Activation of Carbon Dioxide, VI[◇]

Ligand Effects in the Catalytic Hydrogenation of Carbon Dioxide to Formic Acid Using in situ Catalysts Formed from [{(cod)Rh(μ-Cl)}$_2$] and Monodentate and Bidentate Phosphorus Ligands

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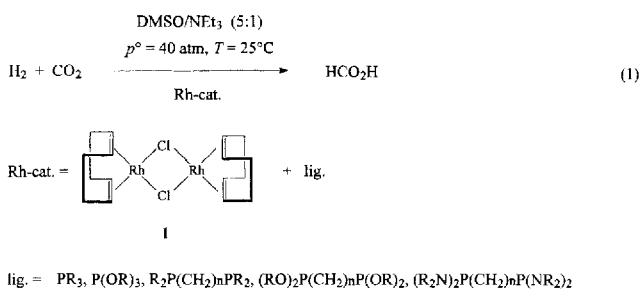
Highly active catalysts for the hydrogenation of CO_2 to formic acid in DMSO/NEt_3 are formed in situ from [{(cod)Rh(μ-Cl)}$_2$] and various monodentate or bidentate ligands with phosphorus as the donor atom. Formic acid concentrations up to 2.3 ± 0.2 mol l^{-1} can be obtained in less than 6 hours at ambient temperature under a total initial pressure of 40 atm by using rhodium concentrations of 5 · 10^{-3} mol l^{-1}. The changes in catalytic activities observed upon structural changes of monodentate ligands are discussed in terms of classical ligand parameters like basicity and steric demand of the PR_3 group, while with bidentate ligands $R_2P(CH_2)_nPR_2$ the chain length n plays a dominant role for the activity of the catalyst. The effects cannot be explained by a direct impact of the ligand on catalytically active intermediates only, but influences on the formation of these species must also be taken into account.

The hydrogenation of carbon dioxide to formic acid catalysed by transition metal complexes in homogeneous phase has recently gained considerable interest as a promising approach to the use of abundant CO_2 as a raw material in chemical synthesis[1,2]. Catalytic systems described in the literature operate in organic solvents[3], aqueous solutions[4], or in a supercritical phase[5]. We introduced a rhodium catalyst formed in situ from [{(cod)Rh(μ-Cl)}$_2$] (**1**) and the bidentate phosphane $Ph_2P(CH_2)_4PPh_2$ as a catalytic system that allowed turnover numbers of >1000 in the CO_2 hydrogenation to formic acid by using mixtures of DMSO and NEt_3 as a solvent[3a,b] (eq. 1). Neutral rhodium hydride complexes are the catalytically active species under these conditions[6], and a number of considerably more active catalysts were developed by using rhodium-containing precursors that allow a more direct access to these species than the dimeric chloro complex **1**[3b,c].



(1)

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lig. = PR_3, $P(OR)_3$, $R_2P(CH_2)nPR_2$, $(RO)_2P(CH_2)nP(OR)_2$, $(R_2N)_2P(CH_2)nP(NR_2)_2$

In the present study, we report on the influence of structural changes of the phosphorus ligand on the efficiency of in situ catalysts based on **1**. Monodentate phosphanes PR_3 and bidentate phosphanes $R_2P(CH_2)_nPR_2$ were investigated systematically, and hetero-substituted ligands with phosphorus as a donor atom were also addressed briefly. Formic acid concentrations obtained after given reaction times under a standard set of reaction conditions were used as a semi-quantitative probe for the catalytic activity. The catalysts formed with chelating ligands were activated with HCO_2H prior to use in order to avoid an induction period[3b]. No such activation was necessary with monodentate ligands as kinetic experiments carried out with selected systems revealed no induction period with this type of ligands. The equilibrium concentration of formic acid[3b] under the given conditions was 2.3 ± 0.2 mol l^{-1}. Some of the results presented here were described briefly as part of a conference report[1c].

