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A Tertiary Phosphonium Salt as a Promoter for the Hydrogenation of CO

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Small amounts of $[HPBu_3]Br$ that are either present as an impurity in commercial $[Bu_4P]Br$ or are added to it promote the hydrogenation of CO catalysed by $[Ru_3(CO)_{12}]$. $[HPBu_3]Br$ may be responsible for the irreproducibility that is sometimes observed in similar CO-hydrogenation reactions.

The homogeneous conversion of synthesis gas into functional chemicals was first reported by Gresham in the 1950s. In these reactions, metal sources were subjected to high temperatures and very high pressures of syngas to form alcohols and polyols.[1] One goal in the research of syngas has been to form C–C bonds from individual molecules of CO whilst retaining some or all of the oxygen functionality. The heterogeneous hydrogenation of CO tends to promote cleavage of the CO bond with the formation of alkanes and alkenes (Fischer–Tropsch chemistry)[2–5] but the early examples from Gresham showed that homogeneous ruthenium catalysts are able to provide oxygenates. Subsequent research by Dombek (Union Carbide) and Bradley (Exxon) found that the activity could be greatly enhanced by the addition of halide promoters, preferably iodide.[6–12] Knifton and co-workers independently found good yields when using molten tetraalkylphosphonium halide salts as solvents instead of the usual organic media.[13–15] Whereas Dombek's system with *N*-methylpyrrolidone and iodide salts was particularly useful for spectroscopic- and mechanistic analysis,[10,16] Knifton focused on tuning the selectivity towards a wide scope of products, such as MeOH,[15,17] EtOH,[18] 1,2-ethanediol,[19–21] and acetic acid[13,22] and their derivatives.[23] Following Dombek's work, Ono et al. found that a remarkable increase in selectivity towards EtOH could be achieved by using phosphoric acid or trimethylphosphate as a promoter.[24,25] Although these systems work well, the problem remains that very high pressures and temperatures are required to achieve reasonable conversions and, therefore, considerable emphasis must continue to be directed towards elucidating the mechanisms of all of these processes and towards finding factors that increase the reaction rates. Herein, we report an interesting promoter that increases the rate of MeOH production.

By using the melt chemistry reported by Knifton et al.[15] with tetrabutylphosphonium bromide as the solvent and $[Ru_3(CO)_{12}]$ as a catalyst precursor at 200 °C, but under milder pressures (CO/H_2, 1:1, 250 bar), MeOH and EtOH are observed as the main products, together with smaller amounts of propanol and 1,2-ethanediol. Qualitative analysis of the gas phase before or after condensing any condensable compounds shows significant amounts of dimethyl-, methylethyl-, and diethyethers, which we have shown elsewhere are formed from the acid-catalysed dehydration of the alcohol products. However, the reproducibility of this system was poor. Marked changes in activity were observed whenever different batches (lot number) of tetrabutylphosphonium bromide were employed. Some batches showed good activity whereas others gave much-poorer activity. Scrutiny of concentrated samples of these different batches of $[PBu_4]Br$ by ^{31}P NMR spectroscopy revealed three peaks (Figure 1). The strongest signal ($\delta = 33.56$ ppm) was from tetrabutylphosphonium bromide.[26] In most batches, another peak was present at $\delta = 37.49$ ppm, owing to tri-*n*-butyl(sec-butyl)phosphonium bromide, which was formed by Markovnikoff addition of the P–H bond across 1-butene during the synthesis of PBu_3 from PH_3 and 1-butene. This peak was more intense in the less-active batch of $[PBu_4]Br$.

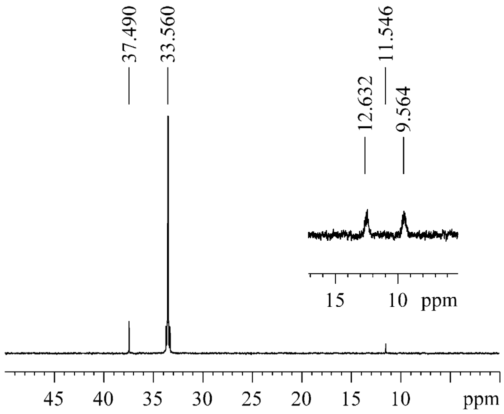

Figure 1. $^{31}P\{^1H\}$ NMR spectrum of an active batch of $[PBu_4Br]$. Inset: H-coupled signal for the resonance at $\delta = 11.55$ ppm.

