Inorg. Chem. **2002**, *41*, 1606–1614

In Situ Formation of Ruthenium Catalysts for the Homogeneous Hydrogenation of Carbon Dioxide

Chih-Cheng Tai,[†] Justine Pitts,[†] John C. Linehan,[‡] A. Denise Main,[‡] Pradip Munshi,[†] and Philip G. Jessop*,[†]

Department of Chemistry, University of California, Davis, California 95616-5295, and Fundamental Sciences Division, Pacific Northwest National Laboratory, PO Box 999, Richland, Washington 99352

Received August 10, 2001

A total of 44 different phosphines were tested, in combination with $[RuCl_2(C_6H_6)]_2$ and three other Ru(II) precursors, for their ability to form active catalysts for the hydrogenation of CO_2 to formic acid. Half (22) of the ligands formed catalysts of significant activity, and only 6 resulted in very high rates of production of formic acid. These were PMe_3, $PPhMe_2$, dppm, dppe, and *cis*- and *trans*-$Ph_2PCH{=}CHPPh_2$. The in situ catalysts prepared from $[RuCl_2(C_6H_6)]_2$ and any of these 6 phosphine ligands were found to be at least as efficient as the isolated catalyst $RuCl(O_2CMe)(PMe_3)_4$. There was no correlation between the basicity of monophosphines (PR_3) and the activity of the catalysts formed from them. However, weakly basic *diphosphines* formed highly active catalysts only if their bite angles were small, while more strongly basic diphosphines had the opposite trend. In situ ^{31}P NMR spectroscopy showed that *trans*-$Ru(H)_2(dppm)_2$, *trans*-$RuCl_2(dppm)_2$, *trans*-$RuHCl(dppm)_2$, *cis*-$Ru(H)(O_2CH)(dppm)_2$, and *cis*-$Ru(O_2CH)_2(dppm)_2$ are produced as the major metal-containing species in reactions of dppm with $[RuCl_2(C_6H_6)]_2$ under catalytic conditions at 50 °C.

Introduction

Carbon dioxide, as its removal from power plant emissions becomes more commonplace, will confirm its position as the cheapest and most readily available carbon feedstock. As such, its conversion to useful organic products is an important alternative to their preparation from fossil fuels. The incorporation of CO_2 into organic products can be achieved by coupling/insertion reactions or by reduction. However, in order for the reduction of CO_2 to be widely adopted as a synthetic strategy, three requirements must first be met; the reduction of CO_2 must be efficient, the range of products and compounds derived therefrom must be wide, and the reductant must be less expensive than the products. While market value largely controls the last requirement, chemical research can contribute greatly to achieving the first two. During the course of our recently renewed investigation of homogeneously catalyzed CO_2 hydrogenation, we have explored the effect of gas pressure, cosolvents, and bases on the rate of the reaction catalyzed by ruthenium trimethylphosphine complexes.[1,2] We now describe a family of in situ catalysts, several of which exhibit high catalytic activity, and a survey of a large number of phosphines evaluated for their competence in forming active in situ catalysts.

From the initial report of CO_2 homogeneous hydrogenation to formic acid by Inoue et al. in 1976,[3] ruthenium(II) catalysts have predominated (Table 1, eq 1). There have been examples with Pd[3,4] or Rh catalysts,[5−10] notably the work of the group of Leitner, who found that Rh complexes were particularly active in DMSO or H_2O. The highest rates of

* Corresponding author. E-mail: jessop@chem.ucdavis.edu.
[†] University of California.
[‡] Pacific Northwest National Laboratory.

(1) Thomas, C. A.; Bonilla, R. J.; Huang, Y.; Jessop, P. G. *Can. J. Chem.* **2001**, *79*, 719−724.
(2) Munshi, P.; Main, A. D.; Linehan, J.; Tai, C. C.; Jessop, P. G. Submitted for publication.
(3) Inoue, Y.; Izumida, H.; Sasaki, Y.; Hashimoto, H. *Chem. Lett.* **1976**, 863−864.
(4) Kudo, K.; Sugita, N.; Takezaki, Y. *Nihon Kagaku Kaishi* **1977**, 302−309.
(5) Yamaji, T. (Teijin Ltd.). Japan Kokai Tokkyo Koho 166,146, 1981.
(6) Tsai, J.-C.; Nicholas, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 5117−5124.
(7) Graf, E.; Leitner, W. *J. Chem. Soc., Chem. Commun.* **1992**, 623−624.
(8) Burgemeister, T.; Kastner, F.; Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 739−741.
(9) Gassner, F.; Leitner, W. *J. Chem. Soc., Chem. Commun.* **1993**, 1465−1466.
(10) Leitner, W.; Dinjus, E.; Gaßner, F. *J. Organomet. Chem.* **1994**, *475*, 257−266.

10.1021/ic010866l CCC: $22.00
Published on Web 03/01/2002

Table 1. Reports of Homogeneous Hydrogenation of CO_2 to Formic Acid Catalyzed by Ru(II) Complexes, Listed in Order of Increasing TOF[a]

catalyst precursor	solvent	reagents	P_{H_2,CO_2}, bar	T, °C	TOF, h^{-1}	ref
$[(C_5H_4(CH_2)_2NMe_2)Ru(dppm)]BF_4$	THF		40, 40	80	0.4	14
$RuH_2(PPh_3)_4$	C_6H_6	NEt_3, H_2O	25, 25	rt	4	3
$RuCl_2(PTA)_4$	H_2O	HCO_3	60, 60	25	25	17
$RuH_2(PPh_3)_4$	C_6H_6	Na_2CO_3	25, 25	100	42	18
$TpRuH(MeCN)(PPh_3)$	THF	H_2O, NEt_3	25, 25	100	63	19
$Ru_2(CO)_5(dppm)_2$	Me_2CO	NEt_3	35, 35	rt	207	20
K[Ru(EDTA-H)Cl]	H_2O		3, 17	40	250	21
$[Ru(Cl_2bpy)_2(H_2O)_2](CF_3SO_3)_2$	EtOH	NEt_3	30, 30	150	625	22
$[Ru(CO)_2Cl_2]_n$	H_2O, ^{i}PrOH	NEt_3	81, 27	80	1300	23
$RuH_2(PMe_3)_4$	$scCO_2$	NEt_3, H_2O	80, 130	50	1400	12
$RuH_2(PMe_3)_4$	$scCO_2$	NEt_3, MeOH	80, 130	50	4000	11
$RuCl(OAc)(PMe_3)_4$	$scCO_2$	NEt_3, C_6F_5OH	70, 120	50	95000	2

[a] Abbreviations: Cl_2bpy = 6,6′-dichloro-2,2′-bipyridine; DMSO = dimethyl sulfoxide; dppm = $Ph_2PCH_2PPh_2$; EDTA-H = monodeprotonated ethylenediaminetetraacetic acid; PTA = 1,3,5-triaza-7-phosphaadamantane; rt = room temperature; TOF = turnover frequency ((mol of formic acid/mol of transition metal)/h); Tp = hydrotris(pyrazolyl)borate.

hydrogenation were obtained by Jessop et al. using $RuXY(PMe_3)_4$ catalysts (X, Y = H, Cl, or O_2CMe) in supercritical CO_2 solution.[11,12] The high rates of reaction were due to the very high H_2 and CO_2 concentrations[1] and also in large part due to the choice of PMe_3 ligands. Those ligands were originally chosen not for their electronic or steric properties but because they imparted upon the catalyst far greater solubility in supercritical CO_2 ($scCO_2$) than could be obtained with triphenylphosphine. The effectiveness of other phosphines was not measured. However, it is likely that the rate of CO_2 hydrogenation is a strong function of the properties of the phosphine ligands. Also, the use of diphosphines has not been explored, beyond a few disappointing tests of dmpe[11] and the more recent discovery by Baiker[13] that dppe complexes of Ru are very active for the related reaction of formamide synthesis (eq 2, dmpe = $Me_2PC_2H_4PMe_2$, dppe = $Ph_2PC_2H_4PPh_2$). More recent efforts have included testing Ru complexes containing dangling or functionalized phosphine ligands.[14] It is likely that the most active Ru(II) catalysts have not yet been discovered.

$$CO_2 + H_2 \xrightarrow[\text{base}]{\text{catalyst}} HCO_2H \qquad (1)$$

$$CO_2 + H_2 + NHMe_2 \xrightarrow{\text{catalyst}} HCNMe_2 + H_2O \qquad (2)$$

We have developed a series of in situ catalysts for CO_2 hydrogenation that incorporate Ru(II) precursors with various phosphines or other ligands. Using this series, we have screened over 40 phosphines, a number of other ligands, and combinations of ligands, for their effectiveness in making active catalysts for reaction 1. The in situ catalysts were prepared from the Ru(II) precursor and the ligands in MeOH/NEt_3 or MeOH/NPr_3 mixed solvent under H_2 pressure, and the success of the combination was judged by the yield of formic acid after 1 h of exposure to a mixture of H_2 and CO_2 gases.

