in the presence of 0.5 equiv of benzoic acid as cocatalyst, reaching 100% yield after just 2 h of reaction time (entry 7). The selectivity decreases to an *E*:*Z* ratio of 92:8, though. When using just 0.1 equiv of benzoic acid, quantitative olefin formation is observed within 4 h, displaying the same *E*:*Z* ratio.

Ketone olefination with stabilized ylides, such as $PPh_3{=}CHCO_2Et$, is usually a sluggish process and requires both harsh reaction conditions and/or long reaction times[24] to obtain reasonable yields. Exceptions to this rule are trifluoromethyl ketones, in which the carbonyl group is sufficiently electron deficient to undergo fast nucleophilic attack by the phosphorus ylide.[4c,25]

The olefination of α,α,α-trifluoroacetophenone proceeds smoothly at 80 °C in toluene, producing a 85% olefin yield after a reaction time of 5 h (entry 8). With an *E*:*Z* ratio of 88:12, the selectivity of this reaction is not as high as that observed for aldehyde olefination, but considerably higher than that obtained applying nonactivated ketones (see below).

The set of ketones tested included nonactivated aromatic rings (**VIII**), activated aromatic rings (**IX**), deactivated aromatic rings (**X**), and cyclic ketones (**XI** and **XII**) (using the same terminology as applied for the aldehydes). To increase the reaction rates, benzoic acid (0.5 equiv) was added as cocatalyst.

The yields obtained with aromatic ketones range from 92% for 4-nitroacetophenone to 57% for 4-methoxyacetophenone. Activated ketone **IX** reacts relatively fast (44 h) and shows the best selectivity observed for the aromatic ketones under examination, with an *E*:*Z* ratio of 35:65. Ketones **VIII** (entry 9) and **X** (entry 11) require long reaction times to obtain moderate yields, 78% and 57%, respectively, having very similar *E*:*Z* ratios. Moreover, the use of an initial excess of ketone **VIII** (3 equiv) produces a 72% olefin yield with an *E*:*Z* ratio of 42:58, after 72 h of reaction time, which is not an improvement over our standard reaction conditions. The lack of electron-withdrawing groups seems to be responsible for the lack of reactivity of this type of ketones.

Cyclic ketones can also be olefinated by this method. Cyclohexanone is olefinated with 84% yield (entry 12) within 24 h, while for **XII** as substrate only a moderate yield of 58% is achieved.

Complex **7** catalyzes efficiently the aldehyde olefination, giving high yields and excellent selectivities in short reaction times, while for the olefination of some ketones only moderate yields could be obtained, even in the presence of benzoic acid as cocatalyst. With respect to selectivity the results obtained with $Cp^*RuCl(PPh_3)_2$ for ketone olefination are the same order of magnitude as those obtained by other good catalysts,[4g,6d] unlike the case of aldehyde olefination, where compound **7** is clearly the most selective system reported so far.

Mechanistic Studies. In a previous communication[9] we suggested a possible mechanism for the aldehyde olefination with $Cp'RuCl(PPh_3)_2$ type complexes based on published results[8] and our own ^{31}P NMR spectroscopy studies. The proposed mechanism involves a $Cp^*RuCl({=}CHCO_2Et)(PPh_3)$ (**8**) carbene intermediate.

Following the reaction of complex **7** with EDA by ^1H NMR and ^{31}P NMR in CD_2Cl_2 at low temperatures, the existence of complex **8** is evident. At −15 °C a doublet at $\delta_H = 14.88$ ppm appears in the ^1H NMR, suggesting the formation of a $Cp^*RuCl({=}CHCO_2Et)(PPh_3)$ carbene.[8] Simultaneously the intensity of the methyl groups peak of Cp* of complex **7** ($\delta_H(Cp^*) = 0.98$ ppm) decreases, while a new one appears around $\delta_H = 1.30$ ppm. At the same temperature the ^{31}P NMR shows a steady decrease of the peak of complex **7** ($\delta_P = 41$ ppm) while two new peaks arise: a peak at 50.3 ppm for carbene complex **8** and a somewhat broader peak at 17.9 ppm, which splits into

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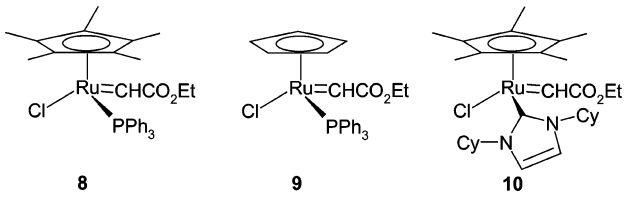
Chart 3



8 **9** **10**

two peaks after 20 min at −10 °C. The latter peaks, at δ_P = 18.4 and δ_P = 16.7 ppm, correspond to the *cis* and *trans* isomers of the phosphorus ylide,[26] as further confirmed by the ^{1}H NMR.