The $^{31}P\{^1H\}$ NMR spectrum of the active batch revealed an additional peak at $\delta = 11.55$ ppm, which split into a doublet ($J(H,P) = 487$ Hz) in the proton-coupled ^{31}P NMR spectrum (Figure 1). Likewise, careful scrutiny of the ^1H NMR spectrum (see the Supporting Information, Figure S2) of the same sample revealed a low-intensity doublet ($\delta = 6.83$ ppm, $J(H,P) = 487$ Hz) in addition to the signals from the butyl groups. These signals were assigned to tributylphosphonium bromide, $[HPBu_3]Br$, which is a protonated form of tributyl phosphine. This impurity is presumably formed during the synthesis of tetrabutylphosphonium bromide when tributylphoshine reacts

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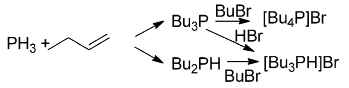


Scheme 1. Process for the production of $[Bu_4P]Br$ and how this process can lead to the formation of small amounts of $[HPBu_3]Br$ as an impurity.

with free HBr or when *n*-butylbromide reacts with traces of di(*n*-butyl)phosphine (Scheme 1); it is not present in the batches of $[PBu_4]Br$ that provide lower hydrogenation activity. The sec-butyl isomer of $[Bu_4P]Br$ should have little effect on the catalysis in the system, but $[HPBu_3]Br$ was not so innocent during the catalysis.

Because the batch of $[Bu_4P]Br$ that contained $[HPBu_3]Br$ was more active, we purified a sample of the active batch by reprecipitating it from acetone with Et_2O. This procedure effectively removed almost all of the $[HPBu_3]Br$. We also synthesised pure $[HPBu_3]Br$ from tri(*n*-butyl)phosphine and HBr and used it in a series of reactions in which we increased the amount of $[HPBu_3]Br$ that was present in $[PBu_4]Br$. The results of this series of experiments (Figure 2, empty symbols) clearly demonstrate that $[HPBu_3]Br$, in a limited- and low concentration range, acts as a promoter for the CO-hydrogenation reaction in this system. The activity towards MeOH increases as the $[HPBu_3]Br$/Ru ratio is increased to 0.5 and then falls at higher ratios.

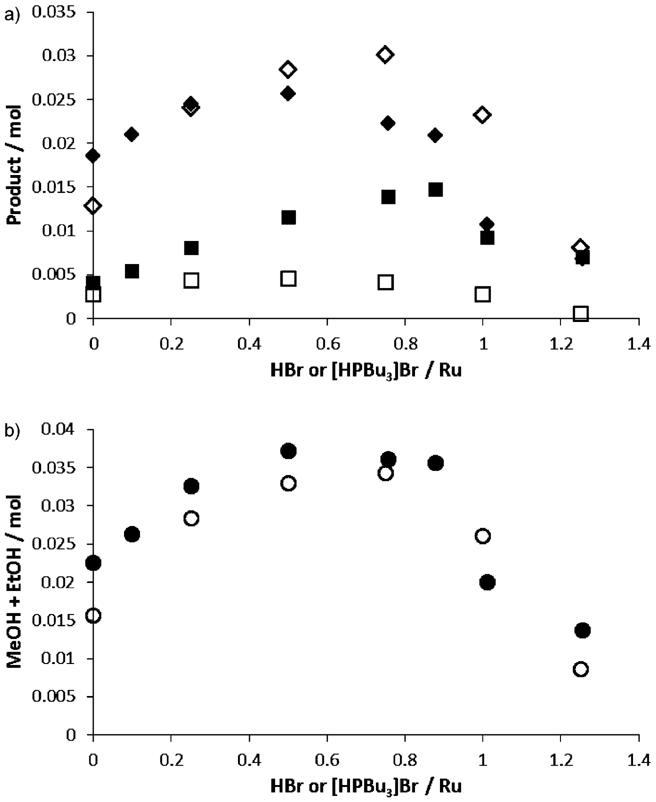


Figure 2. a) Yields of MeOH (◇, ◆) and EtOH (□, ■) from the hydrogenation of CO catalysed by $[Ru_3(CO)_{12}]$ (0.25 g, 0.39 mmol) in $[PBu_4]Br$ (15 g) with added $[HPBu_3]Br$ (empty shapes) or HBr (filled shapes); CO/H_2 (1:2, 250 bar), 200 °C. b) Yield of MeOH+EtOH from the reactions shown in Figure 2a with added $[HPBu_3]Br$ (○) or HBr (●).

