P,N-Chelate Complexes of Pd(II) and Pt(II) Based on a Phosphaalkene Motif: A Catalyst for the Overman−Claisen Rearrangement

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The reaction of *E*/*Z*-MesP═C(Ph)(Py) (**1**, Mes = 2,4,6-$Me_3C_6H_{2-}$) with (cod)$PtCl_2$ or (cod)$PdCl_2$ affords P,N-chelate complexes [MesP═C(Ph)(Py)$PtCl_2$] (**2a**) and [MesP═C(Ph)(Py)$PdCl_2$] **(2b**), respectively. Compounds **2a** and **2b** were fully characterized spectroscopically, and both were characterized by X-ray crystallography. The molecular structures exhibited almost identical metrical parameters. The P═C bond lengths in **2a** and **2b** [1.672(4) and 1.675(3) Å, respectively] were shortened substantially with respect to that of **1** [1.7043(16) Å]. Complex **2b** was explored as a catalyst for the Overman−Claisen rearrangement. Several allyl trichloroacetimidate substrates [HN═C(CCl_3)OCH_2CH═CHR_1: **3a**, R_1 = Me; **3b**, R_1 = *n*-Pr; **3c**, R_1 = *n*-Hep; **3d**, R_1 = CH_2CH_2Ph; **3e**, R_1 = *i*-Pr] were successfully rearranged to their respective branched amides [H_2C═$CHCH(R_1)NHC(O)CCl_3$: **4a**−**e**] using 5 mol % **2b** as catalyst. Isolated yields ranged from a low of 33% for the bulky **4e** to a high of 91% for **4a**.

Introduction

The development of tailor-made phosphorus-containing ligands has played a major role in the immense impact that homogeneous catalysis has made on synthetic organic chemistry. Although trivalent phosphines still dominate the field of late-transition metal-based catalysis, there is growing interest in the development of ligands containing low-coordinate phosphorus.[1] Low-coordinate phosphorus compounds are attractive because their unique π-acceptor properties impart desirable characteristics to electron-rich transition metal centers.[1b]

Some examples of ligands having low-coordinate phosphorus atoms are shown in Chart 1. Significant contributions to this area have stemmed from the development of cyclic divalent phosphorus systems. As examples, phosphinines (**A**[2,3] and **B**[4,5]), phosphaferrocenes (**C**[6,7]), and α-iminophospholyl (**D**[8]) compounds have all been employed successfully as ligands for metals, and complexes of **A**, **B**, and **C** have been successfully employed in catalysis. Examples that have an acyclic phosphaalkene motif are more limited in scope. Most acyclic phosphaalkene-based ligands employed in catalysis utilize the sterically encumbering Mes* ligand (Mes* = 2,4,6-tri-*tert*-butylphenyl) to confer kinetic and thermodynamic stability to the P═C bond (**E**[9−11] and **F**[12]).[13] Particularly relevant to the present studies are 2-pyridyl-substituted phosphaalkenes **G**[14] and **H**[15,16] where the P═C bond is similarly flanked by the Mes* substituent. Although P(sp^2),N(sp^2) compounds containing acyclic phosphaalkenes have been coordinated to transition metals, to our knowledge, only **E** (X = N) has been employed in catalysis.

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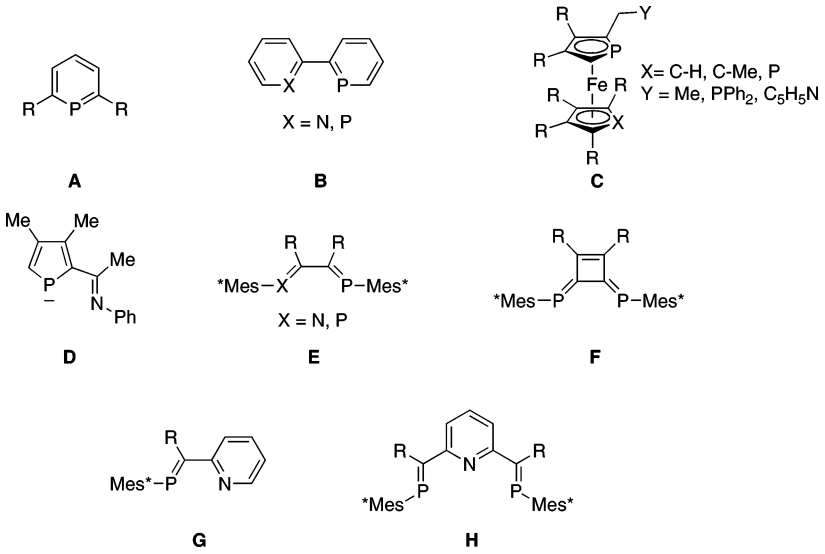
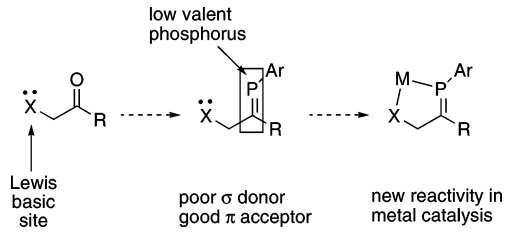
Chart 1



