

Bimetallic hydroformylation: a zwitterionic Rh^{−I}Rh^I tetraphosphine ligand-based bimetallic complex exhibiting facile CO addition and phosphine ligand rearrangement equilibrium

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The X-ray structure of an unsymmetrical tetraphosphine bridged zwitterionic Rh^{−I}Rh^I dinuclear tetracarbonyl complex is reported along with the facile CO addition equilibrium to form an Rh⁰ tetraphosphine pentacarbonyl bimetallic species; both of these are poor hydroformylation catalysts due to the relatively high electron density on the rhodium centres, in marked contrast to a dicationic bimetallic Rh^{II} complex based on the same tetraphosphine ligand that is a highly active and regioselective hydroformylation catalyst.

Perhaps the most dramatic example of bimetallic cooperativity in homogeneous catalysis is the homobimetallic rhodium complex *rac*-[Rh₂(ndb)₂L][BF₄]₂ **1** [ndb = norbornadiene, L = (Et₂PCH₂CH₂)PhPCH₂PPh(CH₂CH₂PEt₂)], which is a precursor for a highly active and regioselective hydroformylation catalyst for alk-1-enes.^{1,2} The initially proposed mechanism¹ for this novel catalyst assumed the presence of the neutral Rh^I hydrido-carbonyl bimetallic complex *rac*-[Rh₂H₂(CO)₂L], in direct analogy with monometallic hydroformylation catalysts that have the generic formula [RhH(CO)₂(P₂)] [P₂ = two monodentate or one chelating bis(phosphine) ligand].³ *In situ* FTIR and NMR studies on **1**, however, indicate that the active catalyst for bimetallic hydroformylation is the unique dicationic Rh^{II}–Rh^{II} bonded complex *rac*-[Rh₂H₂(μ-CO)₂(CO)₂L]²⁺.⁴ In keeping with this observation, we have found that if one starts with a neutral dinuclear precursor, e.g. *rac*-[Rh₂(η³-allyl)₂L] **2**, one accesses a different oxidation state manifold and a very poor bimetallic hydroformylation catalyst is generated.

rac-[Rh₂(η³-allyl)₂L] **2** is prepared from the reaction of 20 equiv. of (allyl)MgCl with 1 equiv. of *rac*-[Rh₂(ndb)₂L][BF₄]₂, **1**. All spectroscopic data support the proposed bimetallic structure and this has been confirmed by an X-ray structure of **2**.[‡] Much to our surprise **2** produces a very slow and non-selective hydroformylation catalyst [90 °C, 90 psi H₂–CO, 1 mM catalyst, 1.5 M hex-1-ene, thf solvent, initial turnover frequency of 35 h^{−1} after a 3 h induction period, 2.4 : 1 linear to branched aldehyde ratio, 14% alkene isomerization, 5% alkene hydrogenation (psi ≈ 6.894 × 10³ Pa)]. This is in marked contrast to dicationic **1** which generates a highly active and regioselective catalyst (90 °C, 90 psi H₂–CO, hex-1-ene, 640

turnovers h^{−1} initial rate, 28 : 1 linear to branched aldehyde ratio, 8% alkene isomerization, 4% hydrogenation).¹

In situ FTIR studies of the reaction of **2** with CO using a Spectratech Circle reaction cell, showed that **2** cleanly reacts with 2 equiv. of CO to produce *rac*-[Rh₂(η³-allyl)₂(CO)₂L] **3**, which has a symmetrical ³¹P NMR and a single terminal CO band at 1930 cm^{−1}.[§] With excess CO, the bis-acyl *rac*-[Rh₂(COC₃H₅)₂(CO)₄L] **4**, is the only product initially formed, presumably going through an η¹-allyl intermediate followed by CO insertion to produce the unsaturated bis-acyl.¶ The weak acyl IR bands are at 1648 and 1623 cm^{−1}, similar to that seen for other Rh–acyl complexes.^{5,6} Complex **4** is relatively stable and does not easily dissociate CO in solution, although it does eventually lose four CO ligands to reform **3** when solvent is removed *in vacuo*.

