Complexes [(P_2)Rh(hfacac)] (P_2 = Bidentate Chelating Phosphane, hfacac = Hexafluoroacetylacetonate) as Catalysts for CO_2 Hydrogenation: Correlations between Solid State Structures, ^{103}Rh NMR Shifts and Catalytic Activities†

Roland Fornika,[a] Helmar Görls,[a] Bernd Seemann[b] and Walter Leitner*‡[a]

[a] *Max-Planck-Gesellschaft zur Förderung der Wissenschaften, Arbeitsgruppe CO_2-Chemie an der Universität Jena, Lessingstrasse 12, 07743 Jena, Germany*

[b] *BRUKER Analytische MeÅtechnik GmbH, , Silberstreifen, 76287 Rheinstetten, Germany*

Complexes [(P_2)Rh(hfacac)] **1a–h** are the most effective catalyst precursors for catalytic hydrogenation of CO_2 to formic acid in organic solvents allowing turnover frequencies of up to 1335 h^{-1}; ^{103}Rh NMR shifts of these complexes in solution are mainly determined by the P–Rh–P angle as obtained from solid state structures and have predictive potential for the catalytic activity of structurally related phosphanes P_2.

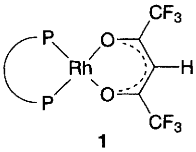
The catalytic hydrogenation of CO_2 to formic acid (Scheme 1) is a promising approach to the use of CO_2 as a building block in chemical syntheses.[1,2] We have reported that rhodium phosphane complexes may serve as very efficient catalysts for this process in organic solvents[2b,d,f] and aqueous solutions.[2e]

Rhodium formate complexes **2** have been inferred as possible key intermediates during the catalytic cycle of CO_2 hydrogenation in $Me_2SO–NEt_3$ mixtures.[2d,f] We now introduce complexes [{R_2P-(X)-PR_2}Rh(hfacac)] **1** as stable model compounds for **2**.[3] The first coordination sphere at rhodium is very similar in **1** and **2** and the pK_a values of hfacacH (4.35) and HCO_2H (3.75) are also compatible. Furthermore, complexes **1** should be able to enter the catalytic cycle of CO_2 hydrogenation *via* hydrogenolysis in analogy to **2**.[4]

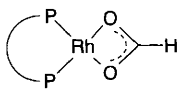
Indeed, very rapid formation of HCO_2H is observed when a solution of [{$Ph_2P(CH_2)_4PPh_2$}Rh(hfacac)] **1f** (2.5×10^{-3} mol dm^{-3}) in $Me_2SO–NEt_3$ (5 : 1) is stirred under $H_2–CO_2$ (1 : 1, 40 atm) in a stainless steel autoclave at 25 °C. The equilibrium concentration of 2.0 mol dm^{-3} HCO_2H is reached within approximately 5 h. Kinetic measurements carried out as previously described reveal that there is no induction period[2f] and that catalysis starts immediately with a maximum turnover frequency (TOF) of 565 h^{-1} (Fig. 1). The highest TOF reported so far for rhodium catalysts with the same ligand is 365 h^{-1}.[2f]

$$H_2 + CO_2 \xrightarrow[\text{catalyst}]{\text{solvent, }\Delta p} HCO_2H$$

Scheme 1



1



2

Complexes **1a–h** were synthesised in order to further improve the catalytic activity by variation of the ligand structure.[3] Selected analytical data of complexes **1a–h** are summarised together with their catalytic activities in Table 1. All of the complexes **1a–h** were catalytically active and the equilibrium concentration of HCO_2H was reached after appropriate reaction times. As expected, the ligand structure has a marked influence on the catalytic activity of complexes **1** as illustrated in Fig. 1. Replacing the phenyl groups in **1f** by cyclohexyl substituents results in a maximum TOF of 1335 h^{-1} as observed with **1g**, which is the most active catalyst for CO_2 hydrogenation to formic acid ever described.[1c,d] Only the water-

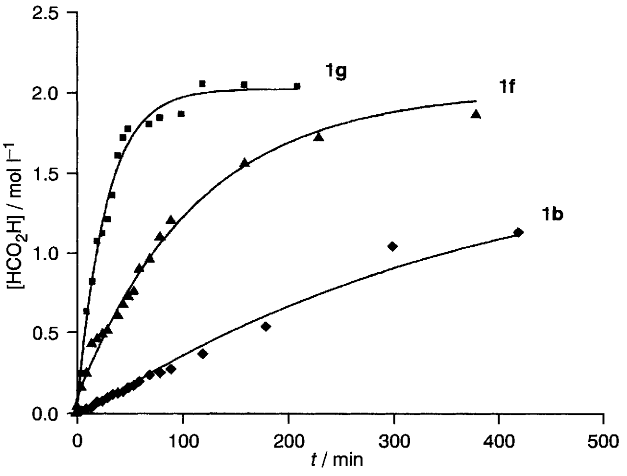
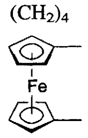