Scheme 1. Strategy for the Preparation of Phosphaalkene Ligands Bearing Unique Donor−Acceptor Properties

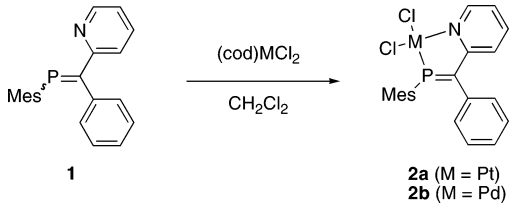


We have recently employed the phospha-Peterson reaction as a general route to phosphaalkenes bearing modest degrees of steric bulk.[17] The relatively mild conditions needed to affect this transformation suggested to us a route to novel chelating phosphaalkene ligands for use in transition metal catalysis. An idealized strategy for the development of phosphaalkene ligands bearing tunable donor−acceptor properties is shown in Scheme 1. An attractive feature of this approach is that the modular nature of the ligand synthesis allows for the facile modification of steric and electronic properties. For example, isolable phosphaalkene ligands bearing varying degrees of steric bulk (i.e., Mes and larger) may be synthesized from a variety of functional ketones using the phospha-Peterson reaction.

Herein, we report two new chelating phosphaalkene-based P(sp^2)−N(sp^2) complexes of palladium(II) and platinum(II): MesP═C(Ph)(Py)$PtCl_2$ (**2a**) and MesP═C(Ph)(Py)$PdCl_2$ (**2b**). These new complexes bear the modestly bulky Mes-substituent at phosphorus as compared to known P(sp^2)−N(sp^2) complexes, which often utilize the larger Mes* substituent to impart stability to the ligand. Moreover, a phosphaalkene ligated palladium(II) complex (**2b**) is demonstrated to be a catalyst for the aza-Claisen rearrangement of trichloroacetimidates (Overman−Claisen rearrangement).

Results and Discussion

Synthesis of Palladium(II) and Platinum(II) Complexes. In an attempt to prepare platinum complex **2a**, C-pyridyl phosphaalkene **1** was treated with (cod)$PtCl_2$ in CH_2Cl_2 at ambient temperature. Analysis of the reaction mixture by ^{31}P NMR spectroscopy revealed that the signals assigned to *E*/*Z*-**1** [δ = 260.1 (*E*), 242.1 (*Z*)] had been replaced by a new signal at 205.6 ppm. Importantly, the observation of ^{195}Pt satellites ($^1J_{PtP}$ = 4486 Hz) provides convincing evidence for coordination of the phosphorus center to the platinum center. The coupling constant is similar to other phosphaalkene complexes such as **F**·$PtCl_2$ ($^1J_{PtP} \approx 4500$ Hz)[18,19] but is higher than the monodentate phosphaalkene in [MesP═CPh_2]$_2PtCl_2$ ($^1J_{PtP}$ = 3950 Hz[20]). Moreover, the downfield ^{31}P NMR chemical shift is consistent with retention of P═C multiple bond character in the ligand upon complexation.



Although the above NMR spectroscopic evidence suggested that **2a** had been formed from **1** and (cod)$PtCl_2$, this was

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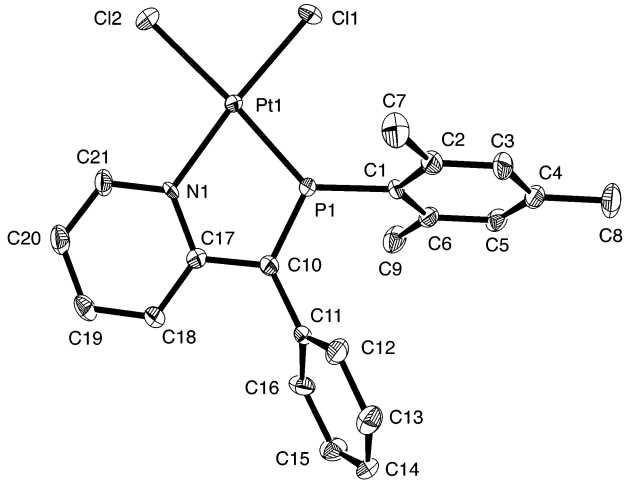