At −10 °C the conversion of complex **7** is quite fast since in less than 30 min it is completely absent from the ^{1}H and ^{31}P NMR. Performing the same procedure in deuterated toluene or THF produces very similar results, with the exception that complex **7** is never fully consumed due to its lower solubility in these solvents.

The reactive complex **8** is isolated in 68% yield by performing all operations at low temperature (−5 °C or below), because at higher temperatures a carbene−carbene coupling reaction easily occurs, leading to diethyl maleate, **7**, and other uncharacterized ruthenium complexes. The properties of **8** can be compared with those of the related compounds **9**[8b] and **10**[27] (Chart 3), which have previously been reported by Baratta et al. Thus, complex **8** is more stable than compound **9**, which was observed only in solution, due to the stabilizing effect of the Cp* moiety, but less stable than complex **10**, containing a stabilizing N-heterocyclic carbene, which was isolated at RT and decomposes in solution after many hours. Complex **8** displays hindered rotation of the phosphane and carbene ligands. At −20 °C the phenyl peaks are broad (^{1}H and ^{13}C−NMR), while at −70 °C the peaks are resolved and the fine structure of the phenyl carbons is observed. The peaks of the carbene ligand change from definite peaks to broad peaks on going from −20 to −90 °C, indicating also a rotation barrier. The rotation restriction is more pronounced for the phosphane ligand, in agreement with its larger bulk.

Complex **8** reacts, as expected, with PPh_3 (Figure 1): the outcome of adding less than 1 equiv of phosphane is a mixture of complex **8**, complex **7**, and $Ph_3P{=}CHCO_2Et$; when using more than 2 equiv of PPh_3, complex **7** is the only Ru species present plus the phosphorus ylide (in a predictable 1:1 ratio) and the excess phosphane.

Noteworthy is the fact that this reaction occurs even at −50 °C. The mixture reacts quantitatively with 2 equiv of 4-nba within 20 min (starting at −30 °C then proceeding to RT) to produce the corresponding olefin with a final *E*:*Z* ratio of 97:3 (determined by GC-MS). For comparison purposes the olefination of 4-nba, using complex **7** as catalyst in CH_2Cl_2 at RT, produces the same results—within the measurement error of the GC-MS technique—the final *E*:*Z* ratio being 96:4. The agreement between the results renders it likely that complex **8** is the active intermediate of the catalytic cycle.

Following a catalytic run by ^{1}H and ^{31}P NMR in both the absence and the presence of benzaldehyde in CD_2Cl_2, the identity of the species formed during the catalytic cycle becomes clearer (see Experimental Section for details). In the absence

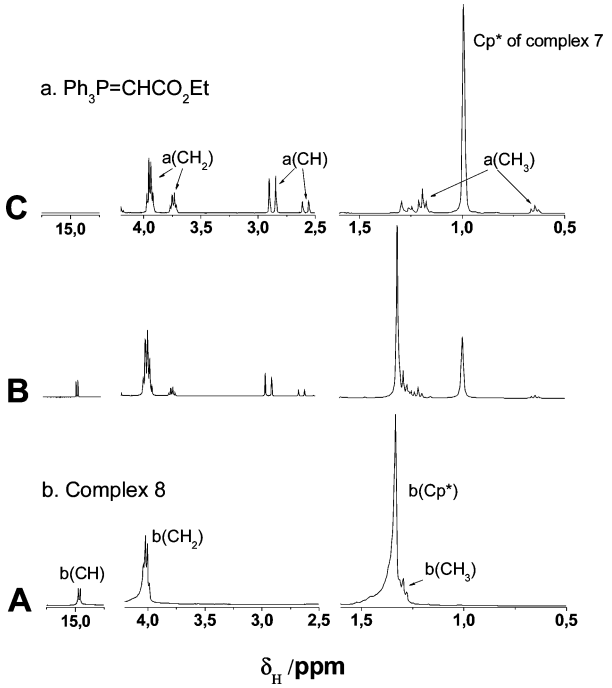


Figure 1. ^{1}H NMR of the reaction of complex **8** with PPh_3 in CD_2Cl_2 at −30 °C: (A) complex **8**; (B) complex **8** after addition of less than 1 equiv of PPh_3; (C) complex **8** with 2.5 equiv of PPh_3. The aromatic region is excluded for simplicity purposes.

