Novel Coupling Reaction of Terminal Acetylenes with a Coordinated $Ph_2PCH_2CH_2NMe_2$ Ligand Involving C−H Activation of the $-CH_2CH_2-$ Chain

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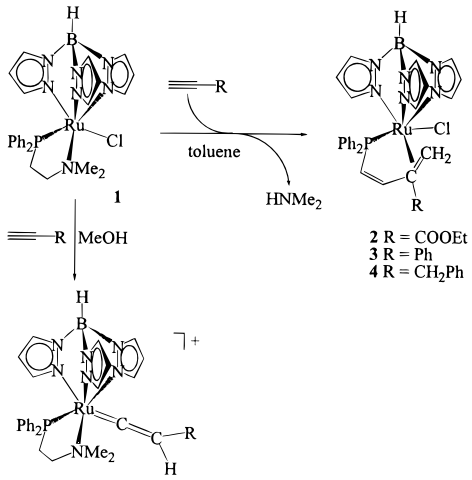
*Summary: RuTp(κ^2(P,N)-$Ph_2PCH_2CH_2NMe_2$)Cl (**1**) reacts with HC≡CR (R = COOEt, Ph, CH_2Ph) to afford the novel coupling products RuTp(Cl)(κ^3(P,C,C)-Ph_2-PCH═CHC(R)═CH_2) (R = COOEt, Ph, CH_2Ph) (**2**−**4**) in high yields. This reaction involves C−H activation of the $-(CH_2)_2-$ chain with concomitant C−N bond cleavage and liberation of $HNMe_2$. **2** has been characterized by X-ray diffraction.*

The chemistry of transition-metal vinylidene complexes has attracted some attention in recent years, especially because of their occurrence as key intermediates in stoichiometric and catalytic transformations of organic molecules.[1] We have previously shown[2] that the neutral vinylidene complex $RuTp(PPh_3)(Cl)(=C=CHPh)$ (Tp = tripyrazolylborate) is capable of initiating the catalytic dimerization of terminal acetylenes to give enynes. This reaction proceeds via the coordinatively unsaturated alkynyl complex $RuTp(PPh_3)(C\equiv CPh)$, which is formed as an intermediate by 1,3-elimination of HCl.[2,3] In the present communication we set out to study the reaction of RuTp(κ^2(P,N)-$Ph_2PCH_2CH_2NMe_2$)Cl (**1**) with terminal acetylenes HC≡CR (R = Ph, CH_2Ph, COOEt), expecting to see one-end cleavage of the $Ph_2PCH_2CH_2NMe_2$ ligand with formation of the vinylidene complex RuTp(κ(P)-$PPh_2CH_2CH_2NMe_2$)(Cl)(=C=CHPh). Phosphino−amine ligands are in fact hemilabile, promoting the formation of vinylidene complexes.[4,5] In addition, the basicity of the NMe_2 moiety should facilitate HCl elimination.

The actual course of reaction turned out to be highly sensitive to the polarity of the solvent, as shown in Scheme 1. In refluxing methanol, the reaction of **1** with HC≡CR led to simple chloride substitution, giving the known cationic vinylidene complexes [RuTp(κ^2(P,N)-$Ph_2PCH_2CH_2NMe_2$)(=C=CHR)]$^+$, without Ru−N bond cleavage.[6] Similarly, **1** reacts in boiling EtCN to give [RuTp(κ^2(P,N)-$Ph_2PCH_2CH_2NMe_2$)(NCEt)]$^+$. In refluxing toluene, on the other hand, an unusual coupling reaction takes place between **1** and an excess of HC≡CR (R = COOEt, Ph, CH_2Ph) to afford, after 7 h, the novel complex RuTp(Cl)(κ^3(P,C,C)-Ph_2PCH═CHC(R)═CH_2) (**2**−**4**) in high yields. This is an insertion reaction of acetylene featuring C−H activation of the $-(CH_2)_2-$ group with concomitant C−N bond cleavage. The difference in reactivity between the methanol and toluene solutions may be sought in terms of the stabilization of the chloride anion in a polar solvent.