Figure 1. Molecular structure of **2a** (50% probability ellipsoids). All hydrogen atoms and the solvent ($^1/_2CH_2Cl_2$) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt1−P1 = 2.1673(11), P1−C10 = 1.672(4), C10−C17 = 1.468(5), C17−N1 = 1.373(5), N1−Pt1 = 2.069(3), Pt1−Cl1 = 2.2923(11), Pt1−Cl2 = 2.3415(11), P1−C1 = 1.787(4); N1−Pt1−P1 = 81.17(10), P1−Pt1−Cl1 = 94.02(4), N1−Pt1−Cl2 = 94.80(10), Cl1−Pt1−Cl2 = 90.02(4), Pt1−N1−C17 = 120.3(3), N1−C17−C10 = 117.4(3), C17−C10−P1 = 112.3(3), C10−P1−Pt1 = 108.64(14), C10−P1−C1 = 116.15(19), Pt1−P1−C1 = 134.76(13).

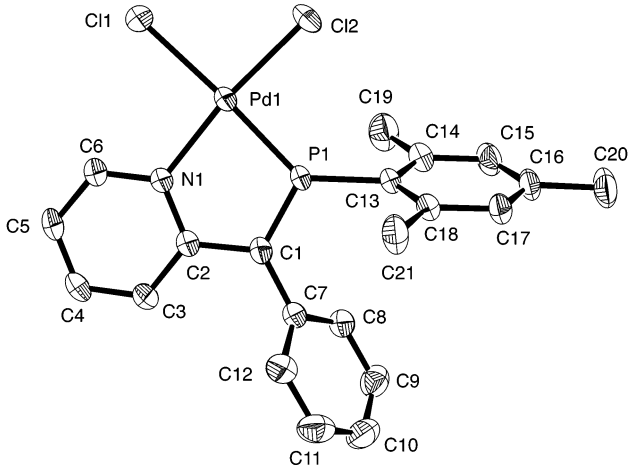

Figure 2. Molecular structure of **2b** (50% probability ellipsoids). All hydrogen atoms and the solvent ($2CH_2Cl_2$) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−P1 = 2.1749(7), P1−C1 = 1.675(3), C1−C2 = 1.470(4), C2−N1 = 1.377(4), N1−Pd1 = 2.076(2), Pd1−Cl1 = 2.3412(7), Pd1−Cl2 = 2.2834(7), P1−C13 = 1.789(3); N1−Pd1−P1 = 81.43(6), P1−Pd1−Cl2 = 91.42(3), N1−Pd1−Cl1 = 95.20(6), Cl1−Pd1−Cl2 = 91.95(3), Pd1−N1−C2 = 119.96(17), N1−C2−C1 = 117.6-(2), C2−C1−P1 = 112.7(2), C1−P1−Pd1 = 108.3(1), C1−P1−C13 = 116.35(13), Pd1−P1−C13 = 135.36(9).

confirmed by an X-ray crystallographic analysis. Crystals suitable for X-ray diffraction were grown by cooling a CH_2Cl_2/hexanes solution to −56 °C. The molecular structure is shown in Figure 1 and confirms that the chelate complex **2a** had been formed successfully (the metrical parameters are discussed below). Despite repeated recrystallizations, according to NMR spectroscopy, there were always traces of (cod)$PtCl_2$ present in samples of **2a**.

Given our success in the preparation of **2a**, we attempted to prepare the analogous Pd-complex **2b**. Under conditions analogous to those described above for **2a**, phosphaalkene ligand **1** was treated with (cod)$PdCl_2$ in CH_2Cl_2. Analysis of the reaction mixture by ^{31}P NMR spectroscopy revealed a single resonance at 230.4 ppm. For comparison, lower field chemical shifts were observed for pyridyl phosphaalkene complexes containing the bulkier P−Mes* moiety (i.e., **G**·$PdCl_2$: R = H, 247 ppm; R = $SiMe_3$, 283 ppm).[14] In contrast, higher field shifts are observed for complexes **F**·$PdCl_2$ (R = C_4H_4S, 149.4 ppm; R = Fc, 134.9 ppm).[18,19,21] Interestingly, the $^{13}C\{^1H\}$ NMR signal assigned to the P═C carbon resonates at 174.8 ppm ($^1J_{PC}$ = 52 Hz) for the complex **2b**, which is further upfield than that found for the free phosphaalkene **1** (δ = 191.3, $^1J_{PC}$ = 40 Hz; i.e., $\Delta\delta$ = 16.5). Similar upfield shifts were observed for the $PdCl_2$ complexes of **G**·$PdCl_2$ (R = $SiMe_3$, $\Delta\delta$ = 4.6)[14] and the phosphaalkene signals for complex **F**·$PdCl_2$ (R = $-(CH_2)_5-$; $\Delta\delta$ = 16.0 and 14.7).[22] Unlike Pt-complex **2a**, the Pd-complex **2b** is readily obtained in analytical purity after recrystallization.

