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Preliminary communication

MIXED LIGAND PLATINUM COMPLEXES AS HYDROGENATION CATALYSTS

HOWARD C. CLARK*, CLAUDE BILLARD and CHUN S. WONG

Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, University of Guelph, Guelph, Ontario N1G 2W1 (Canada)

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Summary

$PtLL'Cl_2$ ($L = PPh_3$, L' = sulphides, amines) are more effective catalysts for the hydrogenation of styrene to ethylbenzene, in the presence of $SnCl_2 \cdot 2H_2O$ than PtL_2Cl_2 or PtL'_2Cl_2; this effect is attributed to the ability of the weaker ligand L' to function as a leaving group in the catalytic hydrogenation cycle.

One valuable aspect of mixed-ligand platinum(II) complexes [1] of the type $PtLL'X_2$ (L,L' = Group V or VI ligands) lies in the opportunity they offer to study the effect on chemical properties of varying just one ligand, L or L′. The complexes PtL_2Cl_2, L = phosphine, arsine or sulphide, have been used extensively as catalysts for the hydrogenation of olefins [2] in the presence of $SnCl_2 \cdot 2H_2O$. In this communication we describe some studies of the catalyzed hydrogenation of olefins using $PtLL'Cl_2/SnCl_2 \cdot 2H_2O$ as catalyst. We show that not only can ligand effects on catalytic activity be examined by varying systematically just one ligand L′, but also that by suitable choice of ligands, catalytic activity can be greatly enhanced, surpassing that of the corresponding bis-ligand complexes.

The results of the catalytic hydrogenation of styrene to ethylbenzene at 60°C, 600 psi H_2 in acetone using various $PtLL'Cl_2/SnCl_2 \cdot 2H_2O$ catalysts are summarized in Tables 1 and 2. Table 1 shows the effect of varying the $SnCl_2 \cdot 2H_2O$ concentration on catalytic activity.

Unlike the $PtL_2Cl_2/SnCl_2 \cdot 2H_2O$ systems, which exhibit [3] maximum catalytic activity at $[SnCl_2]/[Pt] = 10$, the mixed ligand system has maximum activity at $[SnCl_2]/[Pt] = 2$ for $L = Ph_3P$, $L' = SMe_2$ or $L = PPh_3$, $L' = p\text{-}CH_3PhNH_2$. A value of 2 for Sn/Pt was therefore used for all subsequent catalytic hydrogenation studies using mixed ligand complexes as catalysts. Presumably these different Sn/Pt ratios just reflect differences in the equilibria between the chloride and $SnCl_3$ complexes perhaps influenced by the different *trans* effects of the ligands. Several notable trends are apparent from an inspection of Table 2:

1. The dependence on the electronic effect of L, L = phosphine, is the same

TABLE 1

CATALYTIC HYDROGENATION OF STYRENE TO ETHYLBENZENE USING $PtLL'Cl_2/SnCl_2 \cdot 2H_2O$ AS CATALYST AT 60°C, 600 psi H_2, 2 h IN ACETONE. EFFECT OF $SnCl_2 \cdot 2H_2O$ CONCENTRATION

Catalyst	$[SnCl_2 \cdot 2H_2O]/[Pt]$	T.N. obtained
$Pt(PPh_3)(SMe_2)Cl_2$	1	4090
$Pt(PPh_3)(SMe_2)Cl_2$	2	6860
$Pt(PPh_3)(SMe_2)Cl_2$	3	3930
$Pt(PPh_3)(SMe_2)Cl_2$	5	2760
$Pt(PPh_3)(p\text{-}CH_3PhNH_2)Cl_2$	1	2700
$Pt(PPh_3)(p\text{-}CH_3PhNH_2)Cl_2$	2	7040
$Pt(PPh_3)(p\text{-}CH_3PhNH_2)Cl_2$	3	6800
$Pt(PPh_3)(p\text{-}CH_3PhNH_2)Cl_2$	4	6000
$Pt(PPh_3)(p\text{-}CH_3PhNH_2)Cl_2$	5	5100
$Pt(PPh_3)(p\text{-}CH_3PhNH_2)Cl_2$	6	4680
$Pt(PPh_3)(p\text{-}CH_3PhNH_2)Cl_2$	8	4640
$Pt(PPh_3)(p\text{-}CH_3PhNH_2)Cl_2$	10	4720

TABLE 2

CATALYTIC HYDROGENATION OF STYRENE IN ACETONE, AT 600 psi, 60°, 2 h, USING $PtLL'Cl_2/2SnCl_2 \cdot 2H_2O$ AS CATALYST[a]