At the end of the reactions that are depicted in Figure 2a, the colour varied markedly from dark red (no $[HPBu_3]Br$) through orange to yellow ($[HPBu_3]Br$/Ru, 1:1). These final solutions were studied by IR spectroscopy. When no $[HPBu_3]Br$ was added (dark-red colour after the reaction, Figure 3a), the IR spectrum showed peaks at 2112, 2073, 2015, 1988, and 1952 cm^{-1} and there was a peak at $\delta = -12.67$ ppm in the hydride region of the ^1H NMR spectrum. These spectroscopic features can be assigned to $[HRu_3(CO)_{11}]^-$.[27] However, yellow post-reaction solutions that were obtained from reactions with $[HPBu_3]Br/Ru \geq 1$ (Figure 3c) had IR absorptions at 2111, 2048, 2036, 1970, and 1940 cm^{-1}, a less-intense hydride resonance at $\delta = -12.67$ ppm, and a new triplet hydride resonance at $\delta = -6.30$ ppm ($[RuHBr(CO)_2(PBu_3)_2]$).[37] The IR absorptions from these solutions with $[HPBu_3]Br/Ru \geq 1$ mainly correspond to $[Ru(CO)_3Br_3]^-$.[27–29] The spectra (Figure 3b) from successful reactions that contain added $[HPBu_3]Br$ can be assigned as arising from mixtures of $[HRu_3(CO)_{11}]^-$, $[RuHBr(CO)_2(PBu_3)_2]$, and $[RuBr_3(CO)_3]^-$; the relative intensities of the peaks that belong to each compound are dependent on the amount of $[HPBu_3]Br$ that is added. This result suggests that, for higher reactivity, a catalyst composition that contains both $[HRu_3(CO)_{11}]^-$ and $[Ru(CO)_3Br_3]^-$ is needed and that $[HPBu_3]Br$ reacts with $[HRu_3(CO)_{11}]^-$ to give $[Ru(CO)_3Br_3]^-$.

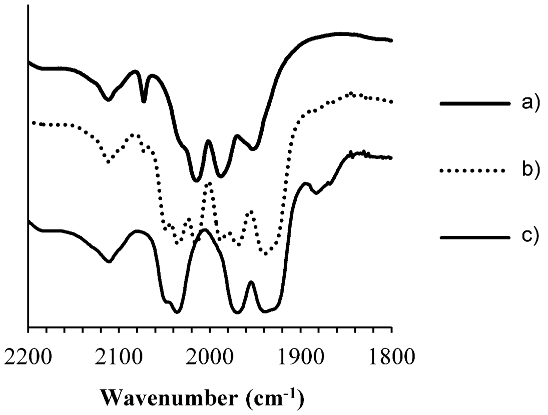


Figure 3. IR spectra that were obtained after the hydrogenation of CO catalysed by $[Ru_3(CO)_{12}]$ (0.25 g, 0.39 mmol) in $[PBu_4]Br$ (15 g) with a) no added $[HPBu_3]Br$; b) $[HPBu_3]Br$ (0.75 mol (mol Ru)$^{-1}$); or c) $[HPBu_3]Br$ (1.25 mol (mol Ru)$^{-1}$). The complete spectra are shown in the Supporting Information, Figures S7–S9.

In a related system with $[Ru_3(CO)_{12}]$ and KI in *N*-methylpyrrolidinone (NMP) as a solvent, Dombek has also shown that both $[HRu_3(CO)_{11}]^-$ and $[RuI_3(CO)_3]^-$ must be present in the solution for it to be active towards CO-hydrogenation.[10,11] He argued that $[HRu_3(CO)_{11}]^-$ donates a hydride moiety to $[RuI_3(CO)_3]^-$ (or a complex that is derived from it) to make the key formyl intermediate, which is not readily made by the direct intramolecular migration of a hydride group onto CO. In support of this argument, Dombek and Harrison showed that a rhenium–formyl complex could be formed by intermolecular hydride-transfer from $[HRu(CO)_4]^-$ to $[CpRe(NO)(CO)_2]$.[30] Some of us also provided support for this intermolecular hydride-transfer mechanism by synthesising $[Ru(CHO)(CO)(dppe)_2][SbF_6]$ (dppe = 1,2-bis(diphenylphosphino)ethane) through hydride-transfer from $[HRu(CO)_9(dppe)_2]^-$ to $[Ru(CO)_2(dppe)_2][SbF_6]_2$.[31,32]