Molecular Structures of 2a and 2b. The molecular structures of **2a** and **2b** are shown in Figures 1 and 2, respectively, and selected metrical parameters are given in the figure captions. Details of the solution and refinement are given in Table 1 and the Supporting Information. Interestingly, the crystal structures of the palladium(II) and platinum(II) complexes contain almost identical metrical parameters. Given that related P,N-chelate complexes of Pt(II) have not been characterized crystallographically, in this section, emphasis will be placed on comparing **2b** to related Pd(II) compounds from the literature. In both **2a** and **2b**, a significant shortening of the P═C bond is observed upon complexation [1.672(4) Å in **2a** and 1.675(3) Å in **2b** vs 1.7043-(16) Å in **1**].[17] In contrast, **E** (X = N), **F**, and **G** showed no significant change or even a slight elongation in P═C bond length upon complexation {i.e., 1.660(11) Å in [**E**·Pd(Me)-(NCMe)]$^+$ vs 1.684(2) Å in **E**;[9] 1.653(12) Å in **F**·$PdCl_2$ vs 1.667(8) Å in **F**;[22] 1.674(4) Å in **G**·PdMeCl vs 1.663(3) Å in **G**}.[14] The palladium−phosphorus bond length in **2b** of 2.1749-(7) Å is similar to those previously observed for phosphaalk-ene−palladium complexes of **E** (X = N) and **G** [avg = 2.179(3) Å].[9,14] However, these are slightly shorter than those observed in **F**·$PdCl_2$ [2.267(2) and 2.256(2) Å].[22] In addition, the N−Pd bond length in **2b** of 2.076(2) Å is shorter than that for **G**·PdMeCl [2.164(4) Å][14] and that for [**E**·Pd(Me)(NCMe)]$^+$ [2.166(8) Å].[9]

The C−P═C angle increases significantly upon coordination of **1** to palladium [107.80(7)° in **1**[17] vs 116.15(19)° in **2a** and 116.35(13)° in **2b**]. Similar increases in C−P═C bond angles were observed for the palladium complexes of **E** [X = N, 104.36(9)° to 113.7(5)°],[9] **F** [99.6(2)° to 114.1(4)°],[22] and **G** [99.15(14)° to 114.26(19)°].[14] The angle between the mean plane of the six carbon atoms of the Mes substituent and the $PdNC_2P$ plane in **2b** is 69°. Not surprisingly, the complexes employing the bulkier Mes* substituent show angles between the Mes* and $PdNC_2P$ planes that are close to orthogonal {87° in [**E**·Pd-(Me)(NCMe)]$^+$,[9] 89° in **G**·PdMeCl[14]}.

Catalytic Activity of 2b. Efforts were then undertaken to establish any catalytic activity for the phosphaalkene palladium-(II) complex **2b**. An important palladium(II)-catalyzed process is the rearrangement of allyl trichloroacetimidates (the Over-man−Claisen rearrangement).[23] This process transforms an allyl

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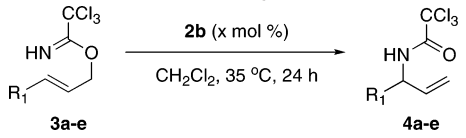
Table 1. X-ray Crystallographic Data for 2a and 2b

	2a	2b
formula	$C_{21}H_{20}NPPtCl_2 \cdot {}^1/_2CH_2Cl_2$	$C_{21}H_{20}NPPdCl_4 \cdot 2CH_2Cl_2$
fw	625.80	664.50
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
color	yellow	orange
a (Å)	9.8721(7)	9.8650(3)
b (Å)	10.2072(7)	11.7091(4)
c (Å)	12.0467(8)	12.5723(5)
α (deg)	105.168(6)	86.292(1)
β (deg)	108.919(6)	88.685(1)
γ (deg)	95.834(6)	69.904(1)
V (Å^3)	1085(1)	1360.96(8)
T (K)	173	173
Z	2	2
μ(Mo Kα) (cm^{-1})	69.17	13.43
cryst size (mm^3)	0.35 × 0.20 × 0.12	0.07 × 0.07 × 0.12
calcd density (Mg m^{-3})	1.916	1.622
2*θ*(max) (deg)	55.2	55.8
no. of reflns	11 319	22 108
no. of unique data	4068	6431
R(int)	0.025	0.031
refln/param ratio	15.41	18.48
R_1[a]	0.026; $I > 2\sigma(I)$	0.037; $I > 2\sigma(I)$
wR_2 (all data)[b]	0.065	0.097
GOF	1.09	1.03