When **4** is placed under 90 psi of H₂–CO (90 °C) the rhodium acyl IR bands are replaced within 10 min by new signals at 1697 and 1733 cm^{−1} representing the elimination of the unsaturated aldehyde products (confirmed by IR, NMR, mass spectroscopy and by comparison to authentic samples). Four new bands in the terminal carbonyl region (1968, 1950, 1928, 1893 cm^{−1}) are generated, compared to only two in the bis-acyl complex, along with a broad and misshapen bridging CO band at 1794 cm^{−1}. After slowly cooling and depressurizing the IR cell, beautiful orange-yellow crystals formed. A single-crystal X-ray structure^{||} revealed the surprising unsymmetrical bimetallic complex *rac*-[Rh₂(μ-CO)(CO)₃(η³ : η¹-L)] **5** (Fig. 1).

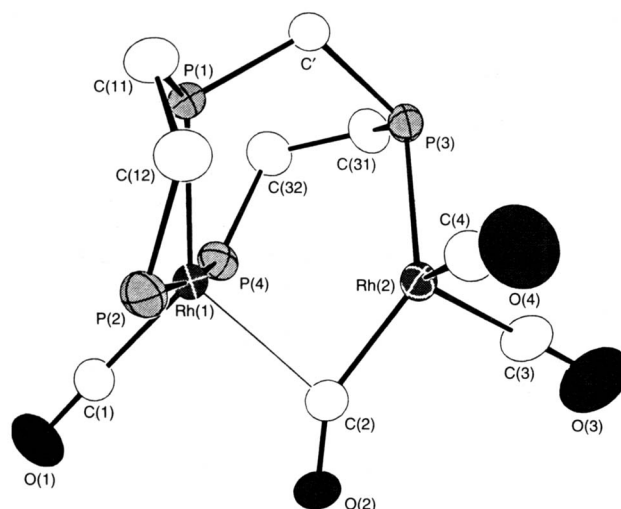
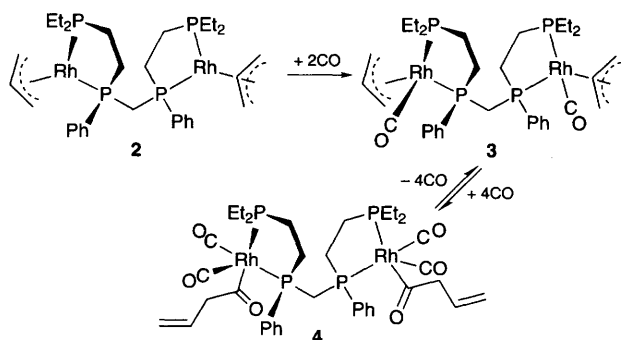


Fig. 1 ORTEP plot of **5** with the phosphine phenyl and ethyl groups omitted for clarity. Selected bond lengths (Å) and angles (°): Rh(1)–Rh(2) 2.9250(3), Rh(1)–P(1) 2.3565(7), Rh(1)–P(2) 2.3080(8), Rh(1)–P(4) 2.3157(8), Rh(1)–C(1) 1.858(3), Rh(1)–C(2) 2.340(3), Rh(2)–P(3) 2.3253(7), Rh(2)–C(2) 1.932(3), Rh(2)–C(3) 1.882(3), Rh(2)–C(4) 1.903(3); P(2)–Rh(1)–P(4) 174.91(3), P(1)–Rh(1)–C(1) 135.74(9), P(3)–Rh(2)–C(2) 132.15(8), P(3)–Rh(2)–C(3) 101.5(1), P(3)–Rh(2)–C(4) 105.55(9), C(2)–Rh(2)–C(4) 109.7(1), C(3)–Rh(2)–C(4) 109.6(1)°.

The ligand **L** in **5** adopts an $\eta^3:\eta^1$ coordination mode where the central bis-(phosphino)methane unit is still bridging the two rhodium centres, but both of the external PEt_2 phosphines and one CO ligand are coordinated to Rh(1). The considerable difference in coordination geometries about the two metals points to a mixed-oxidation state zwitterionic complex. The tetrahedrally coordinated Rh(2) atom is best described as anionic and in the -1 oxidation state (d^{10}). The π back-bonding to the CO ligands on anionic Rh(2) increases the electron density enough so that one acts as a semibridging donor to the formally cationic 16-electron Rh(1) centre producing a distorted square-pyramidal geometry. This drains away a reasonable amount of electron density from Rh(2), increasing the ν_{CO} stretching frequencies by about 40 cm^{-1} from that seen for $[\text{Rh}(\text{CO})_3(\text{PR}_3)]^-$ complexes.⁷ Electron counting with these $+1$ and -1 oxidation state formalisms gives 18-electron configurations for Rh(1) and Rh(2) without invoking any Rh–Rh bonding. The Rh–Rh separation of $2.9250(3)\text{ \AA}$ in **5** is 0.2 \AA longer than a typical $\text{Rh}^0\text{--Rh}^0$ single bond of 2.7 \AA .