Experimental Section

General Methods. Methanol, triethylamine, and tripropylamine were degassed by repeated freeze−vacuum−thaw cycles before use. Hydrogen gas (99.99% purity, Praxair) was used directly. CO_2 gas (99.9999% purity, SFC/SFE grade, Air Products) was passed through an oxygen trap before use. $P(C_6H_4\text{-}p\text{-}C_2H_4(CF_2)_6F)_3$ was a gift from Dr. J.-L. Xiao of Liverpool, U.K. The other phosphines were obtained commercially and used without purification. Catalyst precursors $[RuCl_2(C_6H_6)]_2$ (Aldrich), Ru(methylallyl)$_2$(COD) (Acros, COD = 1,5-cyclooctadiene), and $[RuCl_2(COD)]_n$ (Pressure Chemical) were used as received, while $RuCl_2(DMSO)_4$[15] and $RuCl(OAc)(PMe_3)_4$[16] were prepared by the literature methods.

The high-pressure apparatus is similar to that described earlier.[1,11] In situ catalyst screening was performed by placing 13 small glass vials uncapped and upright in the reaction vessel. Reagents and a micro stir bar were placed in each vial. Coupling of all 13 stir bars to the magnetic stir plate beneath was confirmed visually. Key experiments were performed by this screening method and by the more conventional approach (one glass vial/vessel), with no significant difference in the results. For experiments involving volatile reagents other than methanol and the amine, the conventional approach was used exclusively.

Carbon Dioxide Hydrogenation Method. Under an inert and dry atmosphere, 15 mg of the ruthenium(II) precursor $[RuCl_2(C_6H_6)]_2$, 10 mL of methanol, and 10 mL of tripropylamine were placed in a 50 mL Erlenmeyer flask. The solution was stirred in order to dissolve the ruthenium complex. A 1 mL volume of this solution (3 μmol of Ru, 2.6 mmol of NPr_3, 12.3 mmol of MeOH) was injected into an uncapped and upright glass vial inside a steel vessel. The desired quantity of phosphine or other ligands was also added, as was a micro stir bar. The steel vessel was sealed and flushed three times with 8 bar of H_2, and then H_2 was added to 40 bar. The vessel was placed in a 50 °C water bath. After 1 or 10 h (this time period is referred to as the pretreatment time), CO_2 was introduced until the total pressure reached 100 bar. After 1 h, the reaction was terminated by putting the reaction vessel into an ice water bath and a few minutes later into an acetone/dry ice bath. After the pressure in the vessel dropped lower than the original H_2 pressure, the gases were slowly released and the vessel allowed to warm to room temperature. $CHCl_3$ (0.5 mL) was added to the vial as internal standard. The yield of formic acid was determined by ^{1}H NMR spectroscopy (400 MHz) of the product mixture dissolved in CD_3OD.

(11) Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 344−355.
(12) Jessop, P. G.; Ikariya, T.; Noyori, R. *Nature* **1994**, *368*, 231−233.
(13) Kröcher, O.; Köppel, R. A.; Baiker, A. *Chem. Commun.* **1997**, 453−454.
(14) Chu, H. S.; Lau, C. P.; Wong, K. Y. *Organometallics* **1998**, *17*, 2768−2777.
(15) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204−209.
(16) Mainz, V. V.; Andersen, R. A. *Organometallics* **1984**, *3*, 675−678.

Multinuclear NMR studies on the ruthenium-containing products after reactions of $[RuCl_2(C_6H_6)]_2$ with dppm were performed unlocked using a standard broad-band 5 mm NMR probe in the appropriate solvent on a 7.01 T Varian VXR NMR spectrometer externally referenced to TMS (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). High-pressure ^{31}P and ^1H NMR spectroscopy were conducted using a 10 mm o.d. 3.5 mm i.d. PEEK NMR cell.[24,25]

In a typical experiment 0.05 g (1×10^{-4} mol) of $[RuCl_2(C_6H_6)]_2$ and 0.154 g (4×10^{-3} mol) dppm were suspended in 5 mL of a 0.7:1 molar ratio of MeOH−NEt_3 solution under an inert atmosphere. Portions of this mixture were placed in either the high-pressure NMR cell (0.20 mL) or into a stainless steel reactor (4.0 mL). The vessels were then pressurized with H_2 followed by CO_2 at the desired temperature. In product studies the reactor was cooled and depressurized and the contents were extracted for NMR analysis.

The chemical shifts and splitting patterns of the reaction solutions were compared with authentic compounds synthesized from literature methods.

Safety Warning. Operators of high-pressure equipment such as that required for these experiments should take proper precautions, including but not limited to the use of pressure relief devices, to minimize the risk of personal injury.

Results and Discussion

Formation of in Situ Catalysts. In situ catalysts were prepared from Ru(II) precursors and added phosphines, which were allowed to react with each other, in MeOH/NR_3 solution (R = Et or Pr) and under H_2 pressure (40 bar) at 50 °C for at least 1 h before CO_2 was added. The effectiveness of the in situ catalysts thus prepared was measured by the yield of formic acid obtained after 1 h. Because the usually observed eventual yield is 1.8 mol/mol of amine and the greatest yield obtained after only 1 h in this study was only 0.8, the yield after 1 h should be considered an indication of the rate of the hydrogenation and not an indication of the eventual yield.

Three different dichloro Ru(II) precursors were tested, *trans*-$RuCl_2(DMSO)_4$, $[RuCl_2(COD)]_n$, and $[RuCl_2(C_6H_6)]_2$. With no phosphine ligand added, not one of these complexes was active for CO_2 hydrogenation. However, with even 1 equiv of triphenylphosphine (PPh_3) added/Ru atom, these three complexes were converted into fair catalysts for the hydrogenation of CO_2 into formic acid (Figure 1). The best catalysts were obtained when at least 3 equiv of triphenylphosphine was added. Addition of further equivalents of phosphine did not suppress the hydrogenation with $RuCl_2(DMSO)_4$ and $[RuCl_2(COD)]_n$ and only slightly slowed the reaction with $[RuCl_2(C_6H_6)]_2$. The differences in effectiveness between the three Ru precursors were not large, but because the most effective was $[RuCl_2(C_6H_6)]_2$, this complex was used in all subsequent experiments. The fact that similar catalytic activities were obtained regardless of the choice of Ru(II) precursor suggests that under the reaction conditions the weak ligands (DMSO, COD, or benzene) in the precursors are either entirely displaced or have little effect on the catalytic activity.

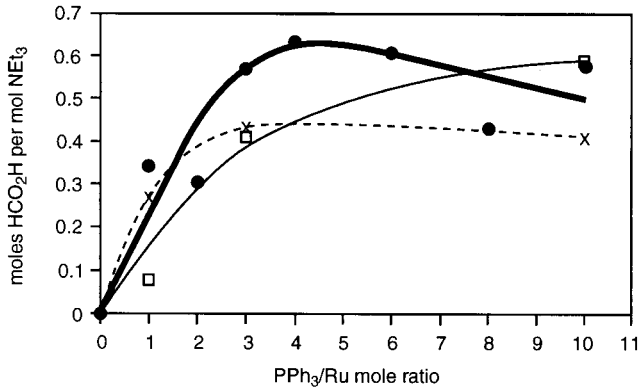


Figure 1. Dependence of the yield in the first 1 h on the choice of Ru(II) precursor and on the number of equivalents of PPh_3 added. The precursors were $RuCl_2(DMSO)_4$ (□ and thin curve), $[RuCl_2(COD)]_n$ (× and dashed curve), and $[RuCl_2(C_6H_6)]_2$ (● and bold curve). The curves are not theoretically derived and are added only to guide the eye. Conditions: 3 μmol of Ru; 0.1 mL of MeOH; 0.5 mL of NEt_3; 40 bar H_2 (during pretreatment time and during reaction); CO_2 added during reaction time only (total pressure 100 bar); pretreatment time 1 h; reaction time 1 h.

