

Letter

The Role of α,ω -Bis(diphenylphosphino)alkanes in Rhodium-catalyzed Hydroformylation of Substituted Terminal Olefins

W. DRENTH

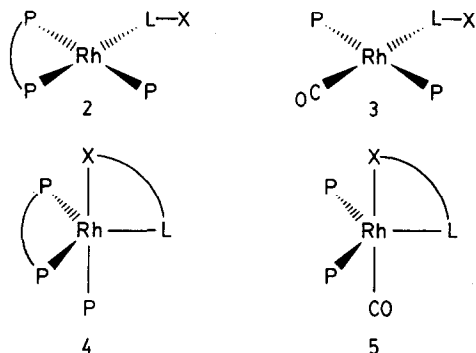
Laboratory for Organic Chemistry of the University, Croesestraat 79, 3522 AD Utrecht (The Netherlands)

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Terminal olefins with a second functional group, such as allyl acetate, are sluggish in hydroformylation with a rhodium catalyst at low pressure. In 1982 Matsumoto and Tamura [1] described the interesting observation that on addition to the rhodium catalyst of a nearly equimolar amount of α,ω -bis(diphenylphosphino)alkane, $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 2 - 4$), **1**, in the presence of a large excess of PPh_3 , the hydroformylation proceeds quite smoothly even at 1 atm. In general, **1** with $n = 3$ gives the best results.

The retarding effect of the second function, *e.g.* the acetate function of allyl acetate, is undoubtedly due to coordination of this function to the rhodium atom, the substrate behaving as a chelating ligand. This chelation would prevent the *cis* oxidative addition of a hydrogen molecule to the rhodium complex. Matsumoto and Tamura ascribe the accelerating effect of added **1** to a suppression of this chelation. We agree with their opinion, but we believe their picture needs some refinement. In Matsumoto and Tamura's explanation it is not clear why the second phosphorus atom in **1** would prevent chelation of the substrate without itself being a retarding ligand.

The combination of high chelating ability of **1** and high concentration of triphenylphosphine will favor the formation of species with three phosphorus atoms in the rhodium ligand sphere [2, 3]. Therefore, we propose



that in the presence of **1** and PPh_3 hydroformylation occurs through complex **2**, whereas in the absence of **1** hydroformylation is generally believed to involve complexes which have only one or two phosphorus atoms (**3**). In these structures L—X is the substrate species, e.g. $-\text{CO}(\text{CH}_2)_3\text{OCOCH}_3$ in the case of allyl acetate. Chelation of L—X will lead to a five-coordinated rhodium, which probably has a trigonal bipyramidal configuration. In this configuration L—X requires two equatorial or one equatorial and one axial position. Thus, starting from **2**, chelation of L—X requires one phosphorus atom to move to an axial position as in **4**. However, in such a bipyramidal configuration the three phosphorus atoms prefer equatorial positions [**3**]. Therefore, chelation of L—X and prevention of further reaction is less likely. Starting from **3** chelation is very possible since CO does not have any objection against an axial position, **5**. Thus, a chelating substrate has a retarding effect when one or two, but not when three phosphine ligands are present in the coordination sphere.

Acknowledgement

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References

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- 3 O. R. Hughes and D. A. Young, *J. Am. Chem. Soc.*, **103** (1981) 6636.