Monodentate Phosphanes PR_3

In earlier studies[3a,b] it was shown that phosphorus ligands are vital components for the formation of active catalysts from **1**, and a maximum was found of the catalytic activity of in situ systems formed with bidentate phosphanes at a ratio of donor groups to rhodium P/Rh = 2:1, i.e. with one equivalent of bidentate ligand per rhodium. In sharp contrast, the catalytic activity of in situ catalysts formed from **1** and monodentate ligands PR_3 steadily increases up to a ratio of P/Rh = 10:1 (Figure 1). Under these conditions the equilibrium concentration of formic acid is already reached within less than 6 hours. The total number

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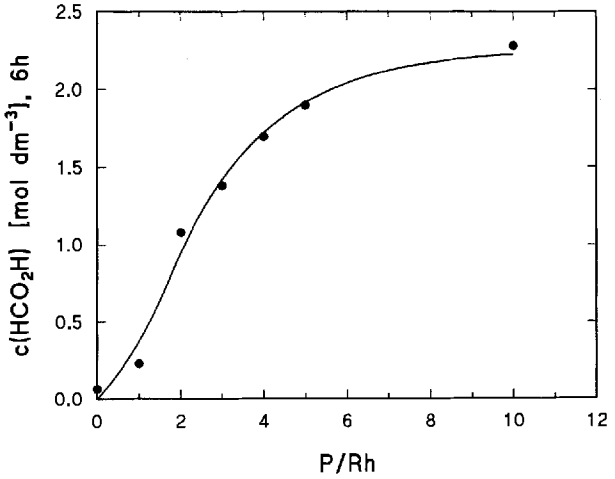
of catalytic turnovers for the formation of formic acid is 440. The limited solubility of the ligand P(4-MeC_6H_4)$_3$ in the reaction mixture prevented experiments at even higher P/Rh ratios and shorter reaction times.

Figure 1. Influence of the ratio of phosphorus donor per rhodium (P/Rh) on the catalytic activity of the in situ catalyst **1**/P(4-MeC_4H_4)$_3$. Reaction conditions: DMSO/NEt_3 (5:1), c(Rh) = 5 · 10^{-3} mol l^{-1}, T = 25°C, p^0 = 40 atm, t = 6 h



A variety of monodentate ligands PR_3 were tested as ligands for in situ catalysts with **1** (Table 1). A P/Rh ratio of 4:1 was used in all experiments, and quenching of the reaction after four hours ensured a formic acid concentration below equilibrium in all cases. The basicity of the phosphanes (given as the pK_a values[7a] of the corresponding acids R_3PH^+) and Tolman's[8] electronic parameter $\Sigma_{\chi i}$ are used for a description of the electronic properties of the ligands, while the cone angle[8] Θ is given as probe for their steric demand.

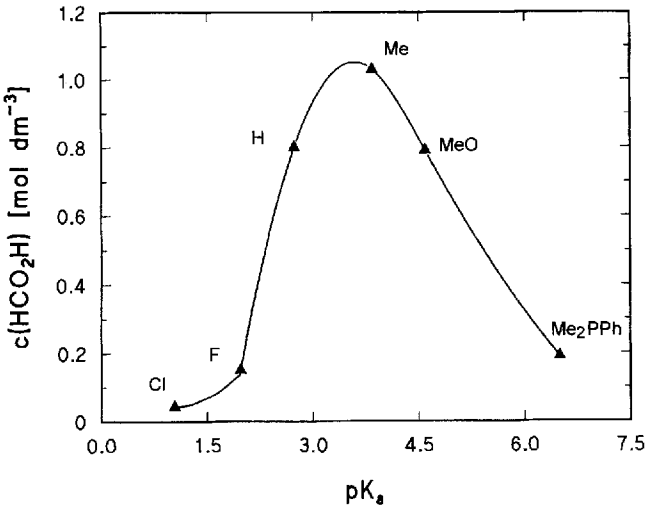
Table 1. Influence of the electronic and steric properties of monodentate phosphanes on the catalytic activity of in situ catalysts **1**/PR_3