These tests of the three dichloro Ru(II) precursors were performed in 0.6 mL of a MeOH/NEt_3 mixture (see caption to Figure 1). All subsequent experiments were performed in 1.0 mL of a MeOH/NPr_3 mixture.

The in situ catalysts presumably formed during the pretreatment time (during which the reaction solution was exposed to 40 bar H_2 pressure) or shortly after the CO_2 gas was introduced. The length of the pretreatment time (1 or 10 h) had little effect on the effectiveness of the catalyst. Of the ligands which had appreciable activity, only two ($P(C_6H_4$-*p*-$F)_3$ and dppe) were significantly affected by variation in the length of the pretreatment time, and in those cases, the 1 h of pretreatment time was found to result in greater formic acid yields. Note, however, that the isolated catalyst precursor $RuCl_2(PMe_3)_4$ was found in an earlier study to be almost inactive in the first 1 h,[11] presumably because that time is required for the substitution of a chloride ligand with a hydride by the action of H_2 and base. The fact that the in situ catalysts are able to produce significant quantities of formic acid in the first 1 h suggests that the induction period, if any, is either complete during the pretreatment with H_2 or is complete shortly after the addition of CO_2.

Screening of Monophosphines. A total of 24 different monophosphines (PR_3) were tested, in combination with $[RuCl_2(C_6H_6)]_2$, for their ability to form active catalysts for the hydrogenation of CO_2 to formic acid (Table 2). Only 11 of the ligands formed catalysts of significant activity (formic acid yield of 0.1 mol/mol of NPr_3 or higher). Only 2 resulted in very high formic acid yields of over 0.6 mol/mol of NPr_3

(17) Laurenczy, G.; Joo, F.; Nadasdi, L. *Inorg. Chem.* **2000**, *39*, 5083−5088.
(18) Yamaji, T. (Teijin Ltd.) Japan Kokai Tokkyo Koho 140.948, 1981.
(19) Yin, C.; Xu, Z.; Yang, S.-Y.; Ng, S. M.; Wong, K. Y.; Lin, Z.; Lau, C. P. *Organometallics* **2001**, *20*, 1216−1222.
(20) Gao, Y.; Kuncheria, J. K.; Jenkins, H. A.; Puddephatt, R. J.; Yap, G. P. A. *J. Chem. Soc., Dalton Trans.* **2000**, 3212−3217.
(21) Khan, M. M. T.; Halligudi, S. B.; Shukla, S. *J. Mol. Catal.* **1989**, *57*, 47−60.
(22) Lau, C. P.; Chen, Y. Z. *J. Mol. Catal., A* **1995**, *101*, 33−36.
(23) Drury, D. J.; Hamlin, J. E. Eur. Patent Appl. 0 095 321, 1983.
(24) Wallen, S. L.; Schoenbachler, L. K.; Dawson, E. D.; Blatchford, M. A. *Anal. Chem.* **2000**, *72*, 4230−4234.
(25) Yonker, C. R.; Linehan, J. *J. Organomet. Chem.*, in press.

Table 2. Results with in Situ Catalysts Derived from Monophosphines and $[RuCl_2(C_6H_6)]_2$[a]

phosphine	pK_a of HPR_3^+	cone angle (deg)	P:Ru mol ratio	pretime, h	yield of HCO_2H
PPh_3	2.7[b,c]	145	3	10	0.13 (3)
			3	1	0.14 (2)
$P(C_6H_4$-*p*-$OMe)_3$	4.6[c]	145	3	1	0.28 (2)
$P(C_6H_4$-*o*-$OMe)_3$	na	∼200[d]	3	1	0.03 (2)
$P(C_6H_4$-*p*-$Me)_3$	3.8[c]	145	3	1	0.21 (2)
$P(C_6H_2$-2,4,6-$Me_3)_3$	6.9[e]	212	3	1	0.00 (2)
$P(C_6H_4$-*p*-$Cl)_3$	1.0[c]	145	3	1	0.33 (2)
$P(C_6H_4$-*p*-$F)_3$	2.0[c]	145	3	10	0.37 (2)
			3	1	0.53 (1)
$P(C_6H_4$-*p*-$CF_3)_3$	na	145	3	1	0.05 (4)
$P(C_6F_5)_3$	na	184	3	1	0.02 (2)
$P(C_6H_4$-*p*-$C_2H_4(CF_2)_6F)_3$	na	145	3	1	0.34 (2)
$P(C_6H_3$(-*m*-$CF_3)_2)_3$	na	na	3	10	0.02 (2)
			3	1	0.02 (1)
$P(C_6H_4$-*m*-$SO_3Na)_3$	na	na	3	10	0.02 (2)
			3	1	0.06 (1)
PPh_2(2-py)	na	na	3	1	0.24 (2)
PPh_2Me	4.6[f]	136[g]	10	1	0.06 (1)
			3	1	0.02 (1)
$PPh_2CH_2CH_2CN$	2.2[h]	141	3	10	0.01 (2)
			3	1	0.07 (1)
$PPh_2CH_2CH_2Cl$	3.6[i]	∼141[j]	3	10	0.13 (3)
			3	1	0.08 (1)
$PPh_2C_3H_6OH$	na	∼141[j]	3	10	0.02 (2)
			3	1	0.08 (1)
$PPhMe_2$	6.5[b]	122	10	1	0.62 (1)
			3	1	0.69 (1)
PMe_3	8.7[b]	118	10	1	0.51 (1)
			3	1	0.70 (1)
PEt_3	8.7[b]	132[k]	3	1	0.15 (1)
PBu_3	8.4[b]	132	3	1	0.16 (1)
P^iPr_3	9.4[i]	160	3	1	0.06 (1)
$P(C_3H_6OH)_3$	na	∼132[l]	3	1	0.03 (1)
PCy_3	9.7[b,c]	170	3	1	0.05 (2)

[a] Experimental conditions: 50 °C; 40 bar H_2; total pressure 100 bar; 0.5 mL of NPr_3; 0.5 mL of MeOH; 0.75 mg of $[RuCl_2(C_6H_6)]_2$; 1 h reaction time after CO_2 added. The "pretime" is the pretreatment time, during which the solution is exposed to H_2 but not CO_2. The yield is in terms of moles of formic acid/mole of amine. The number in parentheses is the number of repetitions of the experiment. Cone angle data are from ref 27. All *para*-substituted triphenylphosphines are assumed to have the same cone angle as PPh_3 itself. na = not available. [b] From ref 28. [c] From ref 29. [d] Estimated in ref 30. [e] Calculated from the $MeNO_2$ data of ref 31 and converted to H_2O scale by the equation $pK_a(H_2O) = 0.7675[pK_a(MeNO_2)] - 3.1705$ obtained by correlation of the data of refs 31, 28, and 32. [f] From ref 32 and references therein. [g] From ref 33. [h] From ref 34. [i] Calculated using the equation of ref 35 and the σ^* values of refs 36 and 37. [j] Assumed to be the same as $PPh_2CH_2CH_2CN$. [k] Reference 38. [l] Assumed to be the same as PBu_3.

in the first 1 h. These were PMe_3 and $PPhMe_2$. The in situ catalysts prepared from $[RuCl_2(C_6H_6)]_2$ and 3 equiv of either of these two phosphines were found to be at least as efficient as the isolated catalyst $RuCl(O_2CMe)(PMe_3)_4$ (0.53 mol/mol of NPr_3 under the same conditions).

It is important to emphasize that the purpose of this study was to survey the competence of the phosphines to form, along with a Ru(II) precursor, an effective in situ catalyst. It is not valid, in the interpretation of the results, to assume that the same structures are formed with the various phosphines, that the phosphines are equally soluble, or even that the mechanism of CO_2 hydrogenation is identical with each phosphine.[26]

(26) Not surprisingly therefore, a QALE (quantitative analysis of ligand effects) analysis of the data in Table 2 did not result in a linear correlation. A summary of the QALE approach can be found in: Fernandez, A. L.; Wilson, M. R.; Prock, A.; Giering, W. P. *Organometallics* **2001**, *20*, 3429−3435 and references therein.