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** shows four well resolved multiplets and two broader, ill-defined resonances.^{**} Addition of CO gas to the NMR tube causes the two broad resonances to sharpen and fully resolve. $^{31}\text{P}\{^1\text{H}\}$ two-dimensional COSY NMR experiments demonstrate that the four multiplets are caused by the four different phosphorus atoms in **5**, while the two other resonances are from a separate more symmetrical bimetallic system, which we formulate as the fluxional Rh^0 dinuclear complex $[\text{Rh}_2(\mu\text{-CO})(\text{CO})_4\text{L}]$ **6**.^{††} The presence of a CO-based equilibrium between these two species has been confirmed by a two-dimensional $^{31}\text{P}\{^1\text{H}\}$ NOESY study.

Both **5** and **6** are somewhat related to $[\text{Rh}_2(\mu\text{-CO})(\text{CO})_2(\text{dppm})_2]$, which has a rather unsymmetrical structure with a semibridging carbonyl.⁸ Our more electron-rich complex, however, picks up one (or two) additional carbonyl ligands and shows even greater differences between the two rhodium coordination environments. $^{31}\text{P}\{^1\text{H}\}$ NMR studies confirm that **6** is favoured at higher CO pressures and temperatures, with the equilibrium shifting back to **5** as the solution is cooled and CO removed. The IR spectrum observed when **4** was placed under $\text{H}_2\text{--CO}$, therefore, represented a mixture of **5** and **6** in equilibrium with one another.

The very different bimetallic catalysts generated from dicationic **1** or neutral **2** can be contrasted with monometallic precursors where it has been demonstrated that the same hydroformylation catalyst is generated from either neutral or cationic precursor complexes.⁹ The poor hydroformylation activity and regioselectivity of neutral **5** and **6** is, however, consistent with previous studies showing that neutral monometallic complexes with electron-donating chelating phosphine ligands are very poor catalysts.¹⁰

These results, in turn, strongly support our proposed formulation of the active bimetallic catalyst as the dicationic complex $\text{rac-}[\text{Rh}_2\text{H}_2(\mu\text{-CO})_2(\text{CO})_2\text{L}]^{2+}$ generated from **1** under hydroformylation conditions,⁴ or from complexes **2–6** by the addition of 2 equiv. of HBF_4 . The stabilization of different bimetallic hydroformylation catalyst oxidation state manifolds (predominately **I** and **II** for **1**; and **I** and **0** for **2**) based solely on the charge of the starting dinuclear complex is both remarkable and completely unexpected based on the vast amount of monometallic hydroformylation work available. It indicates that nature of the bimetallic cooperativity in **1** is considerably more complicated and interesting than initially proposed.¹

Footnotes

[†] $\text{rac-}[\text{Rh}_2(\text{nbd})_2\text{L}][\text{BF}_4]_2$ (2.06 g, 2.0 mmol) in 20 ml of thf was cooled to $-25\text{ }^\circ\text{C}$ and (allyl)MgCl (20 ml of a 2.0 M thf solution, 20 equiv.) added, and

the solution slowly warmed to room temperature, and 30 ml of toluene and 10 ml of hexane added. The flask was placed in a freezer overnight to crystallize out the inorganic salts, which were filtered through a glass frit, and solvents were removed from the filtrate by vacuum evaporation. The product was extracted with toluene–hexane (3:1), the solvents removed, and the residue dissolved in dmf. A total yield of ca. 90% was obtained after repeated recrystallizations from dmf. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , H_3PO_4 ref. δ ppm) 68.5 (dm, J_{PRh} 188 Hz, P_{ext} of all three isomers), 56.4 (dm, J_{PRh} 178 Hz, P_{int} one isomer with twofold symmetry), 55.7 (dddd, J_{PRh} 188, J_{PP} 40, 20, 1 Hz, P_{int} unsymmetrical isomer), 52.3 (dddd, J_{PRh} 194, J_{PP} 40, 19, 1 Hz, P_{int} unsymmetrical isomer), 52.0 (dm, J_{PRh} 194 Hz, P_{int} other isomer with twofold symmetry). Anal. Calc. for $\text{C}_{31}\text{H}_{50}\text{P}_4\text{Rh}_2$: C, 49.48, H, 6.71. Found: C, 49.43, H, 6.51%.