Fig. 1 Increase of formic acid concentration during catalytic hydrogenation of CO_2 using catalysts **1b**, **1f** and **1g** (2.5×10^{-3} mol dm^{-3}) in $Me_2SO–NEt_3$ (5 : 1) under 40 atm $H_2–CO_2$ (1 : 1) at 25 °C

Table 1 Selected analytical data and catalytic activities of complexes [{R_2P-(X)-PR_2}Rh(hfacac)] **1**

Compound	-(X)-	R	Rh–P[a]/Å	P–Rh–P/°	δ(^{31}P)[b]	$^1J_{RhP}$/Hz	δ(^{103}Rh)[b]	TOF[c]/h^{-1}	v_{rel}[d]
1a	$(CH_2)_2$	Ph	2.191(1)	84.34(3)	72.1	196	438	170	8.5
1b	$(CH_2)_2$	Cy	2.193(1)	84.97(2)	91.6	196	368	77	3.9
1c[e]	$(CH_2)_2$	Pr^i	2.183(2)	86.01(7)	101.2	195	323	95	4.8
1d	$(CH_2)_2$	Me	2.176(1)	85.08(5)	54.4	192	370	20	1
1e	$(CH_2)_3$	Ph	2.194(2)	90.77(6)	37.0	183	567	300	15.0
1f	$(CH_2)_4$	Ph	2.206(1)	93.08(3)	48.6	191	646	565	28.3
1g	$(CH_2)_4$	Cy	2 224(2)	98.93(6)	54.1	193	845	1335	66.8
1h		Pr^i	2.228(1)	99.95(3)	44.2	195	1012	687	34.4

[a] The mean value of the two Rh–P distances is given, the difference is less than 0.01 Å in all cases. [b] In [$^2H_8$]THF. [c] Obtained by dividing the initial rate (< 10% of the equilibrium concentration) of formic acid production by the total rhodium concentration (2.5×10^{-3} mol dm^{-3}). Values were reproducible within a less than 10% deviation. [d] Obtained from initial rates under identical reaction conditions. The relative activity, v_{rel}, of the least active catalyst **1d** is defined as 1. [e] Two independent molecules in the unit cell that differ only in the ring puckering of the five-membered chelate.

soluble catalyst $[Rh(tppts)_3Cl]$ exhibits comparable activities under similar mild reaction conditions.[1d] The ruthenium complex $[Ru(PMePh_2)_3(H)_2]$ allows a TOF of 1400 h^{-1} in supercritical CO_2 only under considerably more forcing conditions (50 °C, 204 atm).[2g]

Complexes **1a–h** are ideally suited for a systematic study of structural changes in rhodium phosphane chelates upon small changes in the ligand structure, as there is no steric interaction between the phosphane ligand and the hfacac moiety.§ All the complexes **1a–h** exhibit the expected square planar coordination sphere at rhodium with angles between the P–Rh–P and the O–Rh–O planes varying from 0° (**1d**) to 8.4° (**1h**). No significant changes occur in the Rh(hfacac) fragment throughout the series of complexes **1a–h**. No correlation between the Rh–P bond length and the basicity of the phosphorus donor atom is found in complexes **1a–h**. Furthermore, the P–Rh–P angle remains almost invariant if the groups R are changed in ligands $R_2P(CH_2)_2PR_2$ of complexes **1a–d**. However, the P–Rh–P angle increases with increasing chain length in $Ph_2P(CH_2)_nPPh_2$ (**1a**, **1e**, **1f**) as expected. In contrast to the situation in five-membered chelates, the replacement of phenyl by cyclohexyl in $R_2P(CH_2)_4PR_2$ results in a considerable increase of the P–Rh–P angle from 93.1° (**1f**) to 98.9° (**1g**).

The influence of the ligand on the coordination sphere of rhodium complexes **1a–h** in the solid state is prevalent also in solution, as seen from the linear correlation between the P–Rh–P angles and the ^{103}Rh chemical shifts (Fig. 2) as determined from two-dimensional (^{31}P, ^{103}Rh){^{1}H} NMR experiments.[5]¶ The correlation is in agreement with the generally accepted fact that the paramagnetic contribution of the Ramsey equation σ_p (related to coordination geometry) is more important for the chemical shift of heavy nuclei than the diamagnetic contribution σ_d (related to electron density).[6,7]