Entry	Ligand	pk_a [a]	$\Sigma\chi_i$ [b]	Θ [b]	c(HCO_2H) [c] [mol l^{-1}]
1	$P(C_6H_5)_3$	2.73	12.9	145	0.80
2	$(C_6H_5)_2P(2\text{-}MeOC_6H_4)$	---	9.5	171	0.83
3	$(C_6H_5)P(2\text{-}MeOC_6H_4)_2$	---	6.1	(185)	0.23
4	$P(2\text{-}MeOC_6H_4)_3$	---	2.7	(200)	0.03
5	$P(4\text{-}MeOC_6H_4)_3$	4.59	10.2	145	0.79
6	$P(4\text{-}MeC_6H_4)_3$	3.84	10.5	145	1.03
7	$P(2\text{-}MeC_6H_4)_3$	3.08	10.5	194	0.06
8	$P(3,5\text{-}MeC_6H_3)_3$	(3)	(11)	(180)	0.78
9	$P(2,4,6\text{-}MeC_6H_2)_3$	---	8.1	212	0.04
10	$P(4\text{-}ClC_6H_4)_3$	1.03	16.8	145	0.04
11	$P(4\text{-}FC_6H_4)_3$	1.97	15.0	145	0.15
12	$Me_2P(C_6H_5)$	6.50	9.3	122	0.19

[a] From ref.[7a]; values in parentheses are interpolated. – [b] From ref.[8]; values in parentheses are interpolated. – [c] DMSO/NEt_3 (5:1), c(Rh) = 5 · 10^{-3} mol l^{-1}, P/Rh = 4:1, T = 25°C, p^0 = 40 atm, t = 4 h.

Figure 2 illustrates the influence of ligand basicity on the catalytic activity of **1**/P(4-RC_6H_4) (Table 1, entries 1, 5–6, 10–11). The activity shows a relatively narrow maximum for ligands of medium basicity at a pK_a of the corresponding acids R_3PH^+ of approximately 3.8. The *p*-methyl-substituted ligand P(4-MeC_6H_4)$_3$ forms the most active catalyst within the present series. The formic acid concentration obtained with **1**/P(4-MeC_6H_4)$_3$ (P/Rh = 4:1) is with 1.03 mol l^{-1} almost identical to the one obtained with the standard catalyst **1**/$Ph_2P(CH_2)_4PPh_2$ (P/Rh = 2:1) under the same reaction conditions (Table 2, entry 4b). Replacement of the methyl substituent in *p* position by more electron-donating or electron-withdrawing groups leads to a sharp decrease of the catalytic activity of the systems **1**/P(4-RC_6H_4)$_3$ (P/Rh = 4:1). The influence of basicity seems to generally apply to monodentate ligands of comparable steric demand as indicated by the low activity observed with Me_2PPh (Table 1, entry 12).

Figure 2. Influence of the basicity of ligands (4-RC_6H_4)$_3$P and Me_2PPh on the catalytic activity of in situ catalysts formed with **1**. Reaction conditions see Table 1



The steric demand of monodentate phosphanes is also very important for the activity of catalysts formed in the presence of **1** as illustrated by the results obtained with different methyl-substituted derivatives of PPh_3 (Table 1, entries 1, 6–9; Figure 3). The introduction of the *p*-methyl substituent leads to an increase in activity as outlined above. The electronic and steric effects of two methyl groups in *m* position compensate each other, leading to a similar catalytic activity as with the unsubstituted triphenylphosphane. The methyl group in *o* position gives rise to similar electronic properties of the ligand compared to the *p*-substituted compound, but the considerably more bulky ligand P(2-MeC_6H_4)$_3$ forms a catalyst of very poor efficiency. Finally, hardly any formic acid was formed by using an in situ catalyst obtained from the extremely sterically demanding trimesitylphosphane.