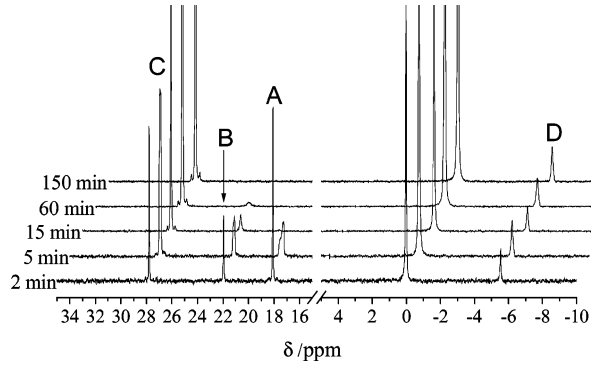


Figure 2. ^{31}P NMR of a catalytic benzaldehyde olefination with complex **7** at RT in CD_2Cl_2: (A) phosphorus ylide; (B) phosphazine **XIII**; (C) $O{=}PPh_3$; (D) PPh_3.

of aldehyde in less than 5 min the quantitative formation of phosphorus ylide and the phosphazine $Ph_3P{=}N{-}N{=}CHCO_2$-Et (**XIII**) in an 86:14 ratio (by integration of ^{1}H NMR peaks, available as Supporting Information) is observed.

The ^{31}P NMR has three main peaks besides the free PPh_3 (excess): a singlet at δ_P = 21.1 ppm and two broad peaks corresponding to the geometrical isomers of the ylide (δ_P = 18.0 and 16.4 ppm), which, as the temperature increases, almost coalesce to a single broad peak at δ_P =17.9 ppm.[26] It is necessary to wait 24 h until the phosphazine is almost entirely consumed, leaving ylide as the main product, observable in both the ^{31}P and ^{1}H NMR spectra.

The same reaction in the presence of benzaldehyde (Figure 2) shows some particular features: the ylide has a single sharp peak (δ_P = 18.1 ppm) in the ^{31}P NMR, a result of its interaction with the aldehyde;[26] the formation of $O{=}PPh_3$ (δ_P = 28.0 ppm) is fast and it is present almost from the beginning of the catalysis; the ylide is consumed completely within 15 min, during which phosphazine **XIII** (δ_P = 22.6 ppm) scarcely reacts. After 150 min at RT the reaction is complete, as there is only

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the peak of $O{=}PPh_3$ in the ^{31}P NMR. These observations lead to two conclusions: (a) the ylide formation is much faster than the phosphazine **XIII** formation and **XIII** is also less reactive; (b) the phosphazine reaction is promoted by the presence of aldehyde.

Bestmann and Göthlich[28] proved that in solution resonance-stabilized phosphazines exist in equilibrium with the original phosphane and diazo starting compounds (Scheme 2). This suggests that even in the presence of phosphazine the actual reaction partner is EDA.

A mixture of phosphazine and complex **7** (ratio 2:1) in CD_2Cl_2 does not show any changes in the ^{31}P or ^1H NMR between −30 and 10 °C. At 15 °C a small doublet at $\delta_H = 14.9$ ppm in the ^1H NMR can be observed, evidencing the presence of complex **8** in solution. At 20 °C there is a small peak at $\delta_P = 51$ ppm in the ^{31}P NMR (complex **8**). However, it is necessary to let the sample react for 20 min at 20 °C to observe the first peak of $Ph_3P{=}CHCO_2Et$ in the ^{31}P NMR.

The conversion of phosphazine into phosphorus ylide should be faster as the equilibrium is shifted to the starting materials. This explains why the presence of aldehyde in solution—which pushes the reaction forward through the formation of the olefin—or a temperature increase enhances the conversion rate since they drive the equilibrium toward the right side of Scheme 2.

For highly active catalysts such as complex **7**, the phosphazine formation is strongly suppressed and should become significant only at very low catalyst loadings; therefore, the main reaction pathway for complex **7** should be the one described in Scheme 3.

