

Table 1. A comparison of selected properties of $[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Co}(\text{tmen})_3]^{3+}$.

Property	$[\text{Co}(\text{en})_3]^{3+}$	$[\text{Co}(\text{tmen})_3]^{3+}$
Colour	Yellow	Red
$\lambda_{\text{max}}/\text{nm} (\epsilon)$	338(85), 464(93)	362(177), 504(177)
$\Delta, \text{B}/\text{cm}^{-1}$ ^a	32 170, 587	21 300, 568
Reduction potential/V vs. n.h.e. ^b	-0.12 ^b	+0.28
Estimated half-life for hydrolysis ^c	3.2 yrs ^c	13.6 s
Estimated half-life for racemization ^c	>3.2 yrs ^c	1.0 ms
First c.d. maximum/nm	489	495
Electron self-exchange rate constant/ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	8×10^{-5} ^d	10^{-7} ^e
⁵⁹ Co Chemical shift/p.p.m.	+ 7088 ^a	+ 8151

^a Calculated according to R. Bramley, M. Brorson, A. M. Sargeson, and C. E. Schäffer, *J. Am. Chem. Soc.*, 1985, **107**, 2780. ^b N.h.e. = normal hydrogen electrode; A. M. Bond, G. A. Lawrance, P. A. Lay, and A. M. Sargeson, *Inorg. Chem.*, 1983, **22**, 2010. ^c In 0.1 M OH⁻ at 25°C; J. A. Friend and E. K. Nunn, *J. Chem. Soc.*, 1958, 1567; W. G. Gehman and W. C. Fernelius, *J. Inorg. Nucl. Chem.*, 1957, **9**, 71. ^d F. P. Dwyer and A. M. Sargeson, *J. Phys. Chem.*, 1961, **65**, 1892. ^e Estimated using the Marcus cross-relationship and data from the $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ reduction.

Reduction of the complex by $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ obeys the rate law: $V = k_1 [\text{Co}(\text{tmen})_3^{3+}][\text{Ru}^{2+}]$, with a rate constant $k_1 = (5.6 \pm 0.5) \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The equilibrium constant for the reaction is only ~ 18 in favour of the $\text{Ru}^{3+}/\text{Co}(\text{tmen})_3^{2+}$ side. Reduction of the complex by Cr^{2+} proceeds readily and obeys a two-term rate law of the form: $V = k_2 [\text{Co}(\text{tmen})_3^{3+}][\text{Cr}^{2+}] + k_3 [\text{Co}(\text{tmen})_3^{3+}][\text{Cr}^{2+}][\text{Cl}^-]$. The rate constants were found to be $k_2 < 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and $k_3 = (5.0 \pm 0.5) \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.

Application of the Marcus cross-relationship⁶ using the Cr data yields an estimate for the self-exchange rate constant k_{11} for $[\text{Co}(\text{tmen})_3]^{2+/3+}$ of $< 10^{-9} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The Ru data, which are considered to be more reliable, yield an estimate of $10^{-7} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for k_{11} . There are several reasons for attributing more significance to the ruthenium data, the main one being that the equilibrium constant for the reaction is very small, and another being that an accurate rate constant is available for the $[\text{Ru}(\text{H}_2\text{O})_6]^{2+/3+}$ self exchange⁷ whereas the same is not true for $[\text{Cr}(\text{H}_2\text{O})_6]^{2+/3+}$. The Marcus relationship

holds best when the difference in the reduction potentials of the two reactants is small, *i.e.* there is a small equilibrium constant for the cross-reaction.¹ Sutin and co-workers have found that cross-reactions with large driving forces generally underestimate the value of the self-exchange rate constant.⁸