Scheme 1



The complexes **2**−**4** are air-stable both in solution and in the solid state. Characterization was by elemental analysis and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR and IR spectroscopy.[7] Accordingly, the ^{1}H and ^{13}C{^{1}H} NMR spectra of **2**−**4** are inconsistent with the presence of a bidentate P,N-coordinated $Ph_2PCH_2CH_2NMe_2$ ligand as follows. The ^{1}H NMR spectrum of **2** no longer shows resonances of a NMe_2 functionality but exhibits two low-field doublets of doublets at 7.90 (dd, $^2J_{HP}$ = 46.2 Hz, $^3J_{HH}$ = 8.6 Hz) and 6.47 ppm (dd, $^3J_{HP}$ = 5.4 Hz, $^3J_{HH}$ = 8.6 Hz) assignable to a PCH═CH moiety with the hydrogen atoms in a *cis* arrangement and two singlets at 5.98 and 4.92 ppm assignable to a terminal ═CH_2 group. In the ^{13}C{^{1}H} NMR spectrum low-field doublet resonances at 157.4 (PCH═*C*H), 126.4 (P*C*H═CH), 91.8 (PCH═CH*C*(COOEt)), and 87.5 (═*C*H_2) ppm diagnose the presence of four inequivalent diene carbon atoms of the Ph_2PCH═CHC(COOEt)═CH_2 ligand.

The structural identity of **2** was unequivocally proven by X-ray crystallography. The result is depicted in

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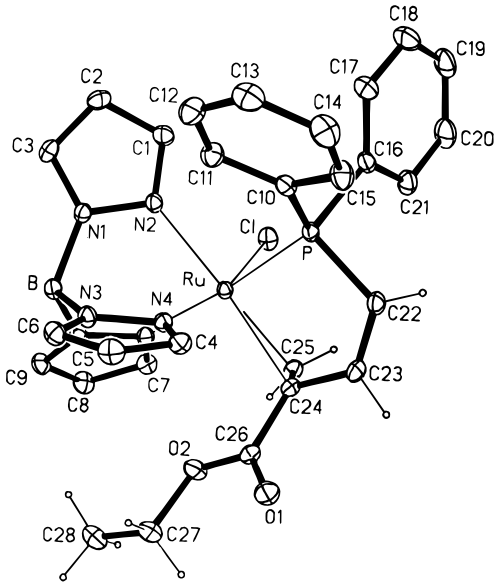

Figure 1. Structural view of RuTp(Cl)(κ^3(*P*,*C*,*C*)-Ph_2PCH═CHC(COOEt)═CH_2) (**2**). Selected bond lengths (Å) and angles (deg): Ru−N(2), 2.111(2); Ru−N(4), 2.113 (2); Ru−N(6), 2.154(2); Ru−P, 2.294(1); Ru−Cl, 2.423(1); Ru−C(24), 2.254(2); Ru−C(25), 2.171(2); C(22)−C(23), 1.320(3); C(23)−C(24), 1.485(3); C(24)−C(25), 1.393(3); P−Ru−Cl, 92.2(1); N(2)−Ru−N(4), 84.8(1); N(2)−Ru−N(6), 82.3(1); N(4)−Ru−N(6), 88.7(1); N(2)−Ru−P, 94.7(1); N(4)−Ru−P 91.1(1).

Figure 1.[8] The coordination geometry around ruthenium is somewhat distorted octahedral, with four coordination positions occupied by the Tp ligand and a chlorine atom, while the remaining two coordination sites are taken by the phosphorus atom and the terminal C═C bond of the 1,3-diene ligand Ph_2PCH═CHC(COOEt)═CH_2. The three Ru−N(Tp) bond lengths show only minor variations and are within the range observed for other ruthenium Tp complexes.[9,10] The Ru−Cl and Ru−P distances are 2.423(1) and 2.294(1) Å, respectively. The diene C−C bonds in Ph_2PCH═CHC(COOEt)═CH_2 adopt a short-long-short pattern (C(22)−C(23) = 1.320(3) Å, C(23)−C(24) = 1.485(3) Å, C(24)−C(25) = 1.393(3) Å), as is the case for many coordinated 1,3-diene ligands. The Ru bond to the terminal carbon atom C(25) (2.171((2) Å) is somewhat shorter than that to the internal carbon atom C(24) (2.254(2) Å).

While a detailed mechanistic proposal of the present reaction cannot yet be given, some conclusions may be drawn from the following observations. The reaction of **1** with HC≡CR proceeds via loss of $HNMe_2$, as monitored by ^{1}H NMR spectroscopy in benzene-d_6 at 80 °C (Scheme 1). In the case of the most reactive acetylene used here, HC≡CCOOEt, the liberated $HNMe_2$ is readily trapped as the enamine Me_2NCH═CHCOOEt. In the further course of reaction no other intermediate could be detected by NMR spectroscopy, aside from the reaction products **2**−**4**. Furthermore, when the deuterated acetylene DC≡CPh is reacted with **1**, again in benzene-d_6 at 80 °C, no deuterium is found to be incorporated into complex **3**. It is thus obvious that the hydrogen atoms of the terminal ═CH_2 group of the Ph_2PCH═CH(Ph)═CH_2 ligand stem from the CH_2CH_2 chain of the phosphino−amine ligand, which is doubly dehydrogenated at the intervention of the metal center. Further mechanistic studies will be reported in due course.

