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Preliminary communication

Isomerization of allyldiphenylphospine to (*Z*)-1-propenyldiphenylphospine in rhodium(I) complexes

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Abstract

Allylic double bonds in $CH_2{=}CHCH_2PPh_2Rh^I$ complexes undergo slow spontaneous isomerization to give (Z)-$CH_3CH{=}CHPPh_2Rh^I$ complexes.

Rhodium complexes are efficient catalysts for carbonylation [1], hydroformylation [2], and isomerization [3,4] of allylamines and allyl ethers. Despite the widespread use of these reactions, the pertinent mechanistic details and reaction intermediates have remained obscure. Our earlier attempts to isolate Rh(acac)(CO)L, acac = acetylacteonate, [5,6], RhCl(cod)L, cod = 1,5-cyclooctadiene [7,8], and $RhCl(CO)_2L$ complexes [9], where $L = CH_2{=}CHCH_2NHR$, R = H, C_2H_5, and C_6H_{11}, have been unsuccessful owing to the inertness of $Rh(acac)(CO)_2$ and $[Rh(cod)Cl]_2$ towards allyl amines, and instability of complexes formed by the reaction of the latter with $[Rh(CO)_2Cl]_2$.

In order to gain some insight into the course of rhodium-catalyzed double bond isomerizations we now use allyldiphenylphosphine complexes in which Rh–P bond can be expected to both facilitate the coordination of the allyl carrying moiety at rhodium, and stabilize the intermediates.

Reaction of $CH_2{=}CHCH_2PPh_2$ (L) with $Rh(acac)(CO)_2$ in diethyl ether gave Rh(acac)(CO)L (**1**) in 65% yield. Complex **1** (m.p. 121°C) was identified from its infrared (ν(CO) 1975 cm^{-1} in nujol mull) and NMR spectra. The latter (C_6D_6, 23°C, ^1H referenced to tetramethylsilane, ^{31}P referenced externally to H_3PO_4) showed the CH_2P group (δ_H 3.16 dd, $J_{H,P}$ 11 Hz, $^3J_{H,H}$ 7 Hz), the vinyl group (δ_H 4.9 m and 6.0 m), and the phosphorus atom (δ_P 43.4 d, $J_{P,Rh}$ 175 Hz).

Analogously, treatment of $[Rh(cod)Cl]_2$ with L in dichloromethane followed by crystallization from dichloromethane/methanol (1/5) afforded RhCl(cod)L (**2**, m.p. 110°C) in 60% yield. The NMR spectra showed an intact allyl group (δ_H 3.49 ddt,

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$J_{H,P}$ 11 Hz, $^3J_{H,H}$ 7 Hz, $^3J_{H,Rh}$ 1 Hz) and the Rh-coordinated phosphorus atom (δ_P 24.1 d, $J_{P,Rh}$ 151 Hz).

The $RhCl(CO)L_2$ complex (**3**) was prepared from $[Rh(CO)_2Cl]_2$ and L in methanol in 85% yield, m.p. 127 °C and identified from its IR (ν(CO) 1986 cm^{-1}) [10] and NMR spectra (δ_H 3.53 apparent triplet, 2H [11,12], 4.90 irregular triplet, 2H, 6.2 m, 1H; δ_P 23.4, $J_{P,Rh}$ 130 Hz).

The stretching vibrations in **1–3**, ν(C=C) 1633 cm^{-1}, indicate that the allylic double bonds are not coordinated to the metal in the solid state. The upfield shift of the CH_2P groups with respect to the signal of the free ligand in the ^{1}H NMR spectra is compatible with the coordination of phosphorus to rhodium and to the increasing $M \rightarrow L$ transfer in the order **3** < **2** < **1**. Comparison of the δ_H of the allylic protons in 1–3 with those in the free ligand (2.70 m, 4.90 m and 5.70 m) shows that the allyl group is not coordinated to rhodium via a stable π-olefinic bond [13–16].

In solution **1–3** undergo slow isomerization with halflives of ca. 3 d at 23 °C, to give the corresponding (*Z*)-propenyl isomers, Rh(acac)(CO)(*Z*)-$CH_3CH{=}CHPPh_2$ (**4**), RhCl(cod)(*Z*)-$CH_3CH{=}CHPPh_2$ (**5**), and RhCl(CO)[(*Z*)-$CH_3CH{=}CHPPh_2]_2$ (**6**), which were identified from their NMR spectra [17]. The propenyl double bonds in **4–6** are not coordinated to rhodium as indicated by the similarity of the δ_H values [17*] with those of the free ligand (1.55 m, 3H, 6.2 m, 1H, 6.7 m 1H) prepared independently [18].

The conversions of **1–3** into **4–6**, respectively, appear to be analogous to the rhodium-catalyzed isomerizations of allylamines, and so the complexes containing allylphosphine ligands serve to model the isomerization step. It is noteworthy that despite the strong coordination of the phosphine to rhodium the latter retains the ability to weakly coordinate the allyl group and induce the isomerization.

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17 4: δ_H 1.52 dt (^2J 7 Hz, ^4J 1.6 Hz, 3H) 6.2 m (1H), 6.7 m (1H); δ_P 42.9 d ($J_{P,Rh}$ 175 Hz). 5: δ_H 1.54 dt (3H), 6.3 m (1H), 6.7 m (1H); δ_P 22.3 d ($J_{P,Rh}$ 151 Hz). 6: δ_H 1.49 m (3H), 6.2 m (1H), 6.7 m (1H); the ^{31}P NMR spectrum showed several signals.
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* Reference number with asterisk indicates a note in the list of references.