[‡] To be reported in a subsequent full paper.

[§] Spectroscopic data for **3**: IR (ν_{CO} , thf, cm^{-1}): 1930. $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{H}_8]$ toluene, H_3PO_4 ref., δ ppm) 56.1 (br d, J_{PRh} 140 Hz, terminal phosphorus atoms), 44.0 (br d, J_{PRh} 147 Hz, internal phosphorus atoms).

[¶] Spectroscopic data for **4**: IR (ν_{CO} , thf, cm^{-1}): 1982m, (axial CO), 1936vs (equatorial CO), 1648w, 1623w (isomeric C=O of Rh–acyl); $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{H}_8]$ toluene, H_3PO_4 ref., δ /ppm) 41.8 (dd, J_{PRh} 72, J_{PP} 27 Hz), 39.2 (dd, J_{PRh} 150, J_{PP} 27 Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{H}_8]$ toluene, SiMe_4 ref., δ /ppm): 241.9 (dd, J_{CRh} 81, J_{CP} 21 Hz, equatorial CO), 199.2 (dm, J values cannot be determined due to complexity of the overlapping peaks of the acyl carbonyl carbon and axial CO carbon); ^1H NMR [C_6D_6 , SiMe_4 ref., δ /ppm, $\text{RhC}(\text{O})\text{CH}_2\text{CH}^{\beta}=\text{CH}_2$ assignment only] 6.2 (m, β), 5.0 (d, J_{HH} 8 Hz, γ trans to β), 4.84 (s, γ cis to β), 3.85 (d, J_{HH} 9 Hz, α).

^{||} Crystal data for **5**: orange–red crystal, $\text{C}_{31}\text{H}_{50}\text{P}_4\text{Rh}_2$, monoclinic, space group $P2_1/n$ (no. 14), $a = 12.4850(6)$, $b = 17.7854(9)$, $c = 14.7921(5)\text{ \AA}$, $\beta = 91.70(1)^\circ$, $U = 3283.2(5)\text{ \AA}^3$, $Z = 4$, $D_c = 1.58\text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 12.12\text{ cm}^{-1}$. Data collection information: CAD4 diffractometer, Mo-K α radiation, 9551 data collected, 7681 unique data with $I > 3\sigma(I)$, $R = 0.028$, $R_w = 0.037$, GOF = 1.872. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/283.

^{**} Spectroscopic data for **5**: IR (ν_{CO} , KBr cm^{-1}): 1968, 1919, 1883, 1787 (br); $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{H}_8]$ toluene, 1 atm CO, H_3PO_4 ref., δ /ppm) 65.6 (dddd, P^1 , J_{PRh} 95.5, $J_{\text{P}^1\text{P}^2}$ 25.8, $J_{\text{P}^1\text{P}^3}$ 10.4 Hz, $J_{\text{P}^1\text{P}^4}$ 327.5 Hz), 53.1 (ddd, P^2 , J_{PRh} 118.8, $J_{\text{P}^2\text{P}^3}$ 217.2, $J_{\text{P}^2\text{P}^4}$ 43.7 Hz), 35.7 (ddm, P^3 , J_{PRh} 139.6, $J_{\text{P}^3\text{P}^4}$ 10.4 Hz), 21.6 (ddd, P^4 , J_{PRh} 95.4 Hz).

^{††} Spectroscopic data for **6**: ν_{CO} (thf, estimated due to overlap with solvent shifted carbonyl bands for **5**, cm^{-1}): 1950, 1928, 1892, 1794 (br); $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{H}_8]$ thf, 1 atm CO, H_3PO_4 ref., δ /ppm) 67.9 (ddd, P_{ext} , J_{PRh} 133.8, J_{PP} 36.6, 15.9 Hz), 46.1 (dm, P_{int} , J_{PRh} 133.1 Hz, J_{PP} is a second-order pattern).