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Supporting Information Available: Text giving full experimental details and spectroscopic analytical data for complexes **3** and **4** and tables of X-ray structural data, including data collection parameters, positional and thermal parameters, and bond distances and angles, for complex **2** (10 pages). Ordering information is given on any current masthead page.

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(7) Preparation and data for **2**: A suspension of **1** (210 mg, 0.35 mmol) in toluene (4 mL) was treated with an excess of HC≡CCOOEt (200 μL) and heated under reflux for 7 h. After removal of the solvent the residue was dissolved in 2 mL of diethyl ether and the product was precipitated with *n*-hexane. Yield: 216 mg (94%). Anal. Calcd for $C_{28}H_{29}BClN_6O_2PRu$: C, 50.97; H, 4.43; N, 12.74. Found: C, 50.92; H, 4.40; N, 12.79. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.04 (d, J = 2.5 Hz, Tp), 7.90 (dd, $^3J_{HHcis}$ = 8.6 Hz, $^2J_{PH}$ = 46.2 Hz, PC*H*═CH), 7.84 (d, J = 2.5 Hz, Tp), 7.68 (d, J = 2.6 Hz, Tp), 7.63 (d, J = 2.6 Hz, Tp), 7.55 (d, J = 2.6 Hz, Tp), 7.42−7.19 (m, 5H), 7.10−6.96 (m, 4H), 6.59 −6.51 (m, 2H), 6.47 (dd, $^3J_{HHcis}$ = 8.6 Hz, $^3J_{PH}$ = 5.6 Hz, PCH═C*H*), 6.26 (pt, J = 2.5 Hz, J = 2.5 Hz, Tp), 6.19 (pt, J = 2.5 Hz, J = 2.5 Hz, Tp), 5.98 (s, ═CH_2), 5.82 (m, Tp), 4.92 (s, ═CH_2), 3.34 (m, 2H, diastereotopic CH_2), 0.30 (t, 3H, CH_3). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 173.3 (*C*OOEt), 157.4 (d, $^2J_{CP}$ = 18.6 Hz, PCH═*C*H), 147.7 (Tp), 146.2 (Tp), 142.2 (Tp), 137.0 (Tp), 135.22 (Tp), 135.17 (Tp), 135.1 (d, $^1J_{PC}$ = 50.7 Hz, Ph^1), 134.3 (d, $^2J_{PC}$ = 9.7 Hz, Ph^{2,6}), 132.9 (d, $^2J_{PC}$ = 9.2 Hz, Ph$^{2',6'}$), 130.7 (d, $^4J_{PC}$ = 2.2 Hz, Ph^4), 130.5 (d, $^1J_{PC}$ = 46.9 Hz, Ph$^{1'}$), 130.3 (d, $^4J_{PC}$ = 2.7 Hz, Ph$^{4'}$), 128.6 (d, $^3J_{PC}$ = 10.4 Hz, Ph^{3,4}), 128.4 (d, $^3J_{PC}$ = 9.8 Hz, Ph$^{3',5'}$), 126.4 (d, $^1J_{PC}$ = 39.8 Hz, P*C*H═CH), 106.5 (Tp), 106.2 (d, $^4J_{PC}$ = 3.3 Hz, Tp), 106.0 (Tp), 91.8 (d, $^3J_{PC}$ = 6.9 Hz, *C*(COOEt)), 87.5 (d, $^4J_{PC}$ = 2.2 Hz, ═CH_2), 60.5 (CH_2), 13.5 (CH_3). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 64.9. IR (diffuse reflectance, cm^{-1}): 2489 (m, B−H), 1702 (s, C═O).

(8) Crystal data for **2**: monoclinic, space group $P2_1/c$ (No. 14), a = 22.108(3) Å, b = 7.995(2) Å, c = 17.063(3) Å, β = 112.09(1),° 2794.6(9) Å^3, Z = 4, R1 = 0.040 (all data), wR2 = 0.063 (all data), no. of reflections 18 260, no. of refined parameters 375.

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