This estimate of the self-exchange rate for the $[\text{Co}(\text{tmen})_3]^{2+/3+}$ couple is almost three orders of magnitude less than the self-exchange rate constant for the parent $[\text{Co}(\text{en})_3]^{2+/3+}$ couple. This corresponds to an increase in activation energy of $\sim 15 \text{ kJ mol}^{-1}$. The elucidation of the various contributions to the activation energy for electron transfer will depend on a complete analysis of the nuclear and electronic factors. However, molecular mechanics calculations⁹ on the $[\text{Co}(\text{tmen})_3]^{3+}$ complex indicate that the energy required to deform the atomic co-ordinates from their equilibrium positions is much higher for $[\text{Co}(\text{tmen})_3]^{3+}$ than for $[\text{Co}(\text{en})_3]^{3+}$. Thus despite the probability that the longer Co-N bonds in $[\text{Co}(\text{tmen})_3]^{3+}$ mean that the Δr value for $[\text{Co}(\text{tmen})_3]^{2+/3+}$ will be less than for $[\text{Co}(\text{en})_3]^{2+/3+}$, it appears that the energy needed to achieve the required deformation will be greater.

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References

- M. Chou, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, 1977, **99**, 5615.
- M. Kojima, H. Funaki, Y. Yoshikawa, and K. Yamasaki, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 2801.
- L. W. Seigle and H. B. Bass, *J. Org. Chem.*, 1940, **5**, 100; J. Bewad, *Ber.*, 1906, **39**, 1231.
- R. G. Pearson, P. M. Henry, and F. Basolo, *J. Am. Chem. Soc.*, 1957, **79**, 5379.
- F. P. Dwyer and E. C. Gyarfás, *Nature*, 1950, **166**, 481.
- R. A. Marcus, *Ann. Rev. Phys. Chem.*, 1964, **15**, 155.
- P. Bernhard, L. Helm, A. Ludi, and A. E. Merbach, *J. Am. Chem. Soc.*, 1985, **107**, 312.
- W. Böttcher, G. M. Brown, and N. Sutin, *Inorg. Chem.*, 1979, **18**, 1447.
- K. Rasmussen, 'Potential Energy Functions in Conformational Analysis,' Springer-Verlag, Berlin, 1985.

Methanol from Synthesis Gas over Iron-rich Iron-Iridium on Silica Catalysts

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Bimetallic FeIr/SiO₂ catalysts with Fe/Ir atomic ratios between 0.1 and 5 produce, under steady state conditions, MeOH from CO + 3 H₂ at 542 K and 4.0 MPa with selectivities of 75% and higher.

Supported bimetallic catalysts consisting of iron and one of the more noble group 8 metals Rh, Pd, and Ir show favourable activities for the production of oxygenates from syngas (CO-H₂) at elevated pressures.¹⁻³ Fukushima *et al.*³ report MeOH selectivities of over 80% for Fe-promoted Ir/SiO₂ catalysts with Fe/Ir atomic ratios between 0.02 and 0.2. For

catalysts of higher Fe content the selectivity falls off rapidly, to only 22% for the 1:1 FeIr/SiO₂ system. Methane and small hydrocarbons are the dominant products here. It should be noted, however, that all data reported by Fukushima *et al.*³ were obtained after a relatively short time on stream (4 h).