A similar trend was observed upon stepwise introduction of methoxy groups in the *o* position of PPh_3 to yield the ligands (2-$MeOC_6H_4$)$_x$P(C_6H_5)$_{3-x}$ (Table 1, entries 1–4). The ligand P(2-$MeOC_6H_4$)$_3$ forms a catalyst that is 26 times less active than the corresponding system with the *p*-substituted phosphane (Table 1, entries 4/5). In general, monodentate phosphanes with cone angles larger than 180° do

Figure 3. Influence of methyl substituents in ligands PAr_3 on the activity of in situ catalysts formed with **1**. Reaction conditions see Table 1

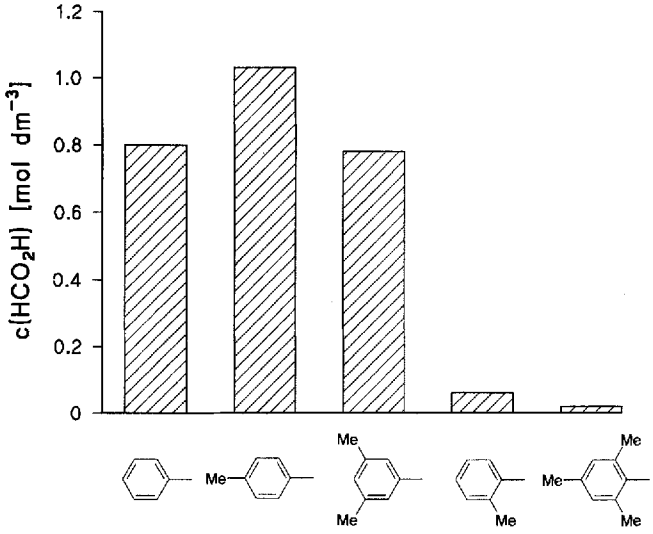


Table 2. Influence of groups R and chain-length n on the activity of in situ catalysts $\mathbf{1}/R_2P(CH_2)_nPR_2$

Entry	Ligand Acronym	R_2P-$(CH_2)_n$-PR_2 n	R	pK_{a1} / pK_{a2} [a]	Θ [b]	t [h]	$c(HCO_2H)$ [c] [mol l^{-1}]
1a	dppm	1	Ph	3.81 / −2.73	121	18	2.58
1b						4	1.58 [d]
2	dppe	2	Ph	3.86 / 0.99	125	18	0.57
3	dppp	3	Ph	4.50 / 2.53	127	18	2.24
4a	dppb	4	Ph	4.72 / 4.28	(130)	18	2.48
4b						4	0.99 [d]
4c						6.5	1.39 [e]
5	dpphx	6	Ph	5.05 / 4.89	---	18	0.56
6	dmpe	2	Me	(8.4 / 5.0)	107	18	0.89
7	dippe	2	iPr	(8.7 / 5.3)	(135)	18	2.01
8	dcpe	2	Cy	(8.8 / 5.4)	142	18	1.78
9	dcpb	4	Cy	(8.8 / 8.3)	(145)	6.5	1.86 [e]

[a] From ref.[7b]; values in parentheses are interpolated. – [b] From ref.[8]; values in parentheses are interpolated. – [c] DMSO/NEt_3 (5:1), $c(Rh) = 10^{-2}$ mol l^{-1}, P/Rh = 2.4, T = 25 °C, p^0 = 40 atm, activation: $c^0(HCO_2H)$ = 0.43 mol l^{-1}, 30 min. – [d] $c(Rh) = 5 \cdot 10^{-3}$ mol l^{-1}, P/Rh = 2.0, no activation. – [e] $c(Rh) = 5 \cdot 10^{-3}$ mol l^{-1}, P/Rh = 2.4, no activation.

not form active catalysts with **1** for the hydrogenation of CO_2 to formic acid in DMSO/NEt_3.