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2[\text{all data}]) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Results of the aza-Claisen Rearrangement Using 2b as Catalyst



3a-e 4a-e

entry	substrate	R_1	**2b** (mol %)	yield (%)[a]
1	**3a**[b]	Me	5	91
2	**3a**[c]	Me	0	0
3	**3a**[c]	Me	5	84
4	**3b**[c]	*n*-Pr	5	86
5	**3c**[c]	*n*-Hep	5	72
6	**3d**[c]	$PhCH_2CH_2$	5	48
7	**3e**[c]	*i*-Pr	5	33

[a] Isolated yield. [b] Purified by distillation. [c] Purified by column chromatography.

alcohol to an allyl amine derivative in concert with a 1,3-allylic transposition. For two principal reasons, this process was deemed to be a useful starting point to examine the potential catalytic reactivity of these complexes. First, the mechanism of the Overman−Claisen rearrangement does not involve changes in the palladium oxidation state, simplifying the overall reaction path. Second, the starting materials for these processes are trivial to obtain.

To our delight, subjecting acetimidate **3a** with 5 mol % of **2b** in CH_2Cl_2 at 35 °C for 24 h led to the production of branched amide **4a** in 91% isolated yield (Table 2, entry 1). Importantly, no background reaction was observed when the reaction was run in the absence of complex **2b** (entry 2). Reactions run with substrate that was not previously purified in any manner tended to be messy, which is presumably a consequence of the sensitivity of **2b**. Purification of the starting material using either distillation (entry 1) or standard silica gel column chromatography (entry 3) gave satisfactory results. Interestingly, the reaction proceeds optimally using acetimidate starting materials possessing linear aliphatic chains (entries 4−6). Substrates containing branched aliphatic groups reacted, although the products were obtained in less satisfactory isolated yield (entry 7). We speculate that the lower yields with bulky substrates may be a consequence of the bulky nature of complex **2b**. A second observation is an overall decrease in the reaction efficiency when the acetimidate substrate contained an aryl moiety. For example, compound **3d** reacted to produce amide **4d** in 48% isolated yield (entry 6). The addition of toluene to the reaction of **3a** also led to a similar decrease in the reaction efficiency. The inhibitory role of the aromatic additives is not clear at the present time. Clearly, efforts to expand substrate scope will necessitate the design of improved phosphaalkene complexes. Still, these results suggest a useful starting point for mixed ligand design using a phosphaalkene as a key structural motif.

Summary

In closing, we have prepared two new palladium(II) and platinum(II) complexes bearing $P(sp^2)-N(sp^2)$ ligands. The phosphaalkene-based ligand bears moderately bulky mesityl substituent. Both compounds were characterized spectroscopically and through X-ray crystallographic analysis. As a proof of concept, the potential use of this ligand class in catalysis was demonstrated by showing that compound **2b** was effective in the Overman−Claisen rearrangement. Future work is underway in efforts to modify the steric and electronic properties of the ligand and to explore the scope and effectiveness of these complexes in a variety of catalytic processes.

Experimental Section

General Procedures. All manipulations of air- and/or water-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk or glovebox techniques. Hexanes and CH_2Cl_2 were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. 230−400 mesh silica was used (Silicycle). The complexes (cod)$PtCl_2$ and (cod)$PdCl_2$ were prepared according to literature procedures.[24,25] Trichloroacetonitrile, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), crotyl alcohol, and trans-2-hexen-1-ol were used as received from Aldrich. Other starting materials were prepared according to the literature procedures, which are cited below. ^{1}H, ^{31}P, ^{13}C{^{1}H} NMR spectra were recorded at room temperature on Bruker Avance 300 or 400 MHz spectrometers. 85% H_3PO_4 was used as an external standard (δ = 0.0 for ^{31}P). ^{1}H NMR spectra were referenced to residual protonated solvent, and ^{13}C NMR spectra were referenced to the deuterated solvent. Elemental analyses were performed in the University of British Columbia Chemistry Microanalysis Facility. Mass spectra were recorded on a Kratos MS 50 instrument in EI mode (70 eV). Melting points are uncorrected.

