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Platinum Dichloride Complexes with (*R*,*R*)-[(Bicyclo[2.2.2]-octane-2,3-diyl)bis(methylene)]bis[diphenylphosphine]- or bis[5H-benzo[b]phosphinindole]: New Catalyst Precursors for Enantioselective Hydroformylation

Giambattista Consiglio* and Sylvia C.A. Nefkens

Swiss Federal Institute of Technology, Department of Industrial and Engineering Chemistry, ETH-Zentrum, CH-8092 Zürich, Switzerland

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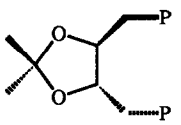
Abstract: The preparation of the platinum dichloride complexes with (*R*,*R*)-[(bicyclo [2.2.2]octane-2,3-diyl)bis(methylene)]bis[diphenylphosphine]- or bis[5H-benzo[b]-phosphinindole] is reported. The complexes have been tested as catalyst precursors for enantioselective hydroformylation of some aromatic olefins. Asymmetric inductions up to 85% have been obtained.

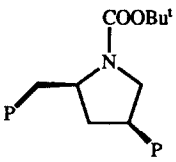
The enantioselective hydroformylation of olefins is a very attractive reaction for the synthesis of valuable optically active aldehydes [1]. However, despite numerous investigations with the classic rhodium catalysts the stereoselectivity remains low [2]. Platinum dichloride-tin dichloride based catalytic systems have shown higher levels of enantioselectivity when modified by Diop **1** (diop is [(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis-(methylene)]bis[diphenylphosphine]), (best ee ~82% using methyl methacrylate as the substrate [3]) or Diop-dbp **2** (Diop-dbp is [(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)bis[5H-benzo[b]phosphinindole]) (best ee ~80% for styrene as the substrate [4]). Similar systems modified by Bppm **3** (Bppm is 1-pyrrolidinecarboxylic acid-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]-*t*-butyl ester) seem to give almost quantitative enantioselectivity, when the hydroformylation reaction is carried out in the presence of ethyl orthoformate in order to convert the formed aldehydes "in situ" to the corresponding acetals which are expected to be optically stable [5,6]. Under these conditions, however, reaction rates are impractical. The aforementioned chiral ligands, which form 7-membered chelation rings, show very high catalytic activity in the platinum catalysed hydroformylation [2-5,7,8]. However, they do not seem to be rigid enough and therefore not the best choice for enantioselective reactions [9].

We report here the preparation of the platinum dichloride complex **4a** and **5a** of Bco-dpp **4** (Bco-dpp is (*R*,*R*)-[(bicyclo[2.2.2]octane-2,3-diyl)bis(methylene)]bis[diphenylphosphine])[10] and of Bco-dbp **5** (Bco-dbp is (*R*,*R*)-[(bicyclo[2.2.2]octane-2,3-diyl)bis(methylene)]bis[5H-benzo[b]phosphinindole]) and some preliminary results concerning their use as catalysts for enantioselective hydroformylation. Ligand **4** was already known [10], whereas ligand **5** was prepared according to literature procedure for analogous compounds [10,11]. The ligands **4** and **5** were reacted with $(C_6H_5CN)_2PtCl_2$ **6** in benzene following literature methods for the synthesis of compounds of the type (diphosphine)$PtCl_2$ [12]. **4** gave the expected chelate compound, (Bco-dpp)$PtCl_2$ **4a**, identified through multinuclear NMR ($CDCl_3$, δ ^{31}P 9.1 ppm, $J_{P\text{-}Pt}$ 3562 Hz) and elemental analysis. In contrast, in the reaction of **5** with **6** two products (in a variable molar ratio) were formed as recognized from ^{31}P

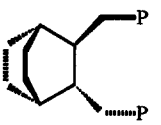
NMR. Both products give single lines accompanied by ^{191}Pt satellites, the coupling constants being about the same for the both products ($CDCl_3$, **5a** : δ ^{31}P 8.8 ppm, $J_{P\text{-}Pt}$ 3404 Hz and **5a'**: δ ^{31}P 1.2 ppm, $J_{Pt\text{-}P}$ 3463 Hz); the latter product shows broader lines in the spectrum. The elemental analysis of this mixture is, however,