Interestingly, Ono et al. have shown that $[Ru_3(CO)_{12}]$ reacts with bis(triphenylphosphine)iminium chloride ([PPN]Cl) under CO/H_2 pressure to give $[HRu_3CO_{11}]^-$ and that, when HCl is added, $[Ru(CO)_3Cl_3]^-$ forms. This latter complex is inactive towards CO-hydrogenation, but the active species in that system is believed to be $[RuH(CO)_4]^-$.[24]

One possible mechanism for the activation of the ruthenium catalysts by $[HPBu_3]Br$ would be for the tertiary phosphonium salt to act as a source of HBr, which might then react with $[HRu_3(CO)_{11}]^-$ to give $[RuBr_3(CO)_3]^-$. To test this possibility, we performed a series of reactions with equivalent amounts of HBr (Figure 2 a, filled symbols) to those of $[HPBu_3]Br$. The shape of the graph of MeOH-production is similar to that when using $[HPBu_3]Br$, except that the yield of MeOH decreases more quickly at higher [HBr].

By using ^{13}C-labelling studies,[33] we have shown that EtOH is formed through MeOH as an intermediate; thus, the overall rate of MeOH-production is represented by the rate of formation of MeOH+EtOH. These data are presented in Figure 2 b for the systems that are promoted by $[HPBu_3]Br$ (open symbols) and by HBr (filled symbols). The very close correspondence of these graphs very strongly suggests that the role of $[HPBu_3]Br$ is to act as a source of HBr. The trend in the yield of MeOH+EtOH, together with IR studies, which show that $[HRu_3(CO)_{11}]^-$ is smoothly converted into $[Ru_3(CO)_3]^-$ as HBr is added, also reinforce the view that both $[HRu_3(CO)_{11}]^-$ and $[RuBr_3(CO)_3]^-$ must be present in the solution to afford good activity in MeOH-production.

The situation for EtOH is different when using HBr compared with that when using $[HPBu_3]Br$. In the presence of HBr, the yield of EtOH increases as [HBr] is increased and only falls when the yield of MeOH becomes low, although the ratio of EtOH/MeOH continues to increase. These observations suggest that $[RuBr_3(CO)_3]^-$, which also increases at the expense of $[HRu_3(CO)_{11}]^-$ as HBr is added, is the major species that is responsible for the conversion of MeOH into EtOH. In contrast, when $[HPBu_3]Br$ is used, the yield of EtOH remains fairly constant as increasing amounts of $[HPBu_3]Br$ are added, before falling at higher concentrations of $[HPBu_3]Br$. $[MePBu_3]Br$ is observed by NMR spectroscopy (Figure 4) at the end of the reaction when $[HPBu_3]Br$ is used as the promoter, but not when HBr is added. This difference suggests that the free PBu_3 that is liberated when HBr is formed from $[HPBu_3]Br$ acts to scavenge MeBr, which is an intermediate in the formation of EtOH, thus lowering the rate of EtOH-formation as more $[HPBu_3]Br$ is added. In a separate experiments, it has been shown that neither PBu_3 nor $[MePBu_3]Br$ acts as a promoter, these reactions are outlined in Scheme 2.

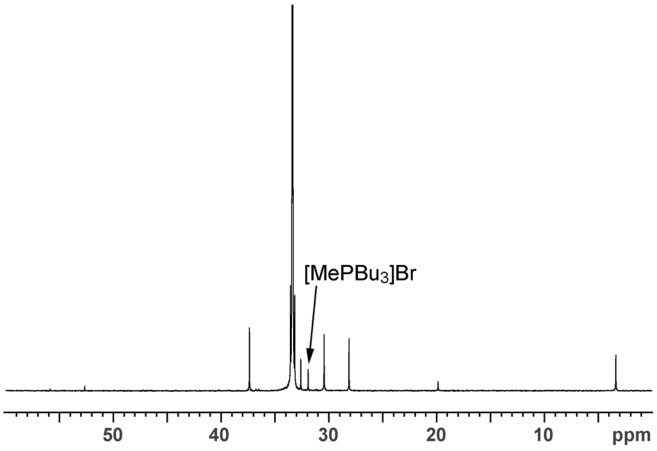
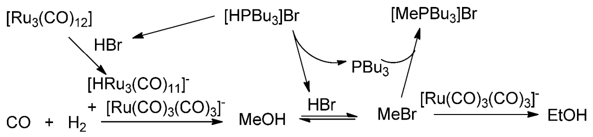