The purpose of this communication is to show that high

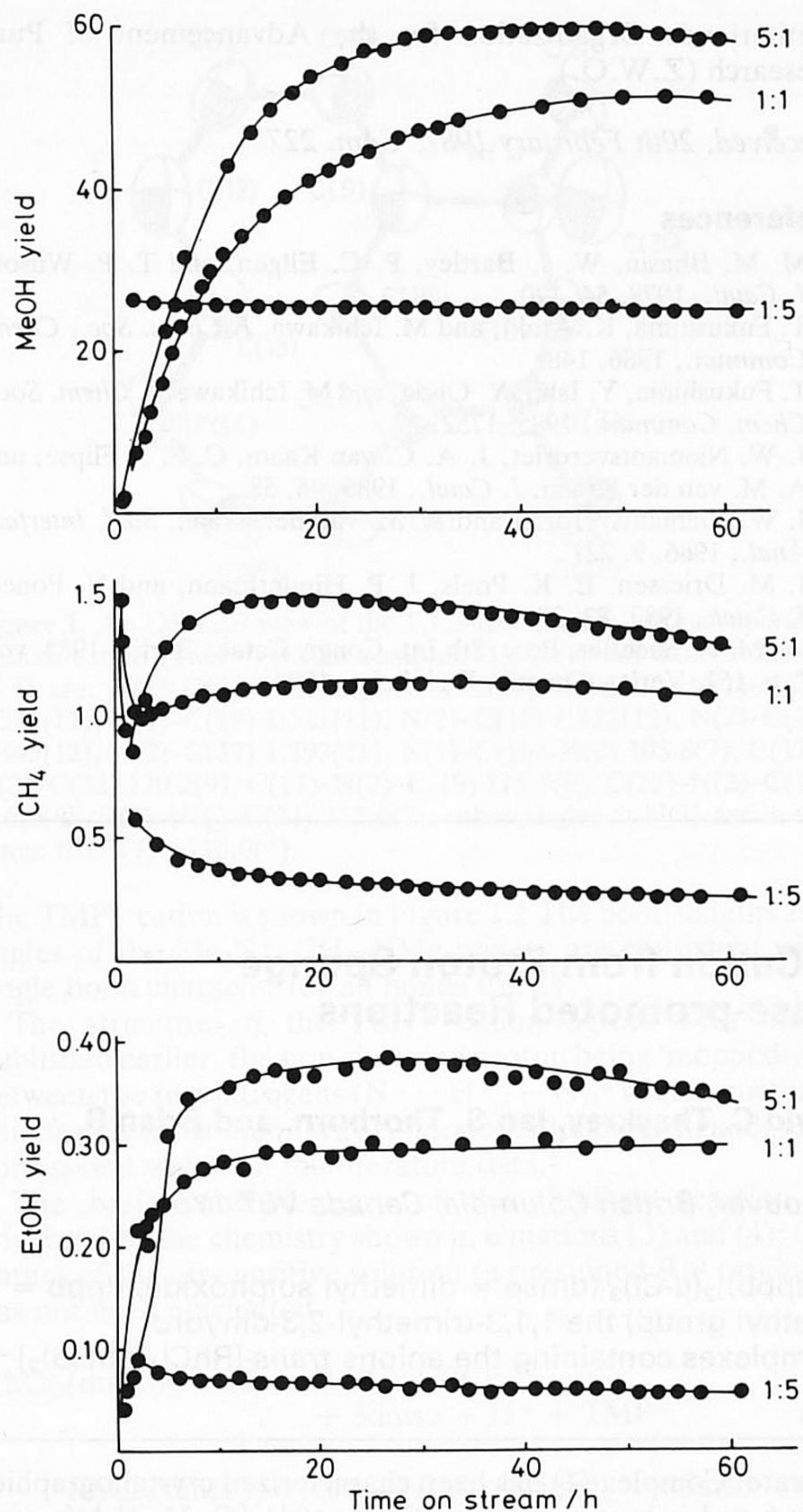


Figure 1. Yields [mmol converted CO (mol Ir s)⁻¹] of methanol, ethanol, and methane in CO hydrogenation over 1:5, 1:1, and 5:1 FeIr/SiO₂ catalysts at 542 K and 4 MPa of 3 H₂ + CO.

MeOH yields can also be obtained with iron-rich FeIr/SiO₂ (Fe/Ir ≥ 1) catalysts. These catalysts, however, need 20–40 h to reach steady state conditions. The results underline the need for time-dependent studies to ascertain steady state conditions and raise the question whether iron is a promoter^{2,3} or a catalyst itself.