L	L'	Total T.N.
$P(p\text{-}CH_3OPh)_3$	as L	1820 [b]
$P(p\text{-}CH_3Ph)_3$	as L	1660 [b]
PPh_3	as L	1600 [b]
$P(p\text{-}ClPh)_3$	as L	850 [b]
$P(p\text{-}FPh)_3$	as L	810 [b]
$P(p\text{-}CH_3OPh)_3$	SMe_2	8210
$P(p\text{-}CH_3Ph)_3$	SMe_2	7450
PPh_3	SMe_2	6860
$P(p\text{-}FPh)_3$	SMe_2	5170
PPh_3	$p\text{-}NH_2PhOCH_3$	6610
PPh_3	$p\text{-}NH_2PhCH_3$	7030
PPh_3	NH_2Ph	7460
PPh_3	$p\text{-}NH_2PhCl$	7960
PPh_3	$p\text{-}NH_2PhNO_2$	8880
PPh_3	SEt_2	8160
PPh_3	SPh_2	8570
PPh_3	$S(p\text{-}PhCl)_2$	8680
$p\text{-}NH_2PhNO_2$	as L	680
SMe_2	as L	370 [c]

[a] [styrene]/[Pt] = 10 000. [b] 10 $SnCl_2 \cdot 2H_2O$ used. [c] There is also some polymerization, estimated 940 equivalent of styrene polymerized.

for both PtL_2Cl_2 and $PtLL'Cl_2$, i.e., electron donating *p*-substituents enhance catalytic activity.

2. In the mixed ligand complexes, the weaker coordinating ligand L' (L' = amine, compared to the stronger coordinating L = PPh_3) exhibits the opposite dependence of catalytic activity on electronic effects. Thus in the amine series, the effectiveness of the catalyst increases as the basicity of the amine decreases.

3. Generally, the mixed ligand complexes, containing one strong ligand, e.g. phosphine, and a weak ligand, e.g. amine, or sulphide, are more effective as catalysts than their corresponding bis(ligand) complexes. Thus, the catalytic activity of $Pt(PPh_3)(SMe_2)Cl$ is more than four times greater than that of $Pt(PPh_3)_2Cl_2$ and 20 times greater than $Pt(SMe_2)_2Cl_2$. Similarly, $Pt(PPh_3)(p\text{-}NO_2PhNH_2)Cl_2$ is more effective that either $Pt(PPh_3)_2Cl_2$ or $Pt(p\text{-}NO_2PhNH_2)_2Cl_2$.

The fact that the two ligands L and L′ show different dependences on the electronic properties of the *p*-substituents suggests that they function quite differently in the catalytic cycle. The increase of catalytic activity with decreasing basicity of the weaker ligand L′ further suggests that L′ functions as a leaving group. This is supported by the ^{1}H NMR spectrum of *cis*-$Pt(PPh_3)(SMe_2)Cl_2$ and $SnCl_2 \cdot 2H_2O$ in CD_3COCD_3. In the absence of $SnCl_2 \cdot 2H_2O$, the SMe_2 resonance appears as a sharp singlet with ^{195}Pt satellites (δ 2.48 ppm, J(PtH) 50.8 Hz). On addition of one equivalent of $SnCl_2 \cdot 2H_2O$ at room temperature, the SMe_2 resonance became broad and the ^{195}Pt satellites are not observable. However, at −60°C two SMe_2 resonances were observed, both with ^{195}Pt satellites, presumably due to two isomers (δ 2.60 ppm, ^3J(PtH) 46.4 Hz (major); δ 2.45 ppm, ^3J(PtH) 46.9 Hz). Thus, at ambient temperatures, the SMe_2 in the complex is labile in the presence of $SnCl_2$. The importance of creating a vacant coordination site in effecting certain chemical reactions has been well documented [4]. In many catalytic hydrogenation systems, e.g. with Wilkinson's catalyst, $Rh(PPh_3)_3Cl$ [5—7], dissociation of a ligand or its displacement by the substrate, is one of the important steps in the catalytic cycle. Thus, in the mixed ligand complexes, the introduction of a weak ligand affords a means of enhancing the catalytic activity of a catalyst, and also demonstrates a new approach to catalyst tailoring.

The present results also describe a different role for the $SnCl_3$ ligand which has previously been thought [8] to act as co-catalyst through its ability to stabilize low energy five coordinate platinum(II) intermediates. The role described here, i.e. labilization of the *trans* ligand, is however, fully consistent with the high *trans* effect [8] of the $SnCl_3$ ligand.

Further study on these interesting systems, particularly with the aim of elucidating the detailed mechanism, is in progress.

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