References

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Conference Diary*

December 1996

14th SCI Process Development Symposium

Manchester, UK December 1-4
Contact: SCI Conference Secretariat, 14/15 Belgrave Square, London, UK SW1X 8PS. Tel +44 (0) 171 235 3681.
 Fax +44 (0) 171 235 7743.
 E-mail conferences@chemind.demon.co.uk

Asymmetric Catalysis

London, UK December 2
Contact: Dr D Craig, Department of Chemistry, Imperial College of Science, Technology & Medicine, London, UK SW7 2AY.
 Tel +44 (0) 171 594 5771. Fax +1 (0) 171 594 5804.
 E-mail d.craig@ic.ac.uk

Fifth Eurasia Conference on Chemical Sciences

Guangzhou, China December 10-14
Contact: Professor Liang-Nian Ji, Biotechnology Research Center, Zhongshan (Sun Yatsen) University, Guangzhou, Canton 510275, China. Tel +86 (20) 418 5461. Fax +86 (20) 418 9173.
 E-mail leiy@bepc2.ihep.ac.cn

Faraday Discussion 105, Catalysis and Surface Science at High Resolution

Reading, UK December 16-18
Contact: Professor M Bowker, Department of Chemistry, University of Reading, Whiteknights Park, Reading, UK RG6 6AD.

Computer Modelling Inorganic Chemicals

London, UK December 18
Contact: Dr Philip Mitchell, Department of Chemistry, University of Reading, Reading, UK RG6 6AD.
 Tel +44 (0) 1734 875123 ext. 7448. Fax +44 (0) 1734 311610.
 E-mail p.c.h.mitchell@reading.ac.uk

Inorganic Mechanisms Discussion Group UK Symposium

York, UK December 19-21
Contact: Professor M B Davies, Applied Sciences, Anglia Polytechnic University, East Road, Cambridge, UK CB1 1PT.
 Tel +44 (0) 1223 363271. Fax +44 (0) 1223 576157.

January 1997

International Symposium on Chemical and Biological Thermodynamics

Amritsar, India January 5-8
Contact: Professor D V S Jain, Department of Chemistry, Panjab University, Chandigarh 160014, India. Tel +91 (172) 541435.
 Fax +91 (172) 541409. E-mail dvs-jain@imtech.ernet.in

Oligonucleotides as Therapeutic Agents

London, UK January 10
Contact: either Dr J F Gibson† at the RSC or Ms J Dempster, The Ciba Foundation, 41 Portland Place, London, UK W1N 4BN.
 Tel +44 (0) 171 636 9456. Fax +44 (0) 171 436 2840.
 E-mail jdempster@cibafound.org.uk

13th Winter Fluorine Conference

St Petersburg Beach, USA January 19-24
Contact: ACS Meetings Department, 1155-16th St, NW, Washington DC 20036-4899, USA. Tel +1 (202) 872 6286.
 Fax +1 (202) 872 6128. E-mail miscmtgs@acs.org

Winter Conference on Medicinal and Bioorganic Chemistry

Steamboat Springs, Colorado, USA January 26-31
Contact: Rose Barbre, Parke-Davis Pharmaceutical Research, 2800 Plymouth Road, Ann Arbor, MI 48105, USA.
 Fax (313) 996 5165. E-mail BARBRER@aa.wl.com

February 1997

10th Australasian Electrochemistry Conference

Surfers Paradise, Australia February 4-7
Contact: Dr David Druskovich, Department of Chemistry, Central Queensland University, Rockhampton, Qld 4702.
 Fax 617 930 9612. E-mail d.druskovich@ucq.edu.au

International Joint Symposium in Chemistry, Biological and Pharmacological Properties of Medicinal Plants from the Americas

Panama City, Panama February 23-26
Contact: Professor Kurt Hostettmann, Chairman, IOCD Working Group on Plant Chemistry, Institute of Pharmacognosy and Phytochemistry, University of Lausanne, B.E.P., CH-1015 Lausanne-Dorigny, Switzerland. Tel +41 21 692 45 61.
 Fax +41 21 692 45 05.

March 1997

British Liquid Crystal Society Annual Meeting

Southampton, UK March 24-26
Contact: Professor T J Sluckin, Faculty of Mathematical Studies, University of Southampton, Southampton, UK SO17 1BJ.
 Tel +44 (0) 1703 593680. E-mail tjs@maths.soton.ac.uk
 WWW <http://www.maths.soton.ac.uk/~blcs97/>

April 1997

4th International Symposium on Applied Bioinorganic Chemistry and the Carmen National Physical Chemistry Conference

Tygerberg, South Africa April 1-4
Contact: Conference Secretariat, 4ISABC, Medical Research Council, PO Box 19070, Tygerberg, 7505 South Africa.
 Tel +27 21 938 0433. Fax +27 21 938 0395.
 E-mail handrews@eagle.mrc.ac.za

30th Annual International Meeting: ESR Spectroscopy of Radicals in Organic and Biological Systems and 5th International Symposium on Spin Trapping: Applications in Chemistry, Biology and Medicine

Lancaster, UK April 6-10
Contact: Dr C C Rowlands, Department of Chemistry, University of Wales, Cardiff, PO Box 912, Cardiff, UK CF1 3TB.