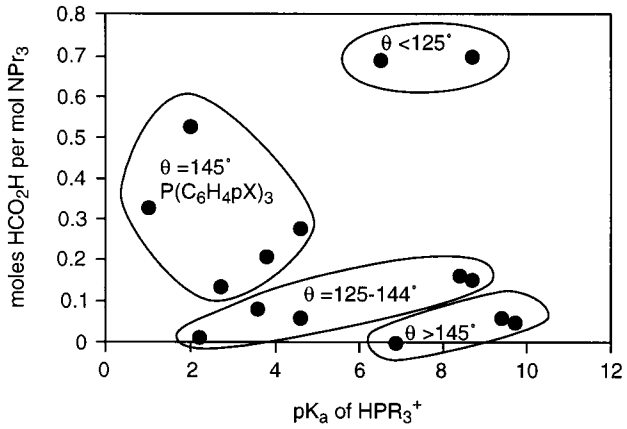


Figure 2. Dependence of the yield in the first 1 h on the pK_a of the phosphine. Conditions: 3 μmol of Ru ($^1/_2[RuCl_2(C_6H_6)]_2$); 9 μmol of phosphine; 0.5 mL of MeOH; 0.5 mL of NPr_3; 40 bar H_2 (during pretreatment time and during reaction); CO_2 added during reaction time only (total pressure 100 bar); pretreatment time 1 h; reaction time 1 h.

The electron-donating ability of the phosphine ligand was related to its effectiveness in forming an active catalyst. The *para*-substituted triphenylphosphines ($P(C_6H_4$-*p*-$X)_3$) had increasing activity in the order CF_3 < H < Me < OMe < $C_2H_4(CF_2)_6F$ = Cl ≪ F. The Hammett constants increase in the order OMe < Me < H < F < Cl < CF_3. The pK_a's of the $[HP(C_6H_4$-*p*-$X)_3]^+$ cations decrease in the order OMe > Me > H > F > Cl. Thus the Hammett and pK_a trends are in agreement with each other but do not bear any relation to the activity of the in situ catalysts. As a result, a plot of the yield of formic acid after 1 h versus the ligand pK_a appears to be close to random (Figure 2). The remarkable effect of fluorine atoms in the *para* positions (causing the rate to more than triple relative to PPh_3) was unexpected. In contrast, perfluorinated PPh_3 was decidedly inferior, perhaps because of steric reasons (vide infra). The progression of ligands PPh_3, PPh_2Me, $PPhMe_2$, and PMe_3 was tested to further explore the effect of ligand basicity on the effectiveness of the in situ catalysts. The rate of formic acid production using these ligands increases in the sequence PPh_2Me < PPh_3 ≪ $PPhMe_2$ = PMe_3. While this trend is more or less consistent with a favorable effect of increasing basicity, it is also consistent with an unfavorable effect of steric bulk. The ligand $P(C_6F_5)_3$, which is an extremely poor base, resulted in a very poor in situ catalyst. Basicity is required probably because (a) the phosphine needs to bind to the metal and (b) the ruthenium hydride needs to be basic enough to be able to transfer hydride to the CO_2 molecule.

Sterically large phosphine ligands created in situ catalysts of poor activity, as illustrated by the trend among the trialkylphosphines (Figure 3). Also, derivatives of triphenylphosphine with groups in the *ortho* positions ($P(C_6H_4$-*o*-$OMe)_3$ and $P(C_6H_2$-*2,4,6*-$Me_3)_3$) were far less effective than those with groups only in the *para* positions ($P(C_6H_4$-*p*-$OMe)_3$ and $P(C_6H_4$-*p*-$Me)_3$). Notably, the most active catalysts were formed from the two ligands with the smallest cone angles, PMe_3 and PMe_2Ph.

The superiority of ruthenium trimethylphosphine catalysts over those with triphenylphosphine has been observed before.[11,12] This superiority is not simply due to the ability

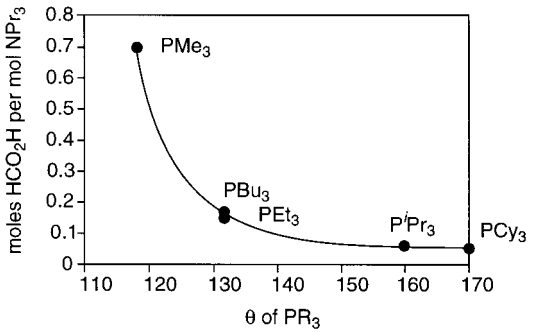


Figure 3. Dependence of the yield in the first 1 h on the cone angle θ of the trialkylphosphine. Conditions are as described in the caption to Figure 2.

of larger numbers of PMe_3 ligands to bind simultaneously to the metal center; even at a fixed Ru:P ratio of 1:3 the PMe_3 ligands produce more active catalysts. However, size is still most certainly a factor (cf. Figure 3), suggesting that a relatively large open area in the catalytic species is vital to the mechanism. In contrast, an earlier study by Angermund et al.[39] found that in some Rh catalysts for CO_2 hydrogenation, the complex with the *smallest* available "solvent accessible surface" around the Rh atom had the greatest activity.

Some ligands had a dangling functional group that could interact with the Ru center or with coligands. For example, Ph_2Ppy (py = 2-pyridyl) was found to make a better catalyst than PPh_3, but this may be related to its chelating ability, its cone angle, or the basicity of the pyridyl group. The results with ligands of the structure $Ph_2PCH_2CH_2X$ (X = Cl, CN, CH_2OH) were disappointing (Table 2). These all had very poor activity but no poorer than the unfunctionalized ligand Ph_2PMe. Trying to incorporate hydroxyl groups onto a trialkylphosphine resulted in lower yields of formic acid ($P(C_3H_6OH)_3 \ll PBu_3$). These functionalized phosphines were of interest because of the accelerating effect of alcohols on CO_2 hydrogenation[1,2,11,12,40] and because of the reported role of a protic ligand in the very rapid hydrogenation of ketones as reported by Noyori.[41]

Table 3. Results with in Situ Catalysts Derived from Monophosphines and $[Ru(methylallyl)_2((cod)]$[a]

phosphine	pK_a of HPR_3^+	cone angle of PR_3 (deg)	P:Ru mol ratio	pretreatment time, h	yield of HCO_2H, mol/mol of base
PPh_3	2.7[b,c]	145	3:1	1	0.07
			6:1	1	0.06
			10:1	1	0.07
$P(C_6H_4$-*p*-F$)_3$	2.0[c]	145	3:1	1	0.52
			6:1	1	0.52
			10:1	1	0.54
PPh_2Me	4.6[d]	136	3:1	1	0.02
			6:1	1	0.02
			10:1	1	0.02
$PPhMe_2$	6.5[b]	122	3:1	1	0.58
			6:1	1	0.58
			10:1	1	0.47

[a] Experimental conditions: 50 °C; 40 bar H_2; total pressure 100 bar; 0.5 mL of NPr_3; 0.5 mL of MeOH; 0.75 mg of $[RuCl_2(C_6H_6)]_2$; 1 h reaction time after CO_2 added. Cone angle data are from refs 27 and 33. [b] From ref 28. [c] From ref 29. [d] From ref 32 and references therein.

A few of the phosphines have unusual solubilities. $P(C_3H_6OH)_3$ and $P(C_6H_4$-*m*-$SO_3Na)_3$ are water soluble, while $P(C_6F_5)_3$, $P(C_6H_3(-m-CF_3)_2)_3$, $P(C_6H_4$-*p*-$CF_3)_3$, and $P(C_6H_4$-*p*-$C_2H_4(CF_2)_6F)_3$ have some solubility in fluorous liquids. Both of the water-soluble ligands failed to produce active catalysts, as did the first three of the fluorinated catalysts. Only $P(C_6H_4$-*p*-$C_2H_4(CF_2)_6F)_3$ produced an effective catalyst, possibly because of the insulating effect[42,43] of the ethylene group in the *para* substituent.

A chlorine-free Ru(II) precursor, $Ru(methylallyl)_2(COD)$, was compared to the $[RuCl_2(C_6H_6)]_2$ precursor (compare Tables 2 and 3). It was anticipated that, in the strongly reducing conditions, the methylallyl ligands would be rapidly displaced by hydride ligands, while the chloride ligands of the $[RuCl_2(C_6H_6)]_2$ precursor might take considerably longer to be so replaced. However, in combination with $P(C_6H_4$-*p*-F$)_3$ and PPh_2Me ligands, the methylallyl precursor gave results virtually identical to those of the $[RuCl_2(C_6H_6)]_2$ precursor. With PPh_3 and $PPhMe_2$ ligands, the methylallyl precursor was slightly less active. These results suggest that the two precursors are equally readily converted to active (presumably hydrido) catalysts.