MesPC(Ph)(Py)$PtCl_2$ (2a). This procedure was performed in a glovebox. To a mixture of (cod)$PtCl_2$ (75 mg, 0.20 mmol) and **1**[17] (65 mg, 0.20 mmol) was added 1 mL of CH_2Cl_2. The resulting dark red solution was stirred for 15 min. Cooling of the reaction mixture to −56 °C with slow addition of 1 mL of hexanes gave yellow crystals. The mother liquor was decanted, and the crystals were washed with hexanes (3 × 1 mL). Recrystallization (CH_2Cl_2/hexanes, twice) followed by drying in vacuo for 6 h gave 41 mg (37%) of the title compound as a solid.

^{31}P NMR (121.3 MHz, $CDCl_3$): δ 205.6 ($^1J_{PtP}$ = 4486 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.34 (dd, $^3J_{HH}$ = 6 Hz, $^3J_{HH}$ = 1 Hz, $^3J_{PtH}$ = 36 Hz, 1H), 7.87−7.79 (m, 1H), 7.50−7.44 (m, 1H), 7.41−7.27 (m, 4H), 7.11−7.08 (m, 2H), 6.90 (d, $^3J_{HH}$ = 4 Hz, 2H), 2.54 (s, 3H), 2.53 (s, 3H), 2.28 (s, 3H).

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MesPC(Ph)(Py)PdCl$_2$ (2b). This procedure was performed in a glovebox. To a mixture of (cod)PdCl$_2$ (100 mg, 0.35 mmol) and **1**[17] (111 mg, 0.35 mmol) was added 1 mL of CH_2Cl_2. The resulting dark red solution was stirred for 15 min. Cooling the reaction mixture to −56 °C with slow addition of 1 mL of hexanes gave orange crystals. The mother liquor was decanted, and the crystals were washed with hexanes (3 × 3 mL) and dried in vacuo at 100 °C for 6 h to give 91 mg (53%) of the title compound as orange crystals.

^{31}P NMR (121.3 MHz, $CDCl_3$): δ 230.4 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.03 (d, $^3J_{HH}$ = 6 Hz, 1H), 7.86 (dd, $^3J_{HH}$ = 4 Hz, $^3J_{HH}$ = 2 Hz, 1H), 7.48−7.44 (m, 1H), 7.39−7.24 (m, 4H), 7.07 (d, $^3J_{HH}$ = 8 Hz, 2H), 6.85 (d, $^3J_{HH}$ = 4 Hz, 2H), 2.50 (s, 3H), 2.50 (s, 3H), 2.25 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 174.8 (d, J_{PC} = 52 Hz), 163.0, 159.7 (d, J_{PC} = 14 Hz), 155.2 (d, J_{PC} = 5 Hz), 145.8 (d, J_{PC} = 3 Hz), 144.0 (d, J_{PC} = 5 Hz), 140.8 (d, J_{PC} = 5 Hz), 134.4 (d, J_{PC} = 13 Hz), 130.3, 129.6, 129.3 (d, J_{PC} = 10 Hz), 128.4 (d, J_{PC} = 14 Hz), 125.9 (d, J_{PC} = 9 Hz), 124.0 (d, J_{PC} = 25 Hz), 120.2 (d, J_{PC} = 38 Hz), 23.5, 23.4, 21.9. Anal. Calcd for $C_{21}H_{20}NPdCl_2$: C, 50.99; H, 4.08; N, 2.83. Found: C, 51.12; H, 4.21; N, 2.80.

Trichloroacetimidate Formation (General Procedure). To a solution of allylic alcohol (1 equiv) in CH_2Cl_2 (0.1 M) at 0 °C were added trichloroacetonitrile (1.5 equiv) and then DBU (0.2 equiv) dropwise. The reaction mixture was stirred at 0 °C for 1 h. The reaction was quenched by the addition of a saturated aqueous solution of sodium bicarbonate. The organic and aqueous fractions were separated, and the aqueous phase was extracted twice with CH_2Cl_2. The combined organic extracts were dried (sodium sulfate) and concentrated by rotary evaporation in vacuo. Further purification of the crude material using flash column chromatography on silica gel was typically necessary.