*Conference Organisers are invited to send details of meetings concerning all aspects of chemistry to: Dr A P Kybett, The Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, UK CB4 4WF. Tel +44 (0) 1223 420066. Fax +44 (0) 1223 420247. E-mail ChemComm@rsc.org

†*Contact:* Dr J F Gibson, The Royal Society of Chemistry, Burlington House, London, UK W1V 0BN. Tel +44 (0) 171 437 8656. Fax +44 (0) 171 734 1227.
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Spring ACS National Meeting

San Francisco, USA April 13-17
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 20th St Station, Washington, DC 20036-8598, USA.

6th International Symposium, Chemistry in the Oil Industry

Ambleside, UK April 14-17
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 Widnes, Cheshire, UK WA8 0JU.

May 1997**11th Noordwijkerhout-Camerino Symposium, Trends in Drug Research**

Noordwijkerhout, The Netherlands May 11-16
Contact: Secretariat 11th Noordwijkerhout-Camerino Symposium,
 c/o Professor H Timmerman, LACDR/Dept. of Pharmacochimistry
 VU, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands.

7th Asian Chemical Congress (7ACC'97)

Hiroshima, Japan May 16-20
Contact: Mr A Nakanishi, Head, Administration Office, 7th Asian
 Chemical Congress, The Chemical Society of Japan, 1-5
 Kanda-Surugadai, Chiyoda-ku, Tokyo 101, Japan.
 Tel +81 3 3292 6161, Fax +81 3 3292 6318.
 E-mail 7acc97@chemistry.or.jp

15th North American Catalysis Society Meeting

Chicago, USA May 18-22
Contact: J Miller, Amoco Corporation, PO Box 3011, Naperville
 IL 60566-7011, USA. Tel +1 (708) 42055818.
 Fax +1 (708) 4203698 (NB. area code changes to 630 after 20
 August 1996). E-mail jmiller@nap.amoco.com
 WWW <http://www.anl.gov/nam/index.html>

EPDIC-5 5th European Powder Diffraction Conference

Parma, Italy May 26-28
Contact: Professor G Artoli, Dipartimento di Scienze della Terra,
 Università di Milano, Via Botticelli, I-20133 Milano, Italy.
 Tel +39 2 23698320. Fax +39 2 70638681.
 E-mail epdic@lummix.terra.unimi.it

June 1997**80th Canadian Society for Chemistry Conference and Exhibition**

Windsor, Canada June 1-5
Contact: Diane Goltz, The Chemical Institute of Canada, 130 Slater
 Street, Suite 550, Ottawa, ON, K1P 6E2. Tel +1 613 232 6252.
 Fax +1 613 232 5862.

4th International Symposium on Bio-organic Chemistry

Biarritz, France June 1-6
Contact: Professor A Marquet, Université Paris, URA CNRS 493,
 Laboratoire de Chimie Organique Biologique, Tour 44/45-4 Pl.
 Jussieu, 75252 Paris Cedex 05, France.

5th International Symposium on Metallomesogens

Neuchâtel, Switzerland June 3-6
Contact: Professor R Deschenaux, Université de Neuchâtel, Institut
 de Chimie, Av. de Bellevaux 51, 2000 Neuchâtel, Switzerland.
 E-mail congrès.ism97@ich.unine.ch

16th Conference on Coordination Chemistry

Smolenice, Slovakia June 9-13
Contact: Professor G Ondrejovič, Department of Inorganic
 Chemistry, Slovak Technical University, Radlinského 9, 812 37
 Bratislava, Slovakia. Tel +42 7 495257. Fax +42 7 493198.
 E-mail sirota@cvstu.cvt.stuba.sk

35th National Organic Symposium

San Antonio, USA June 22-26
Contact: Dr James Rigby, Department of Chemistry, Wayne State
 University, Detroit, MI 48202, USA.
 Tel +1 313 577 3472. Fax +1 313 577 2099.
 E-mail jhr@fourcroy.chem.wayne.edu

10th European Symposium on Organic Chemistry (ESOC 10)

Basel, Switzerland June 22-27
Contact: ESOC 10, Convention Center Basel, PO Box/Messeplatz
 21, CH-4021 Basel, Switzerland. Tel +41 61 686 28 28.
 Fax +41 61 686 21 85.