Therefore, the best catalysts promote the direct formation of $Ph_3P{=}CHCO_2Et$ from EDA and PPh_3, avoiding the production of phosphazine **XIII**, a comparatively sluggish reactant. The first step, release of phosphane and formation of complex **8** by reaction with EDA, occurs at temperatures above −10 °C. The second step, formation of the phosphorus ylide through reaction of complex **8** with PPh_3, is considerably easier and occurs even at −50 °C. The third step, reaction of the phosphorus ylide with the aldehyde, was considered above in terms of ylide structure and reactivity. For this class of ruthenium complexes the different *E*:*Z* ratios obtained with catalysts **1**, **6**, and **7** (Table 1, entries 1, 6, and 7, respectively) show that the catalyst might play a certain role in the third step, influencing the reaction's selectivity. The *E*:*Z* selectivity obtained with complex **7** is (within the experimental error) for several tested aldehydes (**I**, **II**, and **III**) equal to the selectivity obtained in the noncatalyzed Wittig reaction using similar reaction conditions. The NMR studies also did not show any noticeable interaction between this catalyst and the phosphorus ylide, so that it may be concluded that the role of complex **7** in the third step is negligible to the reaction outcome.

To the best of our knowledge, the reaction rate enhancement effected by benzoic acid was never fully understood. Some authors suggest the carbonyl to be protonated by the acid, making it more electrophilic and prone to a nucleophilic attack by the ylide.[6d]

A ^1H and ^{13}C NMR of a mixture of acetophenone/benzoic acid (1:0.5) resemble the arithmetic sum of the spectra of the individual compounds, therefore excluding a significant interaction between the compounds and less likely any activation toward the olefination reaction.

Addition of benzoic acid to the phosphorus ylide changes their NMR spectra considerably (Figure 3 and 4).

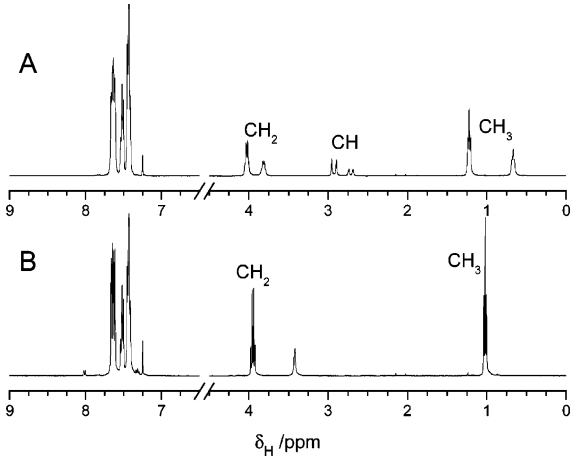


Figure 3. ^1H NMR spectra of the phosphorus ylide: (A) dried over CaH_2; (B) after addition of ca. 0.1 equiv of benzoic acid to A.

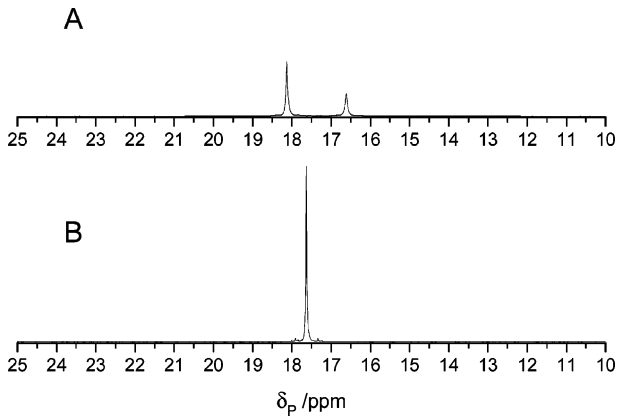


Figure 4. ^{31}P NMR spectra of the phosphorus ylide: (A) dried over CaH_2; (B) after addition of ca. 0.1 equiv of benzoic acid to A.

One of the main features is the collapse of the peaks of the ylide's *cis* and *trans* isomers. This pattern is similar to that observed on addition of benzaldehyde to the ylide.[26a,b] The collapse of the peaks indicates that the interconversion between *cis* and *trans* isomers is very fast (on the NMR time scale).