Screening of Bi- and Polydentate Phosphines. A total of 20 different bi- and polydentate phosphines were tested, in combination with $[RuCl_2(C_6H_6)]_2$, for their ability to form active catalysts for the hydrogenation of CO_2 to formic acid (Table 4). Just over half (11) of the ligands formed catalysts of significant activity (formic acid yield of 0.1 mol/mol of NPr_3 or higher), while only 4 resulted in very high formic acid yields of over 0.6 mol/mol of NPr_3 in the first 1 h. These 4 were dppm, dppe, and *cis*- and *trans*-$Ph_2PCH{=}CHPPh_2$. It has not been determined whether the last two ligands remain unsaturated during the hydrogenation, but note that 1,2-bis(diphenylphosphino)benzene, which is structurally and electronically similar to *cis*-$Ph_2PCH{=}CHPPh_2$ without the readiness to be hydrogenated, had only slightly lower activity. The $Ph_2PC{\equiv}CPPh_2$ ligand, however, is markedly inferior,

(27) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.
(28) Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985−987.
(29) Allman, T.; Goel, R. G. *Can. J. Chem.* **1982**, *60*, 716−722.
(30) Graf, E.; Leitner, W. *Chem. Ber.* **1997**, *129*, 991−96.
(31) Stepanov, B. I.; Bokanov, A. I.; Svergun, V. I. *J. Gen. Chem.* **1971**, *41*, 526−529.
(32) Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981−1991.
(33) Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 53−60.
(34) Fredericks, E. J.; Gindling, M. J.; Kroll, L. C.; Storhoff, B. N. *J. Organomet. Chem.* **1994**, *465*, 289−296.
(35) Henderson, W. A., Jr.; Streuli, C. A. *J. Am. Chem. Soc.* **1960**, *82*, 5791−5794.
(36) Taft, R. W., Jr. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; John Wiley: New York, 1956; p 556.
(37) Stevenson, G. W.; Williamson, D. *J. Am. Chem. Soc.* **1958**, *80*, 5943−5947.
(38) Fernandez, A. L.; Wilson, M. R.; Prock, A.; Giering, W. P. *Organometallics* **2001**, *20*, 3429−3435.
(39) Angermund, K.; Baumann, W.; Dinjus, E.; Fornika, R.; Gorls, H.; Kessler, M.; Kruger, C.; Leitner, W.; Lutz, F. *Chem.—Eur. J.* **1997**, *3*, 755−764.
(40) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259−272.
(41) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97−102.
(42) Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72−75.
(43) Kainz, S.; Koch, D.; Baumann, W.; Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1628−1630.

Table 4. Results with in Situ Catalysts Derived from Diphosphines and $[RuCl_2(C_6H_6)]_2$[a]

phosphine	bite angle	P:Ru mol ratio	pretime, h	yield of HCO_2H
$Cy_2PCH_2PCy_2$ (dcpm)	70[b]	4	1	0.01 (2)
$Cy_2PC_2H_4PCy_2$ (dcpe)	83[c]	6	10	0.03 (3)
		6	1	0.03 (1)
		4	1	0.02 (2)
$Cy_2PC_3H_6PCy_2$ (dcpp)	93[d]	4	1	0.09 (4)
$Cy_2PC_4H_8PCy_2$ (dcpb)	100[e]	6	1	0.42 (3)
		4	1	0.43 (1)
$Ph_2PCH_2PPh_2$ (dppm)	71[f]	4	1	0.63 (2)
$Ph_2PC_2H_4PPh_2$ (dppe)	82[g]	6	10	0.56 (3)
		6	1	0.67 (2)
		4	1	0.71 (3)
		2	1	0.67 (3)
$Ph_2PC_3H_6PPh_2$ (dppp)	91[h]	4	1	0.14 (2)
$Ph_2PC_4H_8PPh_2$ (dppb)	94[i]	4	1	0.00 (3)
$Ph_2PC_5H_{10}PPh_2$	na	6	1	0.12 (2)
		4	1	0.13 (2)
$Ph_2PC_6H_{12}PPh_2$	na	6	10	0.02 (2)
		6	1	0.04 (1)
		4	1	0.03 (2)
$Ph_2PCH{=}CHPPh_2$ (trans)	na	6	1	0.74 (3)
		4	1	0.65 (1)
$Ph_2PCH{=}CHPPh_2$ (cis)	81[j]	4	1	0.62 (2)
$Ph_2PC{\equiv}CPPh_2$	na	4	1	0.13 (2)
$PhHPC_2H_4PHPh$	na	4	1	0.01 (2)
$Ph_2PC_6H_4$-*o*-PPh_2	84[k]	4	1	0.50 (4)
$(Ph_2PC_5H_4)_2Fe$	93[l]	4	1	0.01 (2)
$O(C_6H_4$-*o*-$PPh_2)_2$ (**1**)	na	4	1	0.00 (2)
$(Ph_2PC_2H_4)_2PPh$ (triphos)	na	9	10	0.23 (3)
		9	1	0.20 (1)
		3	1	0.29 (2)
$(Ph_2PC_2H_4)_3P$ (tetraphos)	na	4	1	0.21 (2)
Trost ligand (**2**)	na	6	10	0.01 (2)
		6	1	0.00 (1)

[a] Conditions: 50 °C; 40 bar H_2; total pressure 100 bar; 0.5 mL of NPr_3; 0.5 mL of MeOH; 0.75 mg of $[RuCl_2(C_6H_6)]_2$; 1 h reaction time after CO_2 added. The number in parentheses is the number of repetitions of the experiment. Bite angles are the crystallographically determined P−Ru−P angles of Ru(II) diphosphine complexes. na = not available or not applicable. "Pretime" is the pretreatment time during which the sample is exposed to H_2 and not CO_2. [b] Reference 46. [c] Average of five crystallographically determined angles from refs 47−49. [d] Reference 48. [e] Reference 50. [f] Average of three angles from refs 14 and 51. [g] Average of two angles from ref 52. [h] Reference 53. [i] Average of three angles from refs 54 and 55. [j] Reference 56. [k] Average of two angles from ref 57. [l] Average of two angles from refs 58 and 59.

suggesting that it is not hydrogenated to form dppe or $Ph_2PCH{=}CHPPh_2$. If the nonchelating diphosphine *trans*-$Ph_2PCH{=}CHPPh_2$ is neither hydrogenated nor isomerized during the reaction, then any resulting complexes must necessarily be binuclear, polynuclear, or contain dangling phosphines. Further spectroscopic study is required.

The catalytic activity of ruthenium dppe complexes for CO_2 hydrogenation was first reported by the group of Baiker, who used $RuCl_2(dppe)_2$ as a catalyst precursor for the hydrogenation of CO_2 and dimethylamine to *N*,*N*-dimethylformamide.[13]

We found that, among diphosphines electronically similar to dppe, those with smaller bite angles (dppm, dppe, *cis*-$Ph_2PCH{=}CHPPh_2$, and $Ph_2PC_6H_4$-*o*-PPh_2) were far more successful at forming active catalysts than were those with larger bite angles such as dppp, dppb, dppf, and $O(C_6H_4$-o-$PPh_2)_2$ (Figure 4; Chart 1). The plot of yield versus bite angle for these phosphines is remarkably smooth, suggesting that bite angle is the overriding parameter in determining catalytic

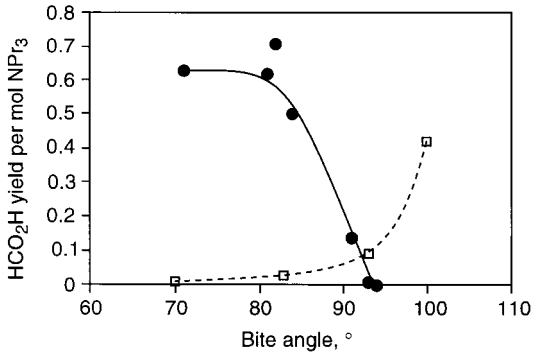
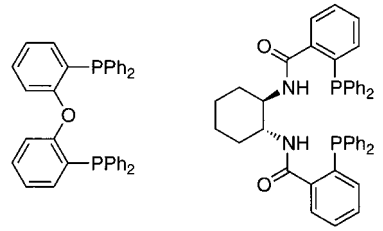


Figure 4. Dependence of the yield of formic acid in the first 1 h on the bite angle of the diphosphine, showing bis(diphenylphosphino) compounds (●) and bis(dicyclohexylphosphino) compounds (□). Conditions: 3 μmol of Ru ($^1/_2[RuCl_2(C_6H_6)]_2$); 6 μmol of diphosphine; 0.5 mL of MeOH; 0.5 mL of NPr_3; 40 bar H_2 (during pretreatment time and during reaction); CO_2 added during reaction time only (total pressure 100 bar); pretreatment time 1 h; reaction time 1 h.