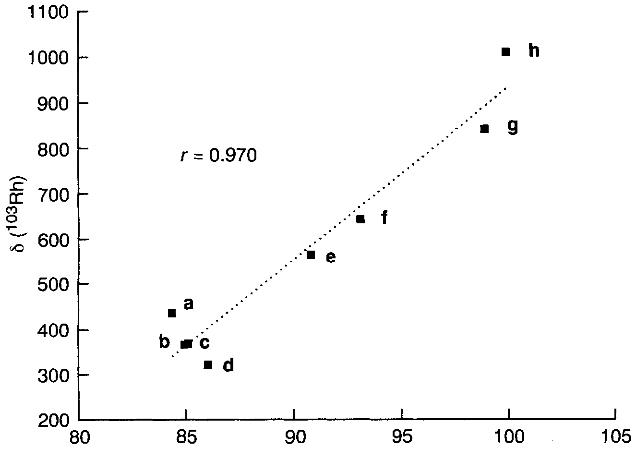


Fig. 2 Correlation between P–Rh–P angles and ^{103}Rh NMR shifts in complexes $[\{R_2P\text{-}(X)\text{-}PR_2\})Rh(hfacac)]$ **1a–h**

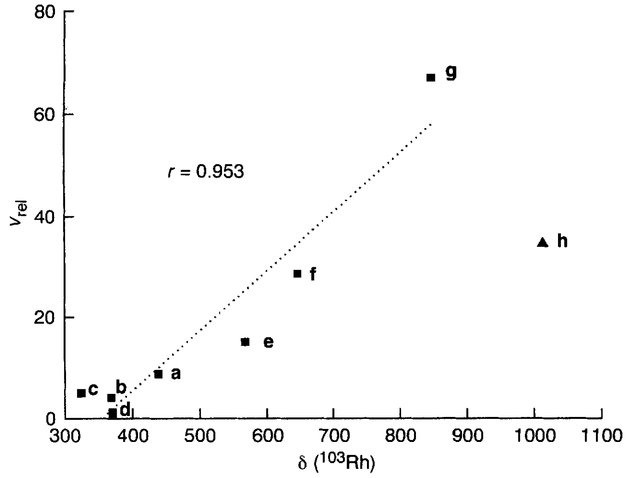


Fig. 3 Relative catalytic activities v_{rel} of complexes **1a–h** plotted against ^{103}Rh NMR shifts. Only data points marked as ■ were used for statistical analysis (dotted line).

The ^{103}Rh chemical shift has been shown to be directly related to rate constants of stoichiometric reactions[7a,c] and qualitative comparisons between the enantioselectivity of chiral rhodium catalysts and the ^{103}Rh shifts of diastereoisomeric intermediates in asymmetric hydrogenation have been reported.[7b] Direct correlations between chemical shifts and catalytic activities have been observed for cobalt complexes.[8] However, despite the widespread use of rhodium phosphane complexes in homogeneous catalysis, no attempts have been reported so far to quantitatively correlated ^{103}Rh chemical shifts with catalytic activities.

For the series of ligands $R_2P(CH_2)_nPR_2$ **1a–g**, an increase of the relative catalytic activity in CO_2 hydrogenation with increasing δ values is observed (Fig. 3). Statistical analysis of the data gave a fairly reasonable linear correlation with a goodness-of-fit, $r = 0.953$ (dotted line). Complex **1h**, however, does not follow this specific pattern. The possible internal movements of a chelate ring with a ferrocenyl backbone are different from a chelate with a $\text{-}(CH_2)_n\text{-}$ backbone. One might speculate on the impact of this difference on a catalytic cycle[2d,f] that has to accommodate several intermediates with different coordination numbers and different requirements for optimum bite angles (dynamic bite angle). However, other factors including electronic effects cannot be ruled out at this preliminary stage of our investigations.

Further work is necessary in order to probe the generality of the observed correlations and in order to further improve our understanding of ligand effects in CO_2 hydrogenation. Appropriate investigations based on the methodologies described herein are under way.

Financial support from the Max-Planck-Society, the BMFT and the Fonds der Chemischen Industrie is greatfully acknowledged. We with to thank Degussa AG for a generous loan of rhodium(III)chloride hydrate and Dr P. A. Chaloner, University of Sussex, for a sample of the ligand dippf. The skillful preparative assistance of U. Beneke is also acknowledged. Special thanks are due to Professor Dr E. Dinjus for his support and for interesting discussions.

Received, 31st March 1995; Com. 5/02061A

Footnotes

† CO_2 Activation, Part 5; for Part 4, see ref. 2*f*.

‡ New address: Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim/Ruhr, Germany.