Figure 4. $^{31}P\{^1H\}$ NMR spectrum of the solution that was recovered from the hydrogenation of CO in the presence of $[Ru_3(CO)_{12}]$ ($[HPBu_3]Br$/Ru. 1.0).



Scheme 2. Proposed outline mechanism for the formation of MeOH and EtOH from CO/H_2, which shows why HBr and $[HPBu_3]Br$ act in a similar manner as promoters in the formation MeOH, but that the formation of EtOH is inhibited when using $[HPBu_3]Br$; PBu_3, which is formed alongside HBr, scavenges MeBr, which is an intermediate in the formation of EtOH.

Quantitatively, if the formation of $[MePBu_3]Br$ were solely responsible for the drop in yield of EtOH when using $[HPBu_3]Br$ instead of HBr, this drop in yield should be equal to the concentration of PBu_3 that is produced or to the concentration of $[HPBu_3]Br$ that is added. However, this result is not the case. For example, with an additive/Ru ratio of 0.75 (0.0009 mol of HBr or $[HPBu_3]Br$ added), the yield of EtOH is lower by 0.01 mol, which is more than 10 times the concentration of the additive. Another contributor to the loss in activity towards EtOH may be that the formed $[RuHBr(CO)_2(PBu_3)_2]$ is inactive and removes $[RuBr_3(CO)_3]^-$ from the system. (We thank a -referee for suggesting this alternative).

Conclusions

We conclude that the irreproducibility that is often observed when studying CO-hydrogenation reactions, especially in molten phosphonium halides, may arise because of minor impurities that are present in the salt. We have discovered that one such impurity, $[HPBu_3]Br$, can act as a promoter of the reaction when added in small amounts (sub-stoichiometric with respect to ruthenium). To the best of our knowledge, the use of such compounds as promoters for catalytic reactions has not been reported before, although P–H phosphonium salts have been used as air-stable alternatives to highly basic phosphines,[34] especially when both phosphines and acids are required in the system.[34–36] In the CO-hydrogenation reactions, $[HPBu_3]Br$ acts to convert $[Ru_3(CO)_{11}]^-$ into $[Ru(CO)_3Br_3]^-$ and both of these ruthenium complexes are required for active catalysis to occur. $[HPBu_3]Br$ appears to act as a source of HBr, which others have shown (in other solvents)[24,25] has similar promoting effects on the production of MeOH. We have also confirmed that this effect is the case in molten $[PBu_4]Br$. The effect of $[PBu_3]Br$ on the production of EtOH is different to that of HBr, partly because PBu_3 that is formed by the loss of HBr sequesters MeBr, the key intermediate in the production of EtOH, and partly because inactive Ru/PBu_3 complexes are formed.

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Keywords: carbon monoxide · hydrogenation · molten salts · ruthenium · salt effect