Bidentate Phosphanes $R_2P(CH_2)_nPR_2$

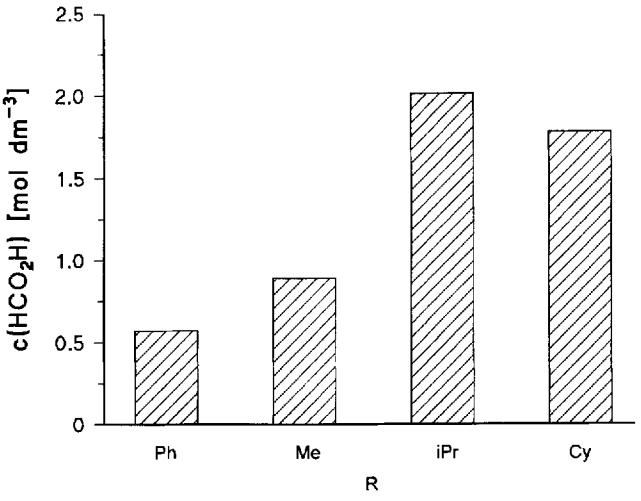
Table 2 summarizes the results obtained with various catalysts formed from **1** and bidentate phosphane ligands $R_2P(CH_2)_nPR_2$ at a rhodium concentration of 10^{-2} mol l^{-1} and a ligand-to-Rh ratio of 1.2 (P/Rh = 2.4). The formic acid concentration after a reaction time of 18 h is given as a qualitative measure of the catalytic activity. The catalysts were activated by treatment with formic acid *prior* to use[3b]. Note that with catalysts of very poor efficiency decomposition of formic acid during the activation procedure is marginal and the concentration of formic acid $c^0(HCO_2H)$ = 0.43 mol l^{-1} used in the activation cannot be neglected compared to the final concentration. In cases where the equilibrium concentration was reached under the standard reaction conditions, additional experiments were carried out in order to get comparable results.

Without activation, the activity of the catalyst $\mathbf{1}/Ph_2P(CH_2)_4PPh_2$ lies exactly in the range predicted from the basicity of the bidentate ligand[7b] (Table 2, entry 4b). However, the results obtained with ligands $Ph_2P(CH_2)_nPPh_2$ being all of similar basicity clearly demonstrate that the influence of bidentate ligands is different from that observed with monodentate phosphanes (Table 2, entries 1–5). The size of the chelate ring formed at the metal centre exerts a strong influence: five-membered and eight-membered rings lead to extremely low activities.

As in related hydrogenation reactions, the low activity induced by $Ph_2P(CH_2)_6PPh_2$ can be explained by intramolecular C–H activation of the long CH_2 backbone yielding catalytically inactive Rh(III) complexes[9]. Other explanations like instability of the entropically disfavoured chelate ring and formation of phosphane-bridged oligomers may also apply. The formation of phosphane-bridged complexes under the reaction conditions must also be taken into account with the ligand $Ph_2P(CH_2)PPh_2$ that forms a very small chelate[10]. However, a sharp maximum of the catalytic activity observed with this phosphane at a P/Rh ratio of 2:1 suggests that it operates as a chelating ligand in CO_2 hydrogenation.

In contrast to the findings obtained by use of monodentate ligands, the catalytic activity of $\mathbf{1}/R_2P(CH_2)_nPR_2$ increases with increasing size and basicity of the PR_2 moiety. Thus, the catalytic activity increases in the order R = Ph < Me < Cy < *i*Pr for ligands $R_2P(CH_2)_2PR_2$ forming five-membered chelate rings at the metal centre (Table 2, entries 2, 6–8, Figure 4). The same trend is observed when the phenyl groups are replaced by cyclohexyl substituents in the ligands $R_2P(CH_2)_4PR_2$ forming seven-membered chelate rings (Table 2, entries 4c, 9).