§ Well formed crystals suitable for X-ray analysis were obtained from saturated solutions in diisoproylether (**1a**, **1c–h**) or acetone (**1b**). Data were collected on an Enraf-Nonius CAD4 diffractometer using Mo-Kα radiation (λ = 0.7107 Å). Data were corrected for Lorentz and polarization effects, but not for absorption. The structures were solved by Patterson methods and refined by full-matrix least-squares techniques. Hydrogen atoms were included at calculated positions with fixed thermal parameters; non-hydrogen atoms were refined anisotropically. The *R* values varied from 0.025 to 0.061. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ Pulse sequence according to ref. 9: F2-domain (^{31}P): SW = 9800 Hz, TD = 4 K; F1-domain (^{103}Rh): SW = 40 000 Hz, TD = 256, digital resolution 78 Hz; mixing time = 2.5 ms ≈ $1/(2J_{RhP})$; experiments were carried out on a Bruker AMX 400 spektrometer. Solutions of *ca.* 25 mg **1** in 0.5 ml

[$^2H_8$]THF were measured using 5 mm NMR tubes, total experimental time was approx. 45 min. Chemical shift values are referenced to Ξ(Rh) = 3.16 MHz.[6]

References

1 (*a*) A. Behr, *Carbon Dioxide Activation by Metal Complexes*, VCH, Weinheim, 1988; (*b*) *Enzymatic and Model Carboxylation and Reduction Reactions for Carbon Dioxide Utilization*, ed. M. Aresta and J. V. Schloss, NATO ASI Series C, 314, Kluwer, Dordrecht, 1990; (*c*) P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1995, **95**, 256; (*d*) W. Leitner, *Angew. Chem.*, in the press.

2 (*a*) Y. Inoue, H. Izumida, Y. Sasaki and H. Hashimoto, *Chem. Lett.*, 1976, 863; (*b*) E. Graf and W. Leitner, *J. Chem. Soc., Chem. Commun.*, 1992, 623; (*c*) J.-C. Tsai and K. M. Nicholas, *J. Am. Chem. Soc.*, 1992, **114**, 5117; (*d*) T. Burgemeister, F. Kastner and W. Leitner, *Angew. Chem.*, 1993, **105**, 781; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 739; (*e*) F. Gaßner and W. Leitner, *J. Chem. Soc., Chem. Commun.*, 1993, 1465; (*f*) W. Leitner, E. Dinjus and F. Gaßner, *J. Organomet. Chem.*, 1994, **475**, 257; (*g*) P. G. Jessop, T. Ikaria and R. Noyori, *Nature*, 1994, **368**, 231.

3 (*a*) R. Fornika, PhD Thesis, Universität Jena, 1994; (*b*) P. J. Fennis, P. H. M. Budzelaar, J. H. G. Frijns and A. G. Orpen, *J. Organomet. Chem.*, 1990, **393**, 287.

4 (*a*) A. A. Oswald, D. E. Hendriksen, R. V. Kastrup, K. Irikura, E. J. Mozeleski and D. A. Young, *Phosphorus Sulfur*, 1987, **20**, 237; (*b*) A. A. Oswald, D. E. Hendriksen, R. V. Kastrup and E. J. Mozeleski, in *Homogeneous Transition Metal Catalyzed Reactions*, (*Adv. Chem. Ser.*, 130), ed. W. R. Moser and D. W. Slocum, American Chemical Society, 1992, S. 395.

5 (*a*) R. Benn, H. Brenneke and R.-D. Reinhardt, *Z. Naturforsch. B Chem. Sci.*, 1985, **40**, 1763; (*b*) R. Benn, H. Brenneke and A. Rufinska, *J. Organomet. Chem.*, 1987, **320**, 115.

6 (*a*) R. Benn and A. Rufinska, *Angew. Chem.*, 1986, **98**, 851; *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 861; (*b*) H. Mason, *Chem. Rev.*, 1987, **87**, 1299; (*c*) B. E. Mann, in *Transition Metal Nuclear Magnetic Resonance*, ed. P. S. Pregosin, Elsevier, 1991.

7 (*a*) M. Koller and W. v. Philipsborn, *Organometallics*, 1992, **11**, 467; (*b*) B. R. Bender, M. Koller, D. Nanz and W. v. Philipsborn, *J. Am. Chem. Soc.*, 1993, **115**, 5889; (*c*) B. Åkermark, R. A. Blomberg, J. Glaser, L. Öhrström, S. Wahlberg, K. Wärnmark and K. Zetterberg, *J. Am. Chem. Soc.*, 1994, **116**, 3405.

8 (*a*) H. Bönnemann, W. Brijoux, R. Brinkmann, W. Meurers, R. Mynott, W. v. Philipsborn and T. Egolf, *J. Organomet. Chem.*, 1984, **272**, 231; (*b*) H. Bönnemann, *Angew. Chem.*, 1985, **97**, 264; *Angew. Chem., Int. Ed. Engl.*, 1984, **24**, 248.

9 A. Bax, R. H. Griffey and B. L. Hawkins, *J. Magn. Reson.*, 1983, **55**, 301.