[1] W. F. Gresham, C. E. Schweizer, US Patent 2,534,018, **1950**.
[2] I. Wender, *Fuel Process. Technol.* **1996**, *48*, 189–297.
[3] R. C. Brady, R. Pettit, *J. Am. Chem. Soc.* **1981**, *103*, 1287–1289.
[4] L. M. Tau, H. A. Dabbagh, B. H. Davis, *Energy Fuels* **1991**, *5*, 174–179.
[5] G. Henrici-Olivé, S. Olive, *Angew. Chem.* **1976**, *88*, 144–150; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 136–141.
[6] B. D. Dombek, *Adv. Catal.* **1983**, *32*, 325–416.
[7] J. S. Bradley, US 4,421,862, **1983**.
[8] J. S. Bradley, *J. Am. Chem. Soc.* **1979**, *101*, 7419–7421.
[9] B. D. Dombek, *J. Am. Chem. Soc.* **1981**, *103*, 6508–6510.
[10] B. D. Dombek, *J. Organomet. Chem.* **1983**, *250*, 467–483.
[11] B. D. Dombek, *Organometallics* **1985**, *4*, 1707–1712.
[12] B. D. Dombek, *J. Organomet. Chem.* **1989**, *372*, 151, and references therein.
[13] J. F. Knifton, *J. Catal.* **1985**, *96*, 439–453.
[14] J. F. Knifton, *ACS Symp. Ser.* **1987**, *328*, 98–107.
[15] J. F. Knifton, R. A. Grigsby, J. J. Lin, *Organometallics* **1984**, *3*, 62–69.
[16] S. H. Han, G. L. Geoffroy, B. D. Dombek, A. L. Rheingold, *Inorg. Chem.* **1988**, *27*, 4355–4361.
[17] J. F. Knifton, US, 4,332,914, **1982**.
[18] J. F. Knifton, US, 4,605,677, **1986**.
[19] J. F. Knifton, *J. Chem. Soc. Chem. Commun.* **1983**, 729–730.
[20] J. F. Knifton, US 4,315,993, **1982**.
[21] J. F. Knifton, *J. Am. Chem. Soc.* **1981**, *103*, 3959–3961.
[22] J. F. Knifton, *Hydrocarbon Process.* **1981**, *60*, 113–117.
[23] J. F. Knifton, *Platinum Met. Rev.* **1985**, *29*, 63–72.
[24] H. Ono, K. Fujiwara, M. Hashimoto, H. Watanabe, K. Yoshida, *J. Mol. Catal.* **1990**, *58*, 289–297.
[25] H. Ono, M. Hashimoto, K. Fujiwara, E. Sugiyama, K. Yoshida, *J. Organomet. Chem.* **1987**, *331*, 387–395.
[26] A. Robertson, *Cytec*, Private Communication.
[27] E. A. Seddon, K. R. Seddon, *The Chemistry of Ruthenium*, Elsevier, Amsterdam, **1984**.
[28] D. F. Gill, B. E. Mann, B. L. Shaw, *J. Chem. Soc. Dalton Trans.* **1973**, 311–317.
[29] M. J. Cleare, W. P. Griffith, *J. Chem. Soc. A* **1969**, 372–380.
[30] B. D. Dombek, A. M. Harrison, *J. Am. Chem. Soc.* **1983**, *105*, 2485–2486.
[31] D. S. Barratt, D. J. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.* **1985**, 1559–1560.
[32] D. S. Barratt, D. J. Cole-Hamilton, *J. Organomet. Chem.* **1986**, *306*, C41–C44.
[33] J. H. Blank, R. Hembre, J. Ponasik, D. J. Cole-Hamilton, unpublished observations.
[34] M. R. Netherton, G. C. Fu, *Org. Lett.* **2001**, *3*, 4295–4298.
[35] A. A. Nunez-Magro, L. M. Robb, P. J. Pogorzelec, A. M. Z. Slawin, G. R. Eastham, D. J. Cole-Hamilton, *Chem. Sci.* **2010**, *1*, 723–730.
[36] D. J. Cole-Hamilton, A. J. Rucklidge, G. E. Morris, A. M. Z. Slawin, *Helv. Chim. Acta* **2006**, *89*, 1783–1800.
[37] Although this compound has not been reported previously, the related $[RuHBr(CO)_2(PCy_3)_2]$ has a hydride resonance at $\delta = -5.9$ ppm; see: F. G. Moers, R. W. M. Tan Hoedt, J. P. Langhort, *J. Inorg. Nucl. Chem.* **1974**, *36*, 2279.

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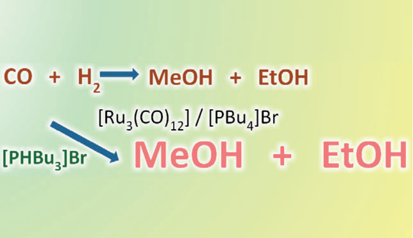
A big promotion: One reason for the irreproducibility that is sometimes found in hydrogenation reactions of CO catalysed by $[Ru_3(CO)_{12}]$ in molten $[PBu_4]Br$ is the possible presence of $[HPBu_3]Br$, which acts as a promoter by providing a source of HBr.



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