Chart 1. Structures of (Oxy-2,2′-diphenylene)bis(diphenylphosphine) (**1**) and the Trost Ligand (**2**)



efficiency, regardless of the other properties of the backbone such as flexibility or degree of saturation. Research led by DuBois has shown that the bite angle of the diphosphine in a hydrido diphosphine complex directly affects the hydride donor ability of the complex.[44] Note that, in our results, the activity of the ligands $Ph_2P(CH_2)_nPPh_2$ drops down to the low activity of the electronically similar but nonchelating Ph_2PMe as the value of *n* increases.

In contrast, the trends with more basic diphosphines were the opposite; that with the greatest bite angle (dcpb) formed the best catalyst of the series dcpm, dcpe, dcpp, and dcpb (Figure 4). The reason for the contrasting behavior is not known. Consistent with the trend is the earlier report by one of us[11] that Ru dmpe complexes (dmpe = 1,2-bis(dimethylphosphino)ethane, bite angle[45] 85°) have extremely low activity for CO_2 hydrogenation.

The complexes [Rh(hfacac)(P−P)] were compared by Fornika et al.[60] for their activity in catalyzing the same reaction. Of those containing $Ph_2P(CH_2)_nPPh_2$ ligands, the

(44) Berning, D. E.; Noll, B. C.; DuBois, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 11432−11447.
(45) Field, L. D.; George, A. V.; Hockless, D. C. R.; Purches, G. R.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1996**, 2011−2016.
(46) Joslin, F. L.; Mague, J. T.; Roundhill, D. M. *Polyhedron* **1991**, *10*, 1713−1715.
(47) Martelletti, A.; Gramlich, V.; Zurcher, F.; Mezzetti, A. *New J. Chem.* **1999**, *23*, 199−206.
(48) Six, C.; Gabor, B.; Gorls, H.; Mynott, R.; Philipps, P.; Leitner, W. *Organometallics* **1999**, *18*, 3316−3326.
(49) Winter, R. F.; Hornung, F. M. *Inorg. Chem.* **1997**, *36*, 6197−6204.
(50) From the structure of (dcpb)(H)Ru(μ-H)(μ-Cl)$_2$Ru(H$_2$)(dcpb): Freed, T.; Jessop, P. G.; Olmstead, M. M. Unpublished material, 1997.
(51) Winter, R. F.; Hornung, F. M. *Organometallics* **1999**, *18*, 4005−4014.

trend was found to be dppe < dppp < dppb, opposite of the trend found in the present case. Of those containing $Cy_2P(CH_2)_nPCy_2$ ligands, the trend was dcpe ≪ dcpb, as found in the Ru system. These trends for the Rh system were explained in a subsequent article[39] as being a function of the size of the open site on the Rh center; the greatest catalytic activity was observed with the complex which had the smallest "solvent accessible surface" around the Rh atom, as calculated by molecular modeling.

The number of equivalents of diphosphine added to the ruthenium precursor had little effect on the effectiveness of the catalyst, as long as the P/Ru ratio was greater than 3. The effect of this ratio with PPh_3 has already been described (Figure 1). The same result was found with the ligands dppe and triphos (Table 4).

The tridentate and tetradentate phosphine ligands triphos and tetraphos were significantly less effective than the electronically similar dppe, a result for which we at present have no explanation. Spectroscopic measurements (see below) suggest that two dppe ligands bind to the Ru in the spectroscopically detectable species. However, it is possible that the catalytically active species contains only one dppe (i.e. a P:Ru ratio of 2), a structure which triphos and tetraphos could not easily reproduce.

Ligands incorporating acidic protons were again put to the test. Introducing a secondary diphosphine ($PhHPC_2H_4PHPh$) instead of tertiary diphosphines resulted in almost complete loss of catalytic activity. Although it was not spectroscopically confirmed, it is possible that CO_2 reacted with the P−H bond. The Trost ligand (Chart 1) places a formamide NH proton near the catalyst; unfortunately no active hydrogenation catalyst was formed from the combination of the Trost ligand with $[RuCl_2(C_6H_6)]_2$. In another attempt to incorporate protic groups into the catalyst, in situ catalysts were prepared from mixtures of $[RuCl_2(C_6H_6)]_2$, a diphosphine, and a bidentate protic ligand (Table 5, Ru:diphosphine ratio 1:1). None of these caused a significant enhancement of the rate of formic acid production over that in the absence of protic ligand. With diols and *o*-phenylenediamine, the rate was essentially unchanged. Ketones lowered the rate slightly, and dithiols and the secondary diphosphine bis(phenylphosphino)ethane had a stronger poisoning effect.

Literature Reports of the Reaction of Ru(II) Precursors with Phosphines. The effectiveness of any one ligand/precursor combination may not only be a function of the activity of the resulting complex but also may be affected by the structure of the complex which is obtained. For this reason, it is important to describe what is known about the reaction products of the dichlororuthenium(II) precursors with phosphines.

Table 5. Results with in Situ Catalysts Derived from a Diphosphine, Another Ligand, and $[RuCl_2(C_6H_6)]_2$[a]

diphosphine	P:Ru mol ratio	ligand	ligand:Ru mol ratio	yield of HCO_2H
none	0:1	HOC_2H_4OH	3:1	0
			10:1	0
		HOC_6H_4-*o*-OH	3:1	0.02
			10:1	0.02
		$H_2NC_6H_4$-*o*-NH_2	3:1	0
			10:1	0
dppe	2:1	none	0:1	0.67
		HOC_2H_4OH	1:1	0.69
		$HOCH_2CH_2CH_2OH$	10:1	0.58
		HOC_6H_4-*o*-OH	10:1	0.64
		$HOCH_2CH_2C(O)CH_3$	10:1	0.49
		$CH_3C(O)CH_2C(O)CH_3$	10:1	0.50
		$HSCH_2CH_2SH$	10:1	0.12
		$HSCH_2CH_2CH_2SH$	10:1	0.37
		$H_2NC_6H_4$-*o*-NH_2	10:1	0.67
		$Ph_2PC_6H_4$-*o*-PPh_2	1:1	0.73
			10:1	0.82
		$PhHPC_2H_4PHPh$	1:1	0.16
dppb	4:1	none	0:1	0.14
	2:1	$H_2NC_6H_4$-*o*-NH_2	10:1	0.03

[a] Condition: 50 °C; 40 bar H_2; total pressure 100 bar; 0.5 mL of NPr_3; 0.5 mL of MeOH; 0.75 mg of $[RuCl_2(C_6H_6)]_2$ (3 μmol of Ru); 3 μmol of dppe; 1 h pretreatment time under 40 bar H_2; 1 h reaction time after CO_2 added.

Reaction of $[RuCl_2(COD)]_n$ with 2 equiv of PCy_3 and excess base in *sec*-butyl alcohol or in toluene under H_2 is known to give $RuH_2(H_2)_2(PCy_3)_2$.[61−63] With PEt_3 in *sec*-butanol, one obtains $RuH_2(PEt_3)_4$, and with PPh_3, one obtains $RuH_2(PPh_3)_3$.[64] This suggests that, under the pretreatment conditions used in this study with $[RuCl_2(COD)]_n$ and PPh_3, at least partial conversion to $RuH_2(PPh_3)_3$ or similar hydridic species could reasonably be expected.