Figure 4. Influence of groups R in ligands $R_2P(CH_2)_2PR_2$ on the activity of in situ catalysts formed with **1**. Reaction conditions see Table 2



Hetero-Substituted Ligands with Phosphorus as the Donor Atom

Phosphorus compounds with P–O or P–N bonds are used less frequently as ligands in homogeneous catalysis than their P–C counterparts[11]. Monodentate trialkyl phosphites form very poor catalysts with **1** for CO_2 hydrogenation (Table 3, entries 1–3). The ligand $(i\mathrm{PrO})_2\mathrm{P(CH_2)_4P(O}i\mathrm{Pr})_2$ is also considerably less effective than phosphanes that form chelates of the same size (Table 3, entry 4). However, the nitrogen-substituted ligand $(\mathrm{Et_2N})_2\mathrm{P(CH_2)_4P(NEt_2)_2}$ allowed the formation of 156 mol of formic acid per mol of rhodium under the given conditions indicating that hetero-substituted ligands with phosphorus as donor atoms can yield promising catalysts for CO_2 hydrogenation (Table 3, entry 5). Attempts to further activate these catalysts by pretreatment with formic acid failed.

Table 3. Compounds with P–O or P–N bonds as ligands for in situ catalysts formed with **1**

Entry	Ligand	pk_a [a]	$\Sigma\chi_i$ [b]	Θ [b]	$c(HCO_2H)$ [c] [mol l^{-1}]
1	$P(OMe)_3$	2.60	20.4	107	0.20
2	$P(OEt)_3$	3.31	23.1	109	0.35
3	$P(O^iPr)_3$	4.08	18.9	130	0.12
4	$(^iPrO)_2P(CH_2)_4P(O^iPr)_2$	---	14.4 [d]	---	0.36
5	$(Et_2N)_2P(CH_2)_4P(NEt_2)_2$	---	5.6 [d]	---	0.78

[a] From ref.[7c]. – [b] From ref.[8]. – [c] DMSO/NEt_3 (5:1), $c(Rh) = 5 \cdot 10^{-3}$ mol l^{-1}, P/Rh = 4:1, $T = 25\,^\circ C$, $p^0 = 40$ atm, $t = 18$ h. – [d] Calculated for $EtPX_2$.

Discussion

Changes in the ligand structure have often a pronounced effect on the efficiency of homogeneous catalysts. It is therefore frequently tried to empirically correlate catalytic activities with so-called "ligand parameters". In a first approximation it is then attempted to describe steric and electronic properties of a ligand separately by using experimentally accessible ligand parameters like the basicity of P donor atoms[7] or the cone angle[8] of the ligand. On a qualitative basis, empirical correlation of this type may give valuable guidelines for the development of more effective catalysts.

Neutral rhodium monohydride complexes were identified as the catalytically active species in CO_2 hydrogenation (equation 2–3)[6]. The formation of such compounds from **1** and phosphorus donor ligands requires the reduction of an initially formed chloro complex, ideally of structure **2**[3b]. However, it is well-known that chloro-bridged diolefin complexes like **1** react with phosphorus compounds to a variety of products, depending on the ligand structure and the reaction conditions[12]. Direct influences on the catalytically active intermediates **3–4** (*intrinsic ligand effects*) and effects on the formation of this species must therefore be considered in attempts to understand the ligand effects observed with **1** and various phosphane ligands. Equilibria between the catalytically active species and inactive shunts

$$\underset{\mathbf{1}}{1/2\,[\{(cod)Rh(\mu\text{-}Cl)\}_2]} + P_n \longrightarrow \underset{\mathbf{2}}{[P_nRh(cod)Cl]} \xrightarrow[NEt_3]{H_2} \underset{\mathbf{3}}{[P_nRhH]} \qquad (2)$$

$$\underset{\mathbf{3}}{[P_nRhH]} \xrightarrow{CO_2} \underset{\mathbf{4}}{[P_nRh(O_2CH)]} \xrightarrow{H_2} [P_nRhH] + HCO_2H \qquad (3)$$

(P = donor atom of mono- or bidentate phosphorus ligand)

during the catalytic cycle can also not be excluded a priori in the present system[11d,13].