1-(1-Imino-2,2,2-trichloroethoxy)-2(*E*)-butene (3a). Crotyl alcohol (1.10 g, 15.3 mmol) was processed as outlined in the general procedure. Purification using column chromatography (5% ethyl acetate:95% hexanes) gave 2.85 g (86%) of a colorless oil. The spectroscopic data for the title compound were identical to the literature.[26]

1-(1-Imino-2,2,2-trichloroethoxy)-2(*E*)-hexene (3b). (*E*)-2-Hexen-1-ol (1.14 g, 11.3 mmol) was processed as outlined in the general procedure. Purification using column chromatography (5% ethyl acetate:95% hexanes) gave 2.05 g (74%) of a colorless oil. The spectroscopic data for the title compound were identical to the literature.[27]

1-(1-Imino-2,2,2-trichloroethoxy)-2(*E*)-decene (3c). (*E*)-2-Decen-1-ol[28] (2.67 g, 17.1 mmol) was processed as outlined in the general procedure. Purification using column chromatography (2% ethyl acetate:98% hexanes) gave 3.84 g (75%) of a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32−8.20 (br s, 1H), 5.87 (dt, $^3J_{HH}$ = 15 Hz, $^3J_{HH}$ = 7 Hz, 1H), 5.66 (dtt, $^3J_{HH}$ = 15 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, 1H), 4.72 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, 2H), 2.05 (q, $^3J_{HH}$ = 7 Hz, 2H), 1.4−1.2 (m, 10H), 0.86 (t, $^3J_{HH}$ = 7 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 162.5, 137.0, 122.9, 91.5, 69.9, 32.2, 31.8, 29.1, 29.0, 28.8, 22.6, 14.0. IR (neat, NaCl): 3347, 1663, 1290 cm^{-1}. MS (EI): *m*/*z* [%] 301 [33, M$^+$], 299 [36, M$^+$], 266 [48, M$^+$ − Cl], 264 [71, M$^+$ − Cl], 216 [85, M$^+$ − C_6H_{13}], 214 [84, M$^+$ − C_6H_{13}], 202 [96, M$^+$ − C_7H_{15}], 200 [100, M$^+$ − C_7H_{15}].

1-(1-Imino-2,2,2-trichloroethoxy)-2(*E*)-5-phenyl-pentene (3d). (*E*)-5-Phenyl-2-penten-1-ol[29] (1.43 g, 8.8 mmol) was processed as outlined in the general procedure. Purification using column chromatography (5% ethyl acetate:95% hexanes) gave 1.85 g (68%) of a colorless oil. The spectroscopic data for the title compound were identical to the literature.[30]

1-(1-Imino-2,2,2-trichloroethoxy)-2(*E*)-4-methyl-pentene (3e). (*E*)-4-Methyl-2-penten-1-ol[31] (0.36 g, 3.6 mmol) was processed as outlined in the general procedure. Purification using column chromatography (5% ethyl acetate:95% hexanes) gave 0.66 g (75%) of a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35−8.20 (br s, 1H), 5.84 (dd, $^3J_{HH}$ = 16 Hz, $^3J_{HH}$ = 6 Hz, 1H), 5.63 (dt, $^3J_{HH}$ = 16 Hz, $^3J_{HH}$ = 6 Hz, 1H), 4.75 (d, $^3J_{HH}$ = 6 Hz, 2H), 2.35 (sept, $^3J_{HH}$ = 7 Hz, 1H), 1.02 (d, $^3J_{HH}$ = 7 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.8, 143.8, 120.3, 91.7, 70.3, 31.0, 22.1. IR (neat, NaCl): 3344, 1663, 1290 cm^{-1}. MS (EI): *m*/*z* [%] 244 [36, M$^+$ − H], 242 [37, M$^+$ − H].

Palladium(II)-Catalyzed Overman−Claisen Rearrangement (General Procedure). This procedure was performed in a glovebox. To a mixture of **2b** (0.05 equiv) and trichloroacetimidate (1 equiv) was added 2 mL of CH_2Cl_2. The reaction mixture was stirred for 24 h. The reaction mixture was removed from inert atmosphere and chromatographed directly on silica gel to afford the trichloroacetamide product.

2,2,2-Trichloro-*N*-(1-methylallyl)acetamide (4a). 3a (96 mg, 0.44 mmol) and **2b** (10 mg, 0.02 mmol) were processed as outlined in the general procedure. Purification using column chromatography (5% ethyl acetate:95% hexanes) gave 87 mg (91%) of a white solid, mp = 37−39 °C (lit. 37−38 °C[32]). The spectral data for the title compound matched the literature data.[30]

2,2,2-Trichloro-*N*-(1-propylallyl)acetamide (4b). 3c (98 mg, 0.40 mmol) and **2b** (10 mg, 0.02 mmol) were processed as outlined in the general procedure. Purification using column chromatography (5% ethyl acetate:95% hexanes) gave 84 mg (86%) of a colorless oil. The spectral data for the title compound matched the literature data.[30]