1
2



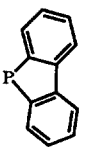
3



4
5

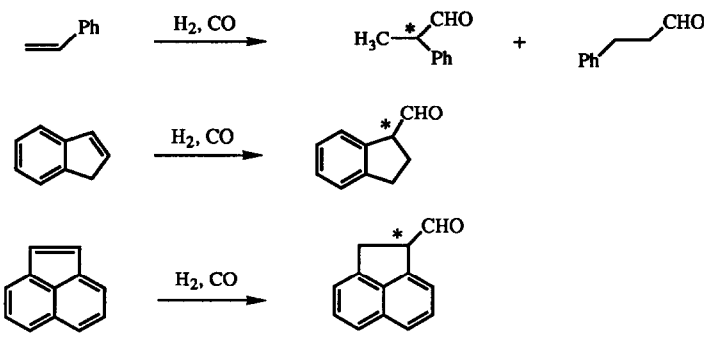
1, 3, 4: P = PPh_2

2, 5: P =



consistent with a product containing the ligand and platinum dichloride in a 1:1 ratio. Attempts to follow the exchange reaction through NMR failed because of precipitation of the product. However, in the analogous reaction of **6** with racemic **5** at the beginning of the reaction only a broad signal can be recognized in the region around 1 ppm, the signal being much larger than that corresponding to product **5a'**. The system slowly evolves to a situation in which this broad signal almost completely disappears, giving rise to a small amount of product **5a** and to the overwhelming formation of another product **5a''** ($CDCl_3$, δ ^{31}P 3.3 ppm, $J_{P\text{-}Pt}$ 3456 Hz) The shape of the signals in ^{31}P-NMR indicates that all the species must be symmetric and the broadness of some of the lines suggests that these might correspond to oligomeric species. Furthermore, there are no signals corresponding to non-bound phosphorus atoms. Species consisting of chlorine bridged platinum dimers appear unlikely [13].We therefore suggest that oligomeric materials form in which the diphosphine behaves as bridging ligand. The oligomerization degree of these associates is not known; for similar compounds dimeric or trimeric structures have been proposed [14]. For the enantiomerically pure ligand the signal at 1.2 ppm (**5a'**) corresponds to a species containing homochiral ligands. In the case of the racemic ligand the signal at 3.3 ppm (**5a''**) therefore should correspond to the analogous species containing heterochiral ligands. Here, we hardly observe any signal corresponding to **5a'**, the exact quantity of which is, however, difficult to ascertain as the signal for the latter compound lies close to the region where we find a very broad signal which is ascribed to higher oligomeric species. Therefore, when the racemic ligand is used, there is a remarkable diastereoselectivity in the formation of this oligomeric product which is in favour of an *ul*-diastereomer [15]. By heating the reaction mixture in a more polar solvent like dimethylsulfoxide or in the presence of $SnCl_2$ all systems (**5a'** and **5a''**) eventually give the signals corresponding to product **5a**. As this is the final product, we assume that it is the chelate compound.

Compounds **4a** and **5a** were tested as catalyst precursors in the presence of $SnCl_2$ for the enantioselective hydroformylation of some aromatic substrates (Table 1 and Scheme 1). Styrene is hydroformylated with high enantioselectiviy and regioselectivity by **5b**. In fact, the enantiomeric excess obtained is the highest observed in the formation of optically active hydratropaldehyde through hydroformylation [5,16,17] at the temperature used. Also the regioselectivity is one of the best reported [18]. Catalytic system **4b** is much less enantio- and regioselective. The new complex [{(*R*,*R*)-Bco-dpp}Pt(Cod)]$(BF_4)_2$ was found to promote hydroformylation, as expected [19]. However, it showed a much lower catalytic activity (~60% conversion after 115 h at 80°C in tetrahydrofuran) and enantioselectivity (~1% ee) than the corresponding tin-containing catalytic system.



Scheme 1

The enantioselective hydroformylation of acenaphthylene has never been reported, in spite of the possible interest in optically active 1-formylacenaphthene as a starting material for products having biological properties[20]. The conversion was kept to a low level in order to avoid racemization of the aldehyde formed, which was suspected to be optically instable [21]. For the determination of the enantioselectivity of the reaction, the formed aldehyde was reduced with $(i\text{-}C_4H_9)_2AlH$ at low temperature and the enantiomeric excess of the formed alcohol was determined by NMR using $Eu(dcm)_3$ (Tris[d,d-dicampholyl-methanato]europium(III)) as the chiral shift reagent. Again the enantioselectivity achieved by **5a** is higher than that of **4a**. It is to note that ligand **3**, which was found to be very effective for many substrates [5], gives a system which is less enantioselective than **5a**.

Table I. Platinum catalysed enantioselective hydroformylation of some aromatic olefins [a]

Substrate	Catalyst precursor	Reaction time (h)	Conversion %	Selectivity [b] %	Isomeric ratio	Enantiomeric excess (%)
styrene	**4a**	20	100	90	57/43 [d]	25(S)
styrene	**5a**	23	95	75	8/92 [d]	85(S)
acenaphthylene	**4a**	48	85	95	--	20
acenaphthylene	**5a**	7	35	89	--	48
acenaphthylene	**3a**	70	33	98	--	43
indene [c]	**5a**	7	22	>95	[f]	45

[a] Reaction conditions: (L-L)$PtCl_2/SnCl_2$ (molar ratio 1:2.75) as the catalyst precursor 0.043 mmol, substrate 43 mmol in 50 ml benzene or toluene as the solvent, 50 °C (unless otherwise stated); p (CO) = 70 atm; p (H_2) = 150 atm; t = 50 °C. [b] moles carbonylation products/moles converted substrate. Competitive hydrogenation of the substrate takes place. [c] Reaction temperature 80 °C. [d] 3-phenylpropanal/2-phenylpropanal. [f] Only 1-formylindane is formed.

We are aware of only one report concerning the enantioselective hydroformylation of indene [22]; the enantioselectivity of the reaction was, however, not determined. Using catalyst precursor **5a** and working at 80 °C we observed a very selective formation of 1-formylindane with no traces of the alternative regioisomer in the gas-chromatographic analysis. The aldehyde was again not isolated but was immediately transformed to the corresponding alcohol through reduction with $(i\text{-}C_4H_9)_2AlH$. The e.e. determined as above was ~45%. Experiments are in progress to extend the use of these catalyst precursors to other olefinic substrates.

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