Catalysts were prepared by adding dropwise an aqueous solution of IrCl₃·xH₂O (53.1 wt% Ir, Drijfhout) and Fe(NO₃)₃·9H₂O (Merck p.a.) to the SiO₂ support (Grace Type 332, 320 m²/g) until the incipient wetness point was reached. The catalysts with atomic ratios Fe/Ir = 1 and lower contained 4 wt% Ir, and those with atomic ratios higher than 1 contained 3 wt% Fe. Impregnated catalysts were dried in air overnight at 295 K, heated at 15 K/h to 400 K, and held at 400 K for 24 h. Dried catalysts were reduced in flowing H₂ (50 ml/min) by linear programming the temperature at 5 K/min to 725 K followed by 1 h at this temperature. CO hydrogenation was carried out in a copper-coated stainless steel reactor in 3 H₂ + CO (flow 1.1 ml/s) at 4.0 MPa (gauge) and 542 K.

Table 1. CO hydrogenation over FeIr/SiO₂ at 542 K and 4.0 MPa of 3 H₂ + CO.

Fe/Ir ratio	Ir, wt%	% Conversion	% Selectivity			Yield ^a		
			MeOH	EtOH	CH ₄	MeOH	EtOH	CH ₄
0	4	0.23	34.8	0.77	50.2	0.09	0.00	0.14
0.05	4	1.22	65.9	2.5	22.1	0.96	0.04	0.32
0.1	4	1.64	79.4	2.1	11.8	1.56	0.04	0.23
0.2	4	2.41	84.7	1.7	8.7	2.44	0.05	0.25
0.33	4	5.75	84.0	2.25	9.1	5.77	0.15	0.63
0.5	4	4.51	80.6	2.2	10.7	4.34	0.12	0.58
1	4	5.69	74.7	4.2	15.3	5.08	0.29	1.04
5	2.1	3.36	74.4	4.4	16.4	5.69	0.34	1.26
10	1.1	2.79	57.7	4.7	27.8	6.99	0.57	3.37
Fe 3 wt%		11.21	13.5	4.0	33.0	—	—	—

^a In mmol converted CO (mol Ir s)⁻¹.

CO hydrogenation results obtained with a few representative FeIr/SiO₂ catalysts are shown in Figure 1. The Ir-rich 1:5 FeIr/SiO₂ catalyst changes only slightly during reaction. This catalyst produces MeOH from the beginning at a favourable selectivity of 80–90%, in agreement with ref. 3. In contrast to this, the iron-rich 1:1 and 5:1 FeIr/SiO₂ start as typical Fischer-Tropsch catalysts with high selectivities for lower hydrocarbons, but change gradually to MeOH-producing catalysts (Figure 1). At steady state, reached after 30–40 h on stream, the 1:1 and 5:1 FeIr/SiO₂ catalysts produce MeOH with a selectivity of about 75% and at a total activity which is significantly higher than that of the catalysts with a low iron content.

Figure 1 illustrates that it is imperative to study the behaviour of FeIr/SiO₂ catalysts as a function of time on stream and to report catalytic data obtained under steady state conditions. If we had compared the behaviour of our catalysts after 4 h on stream, as done by Fukushima *et al.*,³ the favourable performance of the iron-rich FeIr/SiO₂ catalysts would have gone unnoticed.

Table 1 lists the steady state CO conversion, as well as selectivities and yields of the products MeOH, EtOH, and CH₄, for all the FeIr/SiO₂ catalysts. The data show that MeOH selectivities of at least 75% can be obtained for FeIr/SiO₂ catalysts with Fe/Ir ratios between 0.1 and 5. In terms of yield, the iron-rich FeIr catalysts are by no means inferior to the catalysts of low iron content. For completeness we note that high pressure is a prerequisite for appreciable MeOH formation. At atmospheric pressure or even at 3 atm the FeIr/SiO₂ catalysts produced predominantly CH₄, C₂H₄, and C₃H₈ and the MeOH selectivity did not exceed 10%.