2,2,2-Trichloro-*N*-(1-heptylallyl)acetamide (4c). 3c (143 mg, 0.47 mmol) and **2b** (12 mg, 0.024 mmol) were processed as outlined in the general procedure. Purification using column chromatography (1% ethyl acetate:99% hexanes) gave 103 mg (72%) of a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.55−6.45 (br s, 1H), 5.79 (ddd, $^3J_{HH}$ = 17 Hz, $^3J_{HH}$ = 11 Hz, $^3J_{HH}$ = 6 Hz, 1H), 5.28−5.22 (m, 2H), 4.45−4.35 (m, 1H), 1.69−1.56 (m, 2H), 1.40−1.20 (m, 10H), 0.88 (t, $^3J_{HH}$ = 7 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 161.1, 136.7, 116.0, 92.9, 53.5, 34.5, 31.7, 29.2, 29.1, 25.5, 22.6, 14.0. IR (neat, NaCl): 3423, 1694, 1519 cm^{-1}. MS (EI): *m*/*z* [%] 301 [8, M$^+$], 299 [9, M$^+$], 266 [15, M$^+$ − Cl], 264 [23, M$^+$ − Cl], 202 [70, M$^+$ − C_7H_{15}], 200 [100, M$^+$ − C_7H_{15}]. Anal. Calcd For $C_{12}H_{20}Cl_3NO$: C, 47.94; H, 6.71; N, 4.66. Found: C, 47.63; H, 6.50; N, 5.05.

2,2,2-Trichloro-*N*-(1-(2-phenylethyl)-allyl)acetamide (4d). 3d (160 mg, 0.52 mmol) and **2b** (13 mg, 0.027 mmol) were processed as outlined in the general procedure. Purification using column chromatography (2% ethyl acetate:98% hexanes) gave 76 mg (48%) of the title compound as a colorless oil. The spectral data for the title compound matched the literature data.[33]

2,2,2-Trichloro-*N*-(1-isopropylallyl)acetamide (4e). 3e (196 mg, 0.80 mmol) and **2b** (20 mg, 0.04 mmol) were processed as outlined in the general procedure. Purification using column chromatography (2% ethyl acetate:98% hexanes) gave 65 mg (33%) of the title compound as a white solid, mp = 42−43 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73−6.51 (br s, 1H), 5.80 (ddd, $^3J_{HH}$ = 17 Hz, $^3J_{HH}$ = 10 Hz, $^3J_{HH}$ = 6 Hz, 1H), 5.25−5.19 (m,

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2H), 4.31−4.28 (m, 1H), 1.93 (sept, $^3J_{HH}$ = 7 Hz, 1H), 0.97 (d, $^3J_{HH}$ = 7 Hz, 3H), 0.95 (d, $^3J_{HH}$ = 7 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.4, 135.3, 116.9, 93.1, 58.9, 32.2, 18.9, 18.0. IR (neat, NaCl): 3301, 1690, 1530 cm^{-1}. MS (EI): *m*/*z* [%] 245 [16, M^+], 243 [17, M^+], 202 [97, $M^+ - C_3H_7$], 200 [100, $M^+ - C_3H_7$].

X-ray Crystallography. All single crystals were immersed in oil and mounted on a glass fiber. Data were collected on a Rigaku/ADSC CCD diffractometer **2a** or a Bruker X8 APEX diffractometer **2b** with graphite-monochromated Mo Kα radiation. All structures were solved by direct methods and subsequent Fourier difference techniques. All non-hydrogen atoms were refined anisotropically with hydrogen atoms being included in calculated positions but not refined. All data sets were corrected for absorption effects (TwinSolve for **2a**, SADABS for **2b**), Lorentz, and polarization effects. All calculations on crystal **2a** were performed using SHELXL-97,[34] whereas all refinement of **2b** was performed using the SHELXTL[35] crystallographic software package from Bruker-AXS. Compound **2a** crystallizes with one disordered half molecule of dichloromethane residing on an inversion center in the asymmetric unit. Compound **2b** crystallizes with two disordered molecules of dichloromethane in the asymmetric unit. Additional crystal data and details of the data collection and structure refinement are given in Table 1. Further details are included in the Supporting Information.

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Note added in proof: Since this manuscript was accepted an article detailing the use of ligands of type H (Chart 1) in catalyzed conjugate addition reactions. See: Hayashi, A.; Okazaki, M.; Okawa, F. *Organometallics* **2007**, *26*, 5246.

Supporting Information Available: Full details of the crystal structure investigation (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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