Despite these limitations, the ligand effects observed in CO_2 hydrogenation with monodentate phosphanes may be interpreted by influences on the catalytically active intermediate in terms of classical ligand concepts and can be compared to those reported for olefin hydrogenation[4]. In contrast to olefin hydrogenation, an excess of monodentate ligand does not result in a decrease of catalytic activity in CO_2 hydrogenation. A possible reason for this difference is the fact that the interaction of substrate occurs with a Rh(III) dihydride in the first case[14], but with a Rh(I) monohydride under our conditions[6]. Monodentate ligands readily dissociate from neutral rhodium monohydrides **3a** yielding appreciable concentrations of **3b** in solution even at high P/Rh ratios[15]. On the other hand, formation of a $14e^-$ species **3c**, which would result in a *trans* arrangement of the remaining two monodentate phosphanes[16], is avoided under these conditions unless extremely bulky ligands are employed. The *cis* geometry is fixed in **3c** when chelating phosphanes are used and this appears to be a favourable situation for CO_2 hydrogenation[6b]. The different behaviour of H_2 towards rhodium complexes with phosphorus ligands in *cis* or *trans* position was pointed out by Halpern[17a] et al. and Brown et al.[17b]. The low activities of catalysts formed with bulky monodentate phosphanes of cone angles >180° are in agreement with these considerations.

$$\underset{\mathbf{3a}}{[P_4RhH]} \rightleftharpoons \underset{\mathbf{3b}}{[P_3RhH]} + P \rightleftharpoons \underset{\mathbf{3c}}{[P_2RhH]} + 2\,P \qquad (4)$$

The first step of the catalytic cycle of CO_2 hydrogenation involving neutral rhodium monohydrides consists of the insertion of CO_2 into the Rh–H bond yielding a formate complex[6]. The transition state for this reaction requires interaction of the central metal atom with the Lewis-basic oxygen atom of CO_2[6b,18] and should therefore be stabilised by electron-withdrawing phosphane ligands. On the other hand, activation of dihydrogen and also release of formic acid or formate in the product-forming step should be enhanced by electron-donating ligands. The results obtained with *p*-substituted phosphanes $P(4\text{-}RC_6H_4)_3$ are in agreement with the assumption that only ligands of medium basicity allow stabilisation of transition states for all parts of the reaction sequence without suppressing other steps. A steady increase of catalytic activity with electron-releasing

properties of R was observed in olefin hydrogenation by using the same type of ligands[14].

The empirical rules developed for CO_2 hydrogenation catalysts formed from **1** and monodentate ligands do no longer apply to bidentate phosphanes. The decrease in catalytic activity in the presence of an excess of chelating phosphane is readily explained by the formation of stable complexes of type **3a**[3b,6a]. Even more intriguingly, neither the basicities of the ligands nor the steric demand of the PR_2 groups can be directly correlated with catalytic activities in the case of chelating ligands.

A possible explanation for this discrepancy is the fixation of the two PR_2 groups in a flexible, but well-defined chelate ring. The intrinsic ligand effects of chelating phosphanes in rhodium-catalysed CO_2 hydrogenation were studied by CO_2 exchange in $[(P_2)_2Rh][HCO_2]$ model complexes[6a] and most recently by using complexes $[(P_2)Rh(hfacac)]$ as catalyst precursors[3c]. The very low activity of ligands forming five-membered chelate rings was confirmed in these studies, but the relative activities of the ligands $R_2P(CH_2)_2PR_2$ were found to increase in the order Me < Cy < *i*Pr < Ph[3c]. The reactivity order Ph < Me < Cy < *i*Pr observed with the same ligands in the in situ system must therefore be attributed to ligand effects in the formation of the catalytically active species (equation 2). The known tendency of five-membered chelate ring ligands to form complexes of type $[(P_2)_2Rh]^+$ in the reaction with **1** may serve as a possible explanation for this observation[12a-b]. Different reactivities during the activation procedure resulting in different concentrations of active monohydride species may play an important role, too.