Reaction of *trans*-$RuX_2(DMSO)_4$ with 1 or 2 equiv of a monophosphine in refluxing toluene for 30−40 min gives $RuX_2(DMSO)_3(L)$ (where X = Br and L = PPh_3 or PBu_3)[65] or $RuX_2(DMSO)_2(L)$ (X = Cl; L = PPh_3).[15] Complete displacement of the DMSO ligands by a new ligand was demonstrated by Evans et al., who refluxed $RuCl_2(dmso)_4$ in pyridine, obtaining $RuCl_2(pyridine)_4$.[15] Therefore, the in situ catalysts derived from $RuCl_2(dmso)_4$ and excess PR_3 are not expected to contain DMSO ligands.

Reaction of a monophosphine with $[RuCl_2(C_6H_6)]_2$ yields $RuCl_2(C_6H_6)(PR_3)$. This has been observed for a range of alkyl- and arylphosphines and is fairly rapid at 55 °C.[66,67]

(52) Atherton, Z.; Faulkner, C. W.; Ingham, S. L.; Kakkar, A. K.; Khan, M. S.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Organomet. Chem.* **1993**, *462*, 265−270.
(53) Lobana, T. S.; Verma, R.; Singh, R.; Castineiras, A. *Transition. Met. Chem.* **1998**, *23*, 25−28.
(54) MacFarlane, K. S.; Joshi, A. M.; Rettig, S. J.; James, B. R. *Inorg. Chem.* **1996**, *35*, 7304−7310.
(55) Joshi, A. M.; Thorburn, I. S.; Rettig, S. J.; James, B. R. *Inorg. Chim. Acta* **1992**, *200*, 283−296.
(56) Batista, A. A.; Cordeiro, L. A. C.; Oliva, G.; Nascimento, O. R. *Inorg. Chim. Acta* **1997**, *258*, 131−137.
(57) Mashima, K.; Komura, N.; Yamagata, T.; Tani, K.; Haga, M. *Inorg. Chem.* **1997**, *36*, 2908−2912.
(58) Jensen, S. B.; Rodger, S. J.; Spicer, M. D. *J. Organomet. Chem.* **1998**, *556*, 151−158.
(59) Mai, J. F.; Yamamoto, Y. *J. Organomet. Chem.* **1998**, *560*, 223−232.
(60) Fornika, R.; Göris, H.; Seemann, B.; Leitner, W. *J. Chem. Soc., Chem. Commun.* **1995**, 1479−1481.
(61) Belderrain, T. R.; Grubbs, R. H. *Organometallics* **1997**, *16*, 4001−4003.
(62) Wilhelm, T. E.; Berderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867−3869.
(63) Beatty, R. P.; Paciello, R. A. U.S. 5,444,778, 1996.
(64) Nolan, S. P.; Belderrain, T. R.; Grubbs, R. H. *Organometallics* **1997**, *16*, 5569−5571.
(65) Riley, D. P. *Inorg. Chim. Acta* **1985**, *99*, 5−11.
(66) Zelonka, R. A.; Baird, M. C. *Can. J. Chem.* **1972**, *50*, 3063−3072.
(67) Werner, H.; Werner, R. *Chem. Ber.* **1982**, *115*, 3766−3780.

The isolated complex $RuCl_2(C_6H_6)(PMe_3)$ has been found to be inferior to $RuCl_2(PMe_3)_4$ in terms of catalytic activity for the hydrogenation of terminal olefins.[68] Our results show that a 1:1 ratio of Ru to PPh_3 gives an unsatisfactory catalyst (Figure 1). However, higher ratios give much greater yields of formic acid, suggesting that the catalytic species at the higher ratios are different from that obtained at a 1:1 ratio. We initially supposed that the benzene ligand would be displaced during the reaction; spectroscopic evidence (see below) has shown that the displacement of the benzene ligand is temperature, solvent, and pressure dependent.

The first product from the reaction of a diphosphine (P−P) with $[RuCl_2(C_6H_6)]_2$ is either $RuCl_2(C_6H_6)(\eta^1\text{-P}-\text{P})$ or $[RuCl_2(C_6H_6)](\mu\text{-P}-\text{P})$. Zelonka and Baird found that reacting the Ru precursor with 1 equiv of dppm in MeCN at 45 °C for 1 h gave the former product while dppb gave the latter.[66] Reaction of the Ru precursor with *excess* P−P gives $RuCl_2(P-P)_2$, so long as the P−P is nonbulky (e.g. dppe). However, with excess dppb one obtains primarily $[RuCl(C_6H_6)(P-P)]Cl$ and some of the bridged product $[RuCl_2(C_6H_6)](\mu\text{-P}-\text{P})$.[69] The failure of dppb in our tests may be directly related to its inability to displace the benzene and form a $RuX_2(P-P)_2$ complex. That the latter structure would have had some catalytic activity is suggested by the fact that activity for hydrogenation (of imines) has been observed for a range of Ru dppb complexes, including $Ru_2Cl_5(dppb)_2$, $Ru_2Cl_4(dppb)_2$, and $[RuHCl(dppb)]_2$. Only $[RuCl_2(dppb)]_2(\mu\text{-dppb})$ was reported to have very low activity.[70]

Bennett and Ennett[71] found that, in the presence of H_2 and NEt_3, the complex $[RuCl_2(C_6H_6)]_2$ is converted, even at room temperature and low pressure, to $[Ru(C_6H_6)]_2HCl_3$, further suggesting that the $[RuCl_2(C_6H_6)]_2$ precursor readily converts to hydride species under our catalytic conditions.

NMR Spectroscopic Observations of in Situ Catalyst Formation. Results of spectroscopic monitoring of organometallic species during CO_2 hydrogenation will be described in a separate publication. However, the following summarizes the preliminary results relevant to the present discussion.

A series of ^1H and ^{31}P NMR experiments were carried out on reaction mixtures containing $[RuCl_2(C_6H_6)]_2$ and dppm so that a representative sample of the ruthenium-containing species present during the catalytic reaction could be ascertained. The ^{31}P NMR studies of these catalyst systems were complicated by the cis/trans isomers of the $Ru(Y)(Z)(dppm)_2$ which apparently depend on the polarity of the solvent and the substituents. Nonpolar solvents yield predominantly cis isomers, in which A_2MX, for $Y \neq Z$, and pseudotriplets, for $Y = Z$, patterns are observed in the ^{31}P NMR spectrum. Polar solvents, such as alcohols, give predominantly *trans*-$Ru(X)(Y)(dppm)_2$ in which all phosphorus nuclei are equivalent yielding a singlet in the ^{31}P NMR spectrum. For example $RuCl_2(dppm)_2$ is 100% trans when synthesized from $RuCl_3$ in ethanol[72,73] while the cis isomer is isolated from the reaction of dppm with $RuCl_2(dmso)_4$ in toluene.[74]

Room-temperature reactions of $[RuCl_2(C_6H_6)]_2$ and dppm (either Ru:dppm 1:1 or 1:2) in CH_2Cl_2 and in CH_3CN yielded the expected $RuCl_2(C_6H_6)(dppm)$ complex with one phosphorus atom bound to the ruthenium and one phosphorus atom dangling.[66,75] Heating this reaction mixture to 50 °C produced the dimer $[RuCl_2(C_6H_6)(dppm)RuCl_2(C_6H_6)]$. If insufficient dppm (<1 dppm/Ru) was added to these reaction mixtures, then more of the dimer $[RuCl_2(C_6H_6)(dppm)RuCl_2(C_6H_6)]$ was observed even before heating. When the reaction of $[RuCl_2(C_6H_6)]_2$ with excess dppm in CH_2Cl_2 was carried out under 8 bar of H_2 at 50 °C for 16 h, a product NMR study showed a 2:1 mixture of $RuCl_2(dppm)(C_6H_6)$ and *trans*-$RuCl_2(dppm)_2$. In situ ^{31}P NMR spectra of this reaction mixture did show *trans*-$RuHCl(dppm)_2$ while under H_2, but upon release of the pressure, the *trans*-$RuHCl(dppm)_2$ converted to *trans*-$RuCl_2(dppm)_2$. Reaction of $[RuCl_2(C_6H_6)]_2$ with dppm (1:2 Ru:dppm) under 20 bar CO_2 at 50 °C for 20 h in CH_2Cl_2 yielded a 1:1 mixture of $RuCl_2(dppm)(C_6H_6)$ and *trans*-$RuCl_2(dppm)_2$. There was no evidence of any reaction with CO_2.