The fact that iron-rich FeIr/SiO₂ produces MeOH almost as efficiently as catalysts with a low Fe/Ir ratio raises the question whether iron should be considered as a promoter for Ir, as suggested by Fukushima *et al.*,^{2,3} or as a catalyst itself. *In situ* Mössbauer and X-ray photoelectron spectroscopy^{4,5} have shown that a reduced 1:1 FeIr/SiO₂ catalyst contains zero-valent Ir and zero-valent Fe in a face-centred cubic FeIr alloy and highly dispersed iron(III). Mössbauer spectroscopy revealed furthermore that the iron(III) is accessible for and affected by CO. Hence, in principle both unreduced and reduced iron may be involved in catalytic sites for MeOH production.

The time scale on which the 1:1 and 5:1 FeIr/SiO₂ develop their MeOH activity suggests that a chemical or morphological

transformation of the catalyst particles occurs during high pressure CO hydrogenation. It has been suggested that transition metal ions play a key role in the formation of MeOH from syngas.^{6,7} In this respect, it is worthwhile to investigate whether the transformation of the iron-rich FeIr/SiO₂ samples from typical Fischer-Tropsch to MeOH-producing catalysts is accompanied by oxidation of either iron or iridium, caused by H₂O formed during the reaction. *In situ* characterization with EXAFS, Mössbauer, and e.s.r. spectroscopy is in progress to investigate this point.

In conclusion, bimetallic FeIr/SiO₂ with Fe/Ir atomic ratios between 0.1 and 5 produce MeOH from CO + 3 H₂ at 542 K and 4.0 MPa with selectivities of 75% and higher. The iron-rich FeIr/SiO₂ catalysts behave initially as normal Fischer-Tropsch catalysts, but develop their interesting MeOH selectivity during the first 30–40 h of the reaction. The results underline the importance of reporting catalytic data obtained under steady state conditions.

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References

- 1 M. M. Bhasin, W. J. Bartley, P. C. Ellgen, and T. P. Wilson, *J. Catal.*, 1978, **54**, 120.
- 2 T. Fukushima, K. Araki, and M. Ichikawa, *J. Chem. Soc., Chem. Commun.*, 1986, 148.
- 3 T. Fukushima, Y. Ishii, Y. Onda, and M. Ichikawa, *J. Chem. Soc., Chem. Commun.*, 1985, 1752.
- 4 J. W. Niemantsverdriet, J. A. C. van Kaam, C. F. J. Flipse, and A. M. van der Kraan, *J. Catal.*, 1985, **96**, 58.
- 5 J. W. Niemantsverdriet and A. M. van der Kraan, *Surf. Interface Anal.*, 1986, **9**, 221.
- 6 J. M. Driessen, E. K. Poels, J. P. Hindermann, and V. Ponc, *J. Catal.*, 1983, **82**, 20.
- 7 W. M. H. Sachtler, Proc. 8th Int. Congr. Catal., Berlin, 1984, vol. I, p. 151, Verlag Chemie, Weinheim, 1984.