The catalytic activity of **1** in the presence of phosphites is higher than in the absence of any P donor ligands[3b], but much lower than in the presence of phosphanes. Although recent work has thrown some light on the behaviour of neutral rhodium hydrides with phosphite ligands in catalytic hydrogenation[11d], the few data available do not allow the discussion of ligand effects in this case. It should be noted, however, that replacement of O*i*Pr by NEt_2 doubles the catalytic activity of the system **1**/$X_2P(CH_2)_4PX_2$.

Conclusion

Mono- and bidentate phosphanes show a distinct behaviour upon variation of the P/Rh ratio and upon structural changes when used as ligands for in situ catalysts for CO_2 hydrogenation in DMSO/NEt_3. Qualitative correlation between the observed activities and classical ligand parameters led to the conclusion that monodentate phosphanes should possess medium basicity and cone angles <180° in order to form active catalysts. Chelating ligands $R_2P(CH_2)_nPR_2$ should be of medium ring size (n = 3,4) with alkyl or aryl groups R. The most active ligands of these two classes form catalysts of similar efficiency. Ligands with P–O or P–N bonds also show some potential for the formation of in situ catalysts for CO_2 hydrogenation, although activities are at present considerably lower than with phosphane ligands.

For chelating ligands it was demonstrated that the observed ligand effects are partly due to influences on the transformation of **1** and the phosphane into the catalytically active intermediate. Further attempts to understand the influence of phosphane ligands on catalytically active metal centres must therefore concentrate on elucidating intrinsic ligand effects by use of appropriate model approaches[6a,3c].

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Experimental

Reactions involving air-sensitive compounds were carried out under nitrogen by using standard Schlenk techniques. Complex **1** was synthesised according to a known procedure[19]. Monodentate phosphorus ligands were commercial products or synthesised from PCl_3 and the appropriate Grignard reagents[20]. Bidentate phosphanes $R_2P(CH_2)_nPR_2$ were obtained by the reaction of alkyl halides with $LiPR_2$ (R = Ph[21a], Cy[21b]) or of $Cl_2P(CH_2)_2PCl_2$ with Grignard reagents[22]. The ligands $X_2P(CH_2)_4PX_2$ were prepared as described in ref.[23].

Preparation of in situ Catalysts: Under argon, complex **1** (14.8 mg, 60.0 μmol Rh) and the appropriate amount of ligand were dissolved in 10.0 ml of dry and degassed DMSO in a glass liner fitted for a 100-ml stainless steel autoclave and equipped with a vacuum line adapter. Triethylamine (2.0 ml) was added, and the mixture was vigorously stirred for 15 min by using a magnetic stirring bar. When activation was desired, formic acid (0.20 ml, 5.16 mmol) was added with cooling and the solution stirred for another 30 min at room temp.

Catalytic Reactions: The glass liner containing the catalyst solution was inserted into an evacuated and argon-purged commercial 100-ml stainless steel autoclave. Without stirring, the pressure in the reactor was adjusted to 20 atm with CO_2 and then to 40 atm with H_2. The reaction mixture was agitated at a constant stirring rate of 750 rpm at room temp. for the desired reaction time. After venting of the reactor, the formic acid concentration was determined immediately by ^{1}H-NMR spectroscopy (Varian EM-360, unlocked) in an aliquot of the reaction mixture by using mesitylene as an internal standard. Concentration values were reproducible within 10% deviation.

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