Similar reactions between $[RuCl_2(C_6H_6)]_2$ with dppm (1:2 Ru:dppm) conducted in methanol/triethylamine solvent instead of CH_2Cl_2 at 50 °C yielded almost exclusively *trans*-$RuCl_2(dppm)_2$ (>90% isolated yield). Product ^{31}P and ^1H NMR spectra of the reaction mixture of $RuCl_2(dppm)(C_6H_6)$ and dppm in MeOH:NEt_3 after reaction at 50 °C for 8 h under 8 bar of H_2 showed the presence of *trans*-$RuHCl(dppm)_2$ (50%), *trans*-$RuCl_2(dppm)_2$ (30%), and *cis*-$RuCl_2(dppm)_2$ (20%). No $RuCl_2(dppm)(C_6H_6)$ was observed in this reaction mixture by in situ NMR studies. In situ ^{31}P NMR studies conducted under 20 bar of H_2 showed the conversion of $[RuCl_2(C_6H_6)]_2$ to five major species. Heating to 50 °C did not appear to alter the final distribution of these species but had a pronounced effect on the rate at which these species were produced. The species were produced within 1 h at 50 °C, while at room temperature the mixture does not reach "equilibrium" for several hours. All the major species produced under H_2 had trans orientation as detemined by ^{31}P NMR spectroscopy. The species produced include the dihydride (31%), hydrochloride (25%), and the dichloride (2%). Two unidentified species were present at 3.2 ppm (12%) and −7.1 ppm (29%) in the ^{31}P NMR spectrum. These species were produced first and then decreased upon the formation of the known dihydride and hydrochloride. Upon addition of CO_2 (20 bar) both the 3.2 and the −7.1 ppm peaks disappeared and two new major sets of ^{31}P NMR signals showing cis orientation appeared and increased in intensity with the production of formate. An A_2MX pattern

(68) Singer, H.; Hademer, E.; Oehmichen, U.; Dixneuf, P. *J. Organomet. Chem.* **1979**, *178*, C13−C16.
(69) Fogg, D. E.; James, B. R. *J. Organomet. Chem.* **1993**, *462*, C21−C23.
(70) Fogg, D. E.; James, B. R.; Kilner, M. *Inorg. Chim. Acta* **1994**, *222*, 85−90.
(71) Bennett, M. A.; Ennett, J. P. *Organometallics* **1984**, *3*, 1365−1374.
(72) Jung, C. W.; Garrou, P. E.; Hoffman, P. R.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 726.
(73) Mirza, H. A.; Vitaal, J. J.; Puddephatt, R. J. *Inorg. Chem.* **1993**, *32*, 1327−1332.
(74) Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Dalton Trans.* **1984**, 1635.
(75) Zelonka, R. A.; Baird, M. C. *J. Organomet. Chem.* **1972**, *44*, 383−389.

with multiplets centered at 49.5, 19.6, and 9.8 ppm (4%) and a pseudotriplet centered at 9.1 and −11.8 ppm (15%) were observed along with the dihydride (56%) and hydrido chloride (24%) and a small amount of the dichloride. The appearance of these two new sets of ^{31}P NMR resonances corresponding with the catalytic production of formate suggests formato complexes of ruthenium were being formed. Pertuz has observed the formation of *cis*- and *trans*-Ru(H)-(O_2CH)(dmpe)$_2$ and *cis*-Ru$(O_2CH)_2$(dmpe)$_2$ from the reaction of *cis*-RuH_2(dmpe)$_2$ with CO_2.[76] The complex patterns for the dmpe formato compounds are similar to those observed for dppm in this study. The *trans*-Ru(H)(O_2CH)(dppm)$_2$ may have been present as an unidentified minor singlet.

Removal of solvents under vacuum and redissolution of the reaction mixture in $CDCl_3$ yielded deceptively simple ^{31}P and ^{1}H NMR spectra showing only *trans*-dichloride, *trans*-hydrido chloride, and a trace of *cis*-dichloride. The *trans*-dihydride could be detected in small yields with careful solvent removal and the use of C_6D_6 as the solvent. None of the other ^{31}P NMR resonances which were observed by in situ ^{31}P NMR spectroscopy were observed in the product.

While these NMR studies are incomplete and they do not show a definitive active catalytic species, they do demonstrate several important points. First, these NMR studies show that efficient mixing and elevated temperatures are needed for the production of metal hydrides from the ruthenium starting materials used in this study. Hence the need for the 1 h pretreatment time at 50 °C with vigorous stirring in the screening studies in this paper. The low concentration of H_2 in the triethylamine/methanol solvent used in these studies (measured by ^{1}H NMR spectroscopy to be 0.006 mol fraction of H_2 in triethylamine/methanol at 20 bar and 293 K) contributes to the slow conversion of the precursors to hydrides.[77] In situ NMR studies (in which no stirring was possible) show that the reaction to form the ruthenium dihydride or the ruthenium hydrochloride is not complete after 5 h at room temperature. However, ex situ NMR studies of the organometallic products do show that vigorous stirring of the reaction mixture at 50 °C for 1 h is sufficient to produce a near equilibrium mixture of the hydride/dihydride.

Second, hydride and dihydride species are readily formed under these reaction conditions and appear to be the major products under H_2 pressure. The triethylamine presumably acts as a HCl sponge to facilitate the production of hydrides and dihydrides from the chlorides. The unassigned species present under H_2 pressure before the addition of CO_2 may be due to methoxide or methyl carbonate ions present in solution. These would be analogous to the phenoxy compounds previously observed.[78] While we do not observe any direct reaction of the ruthenium chlorides with methanol, the reaction of methanol with the ruthenium hydrides may lead to species containing methoxy and hydride ligands.

The in situ NMR studies are continuing with "cleaner" single component systems. More complete results of the NMR studies will be reported elsewhere.

Conclusions

A total of 44 different phosphines were tested, in combination with [Ru$Cl_2(C_6H_6)]_2$ and three other Ru(II) precursors, for their ability to form active catalysts for the hydrogenation of CO_2 to formic acid. Half (22) of the ligands formed catalysts of significant activity, but only 6 resulted in very high formic acid yields (over 0.6 mol/mol of NPr_3 in the first 1 h). These were PMe_3, $PPhMe_2$, dppm, dppe, and *cis*- and *trans*-$Ph_2PCH{=}CHPPh_2$. The in situ catalysts prepared from [Ru$Cl_2(C_6H_6)]_2$ and any of these 6 phosphine ligands were found to be at least as efficient as the isolated catalyst Ru$Cl(O_2CMe)(PMe_3)_4$. A P:Ru mole ratio of at least 3 was required to create a reasonably active catalyst. Among the monophosphines, the two with the smallest cone angles were the most active. There was no correlation between the basicity of monophosphines and the activity of the catalysts formed from them. However, weakly basic *diphosphines* formed highly active catalysts only if their bite angles were small, while more strongly basic diphosphines had the opposite trend. Ligands incorporating acidic protons were inferior to those without such groups. Studies to spectroscopically identify the major Ru-containing species present during catalysis have begun; preliminary results indicate that, with [Ru$Cl_2(C_6H_6)]_2$ and dppm, RuHCl(dppm)$_2$ and Ru$(H)_2$-(dppm)$_2$ are the primary species present under hydrogen, while the formato species, Ru(H)(O_2CH)(dppm)$_2$ and Ru-$(O_2CH)_2$(dppm)$_2$, grow in as formate is produced under CO_2 and H_2.

Acknowledgment. We acknowledge helpful discussions with Dr. R. H. Morris of the University of Toronto and a kind gift of P$(C_6H_4$-*p*-$C_2H_4(CF_2)_6F)_3$ from Dr. J.-L. Xiao of the University of Liverpool. C.-C.T., J.P., P.M., and P.G.J. also gratefully acknowledge support from the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy (Grant No. DE-FG03-99ER14986). This support does not constitute an endorsement by DOE of the views expressed in this article. J.C.L. and A.D.M. gratefully acknowledge support by the Director, Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract DE-ACO6-76RLO 1830.

IC010866L

(76) Whittlesey, M. K.; Perutz, R. N.; Moore, M. H. *Organometallics* **1996**, *15*, 5166−5169.

(77) The mole fraction of H_2 in methanol at 298 K and 20 bar is reported to be 0.003: Young, C. L., Ed. *Hydrogen and Deuterium*; Solubility Data Series; Pergamon Press: Oxford, U.K., 1981; Vol. 5/6.

(78) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *Organometallics* **1991**, *10*, 1875−1887.