71st Colloid & Surface Science Symposium

Newark, USA June 29-July 2
Contact: E W Kaler, Department of Chemical Engineering,
 Colburn Laboratory, University of Delaware, Newark, Delaware
 19716, USA. Tel +1 (302) 831 3553. Fax +1 (302) 831 4466.

Faraday Discussion 106, Solid State Chemistry: New Opportunities from Computer Simulations

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Limerick, Ireland July 8-11
Contact: RSC†

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Göttingen, Germany July 20-25
Contact: Professor Armin de Meijere, Chairman, OMCOS 9,
 Institut für Organische Chemie, Georg-August-Universität
 Göttingen, Tammannstr. 2, D-37077 Göttingen, Germany.
 Fax +49 (0) 551 399475.

3rd International Conference on Materials Chemistry

Exeter, UK July 21-25
Contact: RSC†

15th International Symposium. Synthesis in Organic Chemistry

Oxford, UK July 22-24
Contact: RSC†

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 E-mail Conferences@rsc.org

8th International Conference on Bioinorganic Chemistry

Yokohama, Japan July 27-August 1
Contact: Professor Masanobu Hidai, Department of Chemistry and Biotechnology, Faculty of Engineering, University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan.
 Tel +81 (3) 3812 2111. Fax +81 (3) 5800 6945.

August 1997**15th International Symposium on Fluorine Chemistry**

Vancouver, Canada August 3-8
Contact: F Aubke or J Shreeve, Department of Chemistry, University of British Columbia, Vancouver, Canada, V6T 1Z1.
 Tel +1 (604) 822 3817. Fax +1 (604) 822 2847.

XXII International Symposium on Macrocyclic Chemistry

Seoul, Republic of Korea August 3-8
Contact: Professor Si-Joong Kim, XXII ISMC, Department of Chemistry, Korea University, 1 Anam-Dong, Sungbuk-Ku, Seoul 136-701, Republic of Korea. Fax +82 2 921 6900.
 E-mail sjkim@kcs.korea.ac.kr

43rd International Conference on Analytical Sciences and Spectroscopy

Montreal, Canada August 10-13
Contact: Claude Marsolais, Exhibit Chairman, Perkin Elmer Canada Ltd. Tel +1 800 361 7815. Fax +1 514 737 9726.

International Biometals Symposium

Calgary, Alta., Canada August 10-14
Contact: Margaret-Anne Stroh, The University of Calgary, Conference Management Services, Olympic Volunteer Centre, 1833 Crowchild Trail N.W., Calgary, Alta. T2M 4S7, Canada.
 Tel +1 (403) 220 6229. Fax +1 (404) 284 4184.

Inorganic Rings International Symposium, IRIS VIII

Loughborough, UK August 10-15
Contact: Professor J D Woollins, Department of Chemistry, Loughborough University, Loughborough, Leicestershire, UK LE11 3TU. Tel +44 (0) 1509 222565. Fax +44 (0) 1509 233163.
 E-mail j.d.woollins@lut.ac.uk

International Society of Heterocyclic Chemistry, 16th ISHC Congress

Bozeman, USA August 10-15
Contact: Professor T Livinghouse, Department of Chemistry, Montana State University, Bozeman, Montana, 59717, USA.
 Tel +1 (406) 994 4801. Fax +1 (406) 994 5407.
 E-mail uchtl@earth.osc.montana.edu
 www http://euch6f.chem.emory.edu/bozeman.html

IUPAC Congress

Geneva, Switzerland August 17-22
Contact: IUPAC '97, c/o AKM Congress Service, PO Box 37, CH-1218 Le Grand-Saconnex/GE, Switzerland.
 Tel +41 22 761 1661. Fax +41 22 761 16 62.