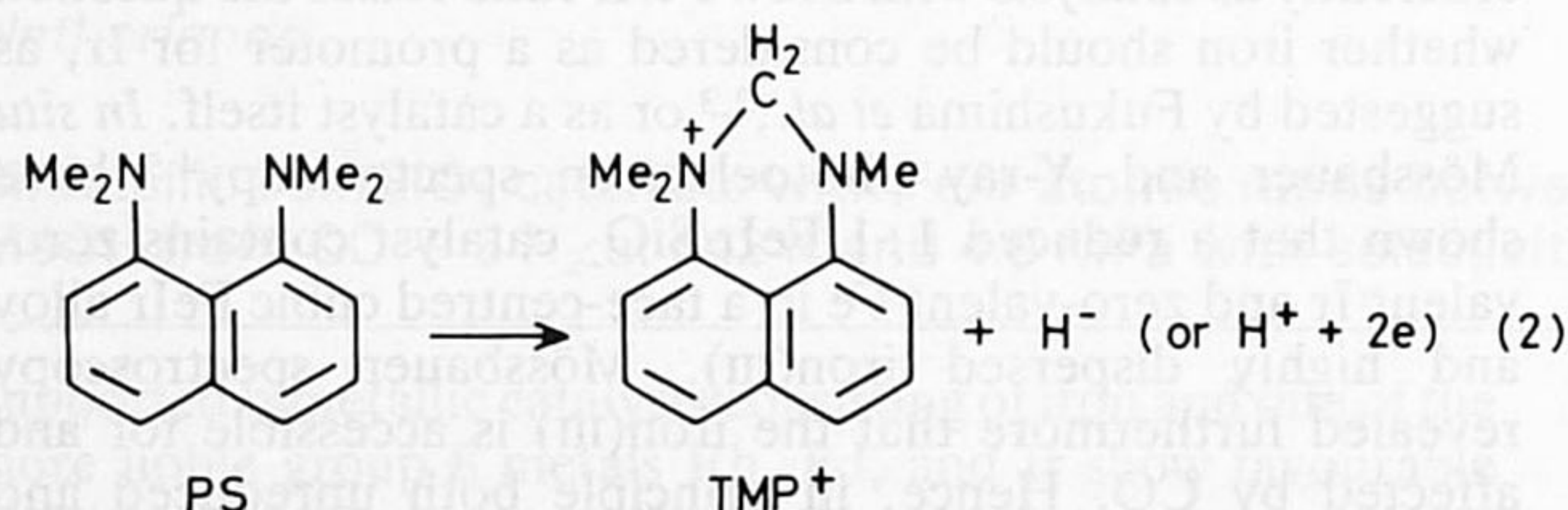
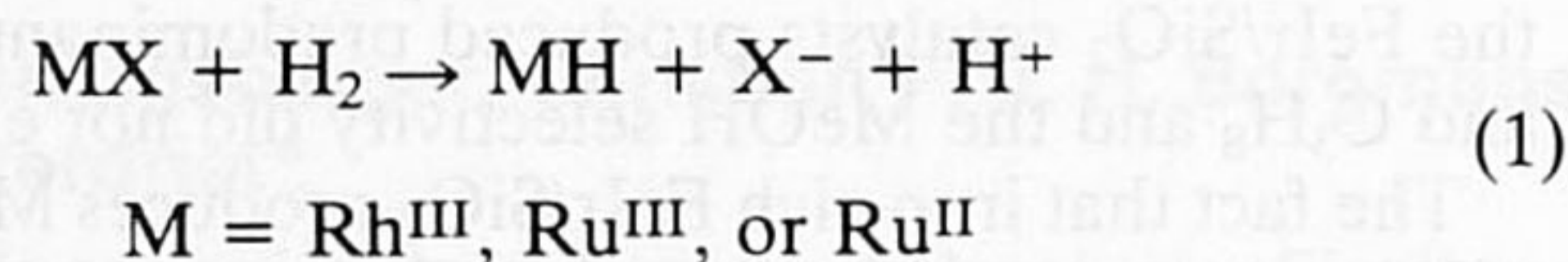
Formation of a Trimethyldihydroperimidinium Cation from Proton Sponge [1,8-Bis(dimethylamino)naphthalene] during Base-promoted Reactions of Rhodium and Ruthenium Complexes