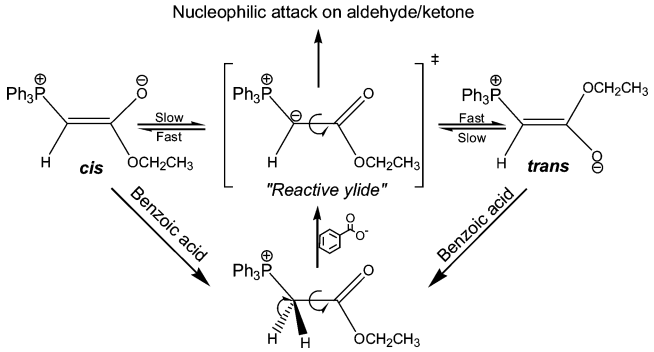
Hooper et al.[26b] suggested that during the Wittig reaction neither the *cis* nor *trans* isomers of the phosphorus ylide seem to readily react with the carbonyl group. Instead the reaction in carried out by an intermediate present during the interconversion of the two isomers, which bears a negative charge on the methine carbon (Scheme 4).[26b] In the presence of traces of water or acidic protons (to promote the protonation of the isomers), the carbonyl of benzaldehyde easily "traps" this reactive intermediate, and thereby the peaks collapse.

Mixing acetophenone with the ylide (1:1) no such collapse is observed, indicating that the ketone cannot "trap" the reactive intermediate due to its low electrophilic character. The benzoic acid, however, greatly increases the concentration of the "reactive ylide" in solution, while not reacting with it (Scheme 4), making it available to nucleophilic attack on a carbonyl group. Still the carbonyl group of ketones is much less electrophilic than the carbonyl of aldehydes, and concomitantly the reactions are considerably slower with ketones than with aldehydes. Nevertheless the trend is clear, the more electrophilic the ketone's carbonyl, the higher the reaction rate.

Other interesting features observed in Figure 3 are the position of the methine proton and its lack of coupling with the

(28) Bestmann, H. J.; Göthlich, L. *Liebigs Ann. Chem.* **1962**, *655*, 1.

Scheme 4. "Activation" of Phosphorus Ylide by Benzoic Acid[a]



[a] Partially adapted from ref 26b.

phosphorus. While the positions of the methylene and methyl protons appear to be the average of the initial positions and relative amounts of each isomer existing before the addition of the benzoic acid, the methine proton is considerably shifted toward lower fields. Further experiments using different amounts of benzoic acid unveil that this peak shifts to lower fields as the relative amount of benzoic acid increases. We conclude that the proton must be switching between the two ylide isomers and the benzoic acid, and the resulting peak is an average of these three contributions. A calculation of the expected position of this peak simply based on the amounts of each component and the peaks' original positions leads to $\delta_H(CH) = 3.48$ ppm as the expected chemical shift of the methine proton and is in very good agreement with the experimental result $\delta_H(CH) = 3.42$ ppm (Figure 3), thus confirming the above-described suggestion. The lack of coupling with phosphorus of the resulting peak stems from this same process, since the proton while coordinated to benzoic acid does not couple with the phosphorus.

Conclusions

Several ruthenium compounds bearing phosphane ligands act as catalysts for the aldehyde olefination starting from diazo compounds, phosphanes, and aldehydes. The phosphane structure has a strong effect on the catalyst performance, bulkier phosphanes leading to better yields and higher selectivities. The replacement of the Cl ligand by a more electron-withdrawing group such as $-OC(O)CF_3$ has a negative effect on the catalyst performance. On the other hand, the replacement of the Cp ligand by bulkier π-ligands such as Cp* or indenyl has a remarkable positive effect on the catalyst activity. Particularly $Cp^*RuCl(PPh_3)_2$ leads to excellent yields and particularly high *E*:*Z* ratios, the latter being the best reported so far. This compound was also found to be a good catalyst for the olefination of activated ketones and a moderate catalyst for the olefination of nonactivated ketones using benzoic acid as cocatalyst. Investigations on the mechanism show the existence of a mixed carbene/phosphane ruthenium intermediate, complex **8**, which was isolated and characterized. The catalytic cycle is triggered by EDA, and the ylide $Ph_3P{=}CHCO_2Et$ is formed by reaction of complex **8** with PPh_3. Under catalytic conditions phosphazine **XIII**, a less reactive reaction partner, is also formed and exists in equilibrium with its precursor compounds. Highly active catalysts such as complex **7** largely suppress phosphazine formation.

Benzoic acid promotes the catalytic reaction with both aldehydes and ketones, by facilitating the transition between *cis* and *trans* isomers of the phosphorus ylide and hence increasing the presence of the "reactive ylide" in solution, making it available to react with otherwise unreactive ketones.

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