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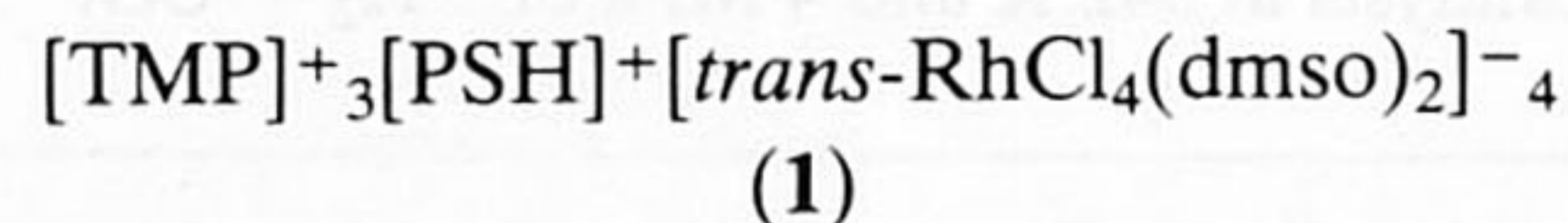
Proton sponge, in the presence of *mer*-RhCl₃(dmsO)₃ or [RuCl(dppb)]₂(μ-Cl)₃ (dmsO = dimethyl sulphoxide, dppb = Ph₂P[CH₂]₄PPh₂), generates (*via* a net hydride loss from one methyl group) the 1,1,3-trimethyl-2,3-dihydroperimidinium cation, which is isolated as the counter-ion in complexes containing the anions *trans*-[RhCl₄(dmsO)₂]⁻ and {[RuCl(dppb)]₂(μ-Cl)₃]⁻.

We reported recently¹ on the facile dehydrogenation of triethylamine in the presence of *mer*-RhCl₃(dmsO)₃ (dmsO = dimethyl sulphoxide), with resulting formation of the ylidic enamine complex RhCl₃(dmsO)₂(σ-CH₂CH=NEt₂). We now find that the widely employed Aldrich reagent, 'proton sponge' (PS), which we were using to promote formation *via* H₂ of monohydride complexes of Rh^{III}, Ru^{III}, and Ru^{II}, equation (1),^{2,3} also 'dehydrogenates' with formation of the 1,1,3-trimethyl-2,3-dihydroperimidinium cation (TMP⁺), equation (2).



Treatment of a suspension of *mer*-RhCl₃(dmsO)₃ in acetone with proton sponge (Rh : PS 1 : 0.8) under Ar precipitates an air-stable, orange-brown product, (1) (which could be recrystallized from dmsO-acetone solutions) and an air-sensitive

filtrate. Complex (1) has been characterized crystallographically,[†] and is best written as [C₁₄H₁₇N₂]⁺₃[C₁₄H₁₉N₂]⁺[*trans*-RhCl₄(dmsO)₂]⁻₄, three of the associated cations being TMP⁺ and one being the protonated form of proton sponge (PSH⁺).



[†] Crystal Data: (1): [C₁₄H₁₇N₂]⁺₃[C₁₄H₁₉N₂]⁺[RhCl₄(dmsO)₂]⁻₄, monoclinic, space group P2₁/n, a = 22.327(2), b = 14.621(1), c = 15.263(2) Å, β = 94.71(1)°, Z = 2, D_c = 1.645 g cm⁻³.

(2): [C₁₄H₁₇N₂]⁺{(μ-Cl)₃[RuCl(Ph₂PCH₂CH₂CH₂CH₂PPh₂)]₂]⁻·2Me₂CO·2H₂O, monoclinic, space group C2/c, a = 21.596(2), b = 16.019(2), c = 22.317(2) Å, β = 106.15(1)°, Z = 4, D_c = 1.431 g cm⁻³.

Intensity data for both compounds were collected at 22 °C on an Enraf-Nonius CAD4-F with graphite-monochromated Mo-K_α radiation (2θ ≤ 55°). The structures were solved by heavy atom methods and refined by full-matrix least-squares procedures to R values of 0.055 and 0.039 for 4287 and 5237 absorption-corrected reflections with I ≥ σ(I) and I ≥ 3σ(I), respectively, for (1) and (2). Cation disorder was encountered in both structures. In (1) there are two crystallographically independent cation sites. One of these is occupied by the TMP⁺ cation, while the disordered second site is occupied half of the time by TMP⁺ and half by PSH⁺. In (2) the TMP⁺ cation is disordered about a crystallographic C₂ axis. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.