13th International Symposium on Plasma Chemistry ISPC-13

Beijing, China August 17-22
Contact: Dr Lin He, Secretary, ISPC-13, The Chinese Society of Theoretical and Applied Mechanics, 15 Zhong Guan Cun Road, Beijing 100080, China. Fax +86-10) 6255 9588.
 E-mail cstam@sun.ihep.ac.cn

ZMPC '97 International Symposium on Zeolites and Microporous Crystals

Tokyo, Japan August 24-27
Contact: Dr Takahashi Tatsumi, Secretary, ZMPC'97, Engineering Research Institute, Faculty of Engineering, The University of Tokyo, Yayoi, Tokyo 113, Japan.

32nd IUPAC International Conference on Coordination Chemistry

Santiago, Chile August 24-29
Contact: Professor J Costamanga, Faculty of Chemistry and Biology, Universidad de Santiago di Chile, Santiago-2, Chile.

14th International Mass Spectrometry Conference

Tampere, Finland August 24-29
Contact: Mr A Hesso, Chairman, University of Helsinki, Department of Chemistry, Vuorikatu 20, 00100 Helsinki, Finland.
 Fax +358 (0) 413 691.

4th International Conference on Calixarenes

Parma, Italy August 31-September 4
Contact: Conference Secretary, 4th International Conference on Calixarenes, Dipartimento di Chimica Organica e Industriale, Università di Parma, Viale delle Scienze, 43100 Parma, Italy.
 Tel +39 521 905409. Fax +39 521 905472.
 E-mail calix@ipruniv.cce.unipr.it
 WWW http://www.unipr.it/~calix/home.html

XIIth FEChem Conference on Organometallic Chemistry

Prague, Czech Republic August 31-September 5
Contact: J Schraml, FEChem, Institute of Chemical Process Fundamentals ASCR, 16502 Prague 6-Suchbát, Czech Republic.
 Tel (+42 2) 24311498. Fax (+42 2) 342073.
 E-mail FEChem@icpf.cas.cz

3rd European Congress on Catalysis (EuropaCat-3)

Krakow, Poland August 31-September 6
Contact: M Czerwenka, Institute of Catalysis and Surfactant Chemistry, Polish Academy of Science, ul Niezapominajek, PL-30239 Krakow, Poland. Tel +48 (12) 252814.
 Fax +48 (12) 251923. E-mail ncczerwe@cyf-kr.edu.pl

September 1997**International School of Organometallic Chemistry**

Camerino, Italy September 9-13
Contact: Professor Stefano Maiorana, Dipartimento di Chimica Organica e Industriale, Università di Milano, Via C Golgi, 19, 20133 Milano, Italy. Tel +39 2 2663978. Fax +39 2 2364369.
 E-mail MAIOR@ICIL64.CILEA.IT

International Phase-Transfer Catalysis Conference

Nagoya, Japan September 25-27
Contact: Professor Takayuki Shioiri, Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467, Japan. Tel +81 52 836 3439.
 Fax +81 52 834 9309. E-mail shioiri@phar.nagoya-cu.ac.jp

CHEMECA '97

Rotorua, New Zealand September 28-October 1
Contact: Professor R S Jebson (Chair), Massey University, Palmerston North, New Zealand. Tel +64 6 350 4228.
 Fax +646 350 5655.

†*Contact:* Dr J F Gibson, The Royal Society of Chemistry, Burlington House, London, UK W1V 0BN. Tel +44 (0) 171 437 8656. Fax +44 (0) 171 734 1227.
 E-mail Conferences@rsc.org

2nd International Conference on the Chemistry of Alkali and Alkaline Earth Metals

Erlangen, Germany September 1997
Contact: Professor P von Ragué Schleyer, Institut für Organische Chemie der Friedrich Alexander Universität Erlangen-Nürnberg, Henkestrasse 42, D-91059 Erlangen, Germany.

RSC Autumn Meeting

Aberdeen, Scotland September 1997
Contact: RSC†

Autumn ACS National Meeting

Las Vegas, USA September 7-11
Contact: American Chemical Society, Meetings, PO Box 18598, 20th St Station, Washington, DC 20036-8598, USA.

4th International Conference on Carbon Dioxide Utilization

Kyoto, Japan September 7-11
Contact: T Inui, Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01 Japan. Tel +81 (75) 7535682. Fax +81 (75) 7717285.

7th European Conference on the Spectroscopy of Biological Molecules

San Lorenzo de El Escorial, Spain September 7-12
Contact: Dr P Carmona, ECSBM'97 Chairman, Instituto de Estructura de la Materia (CSIC), Serrano 121, 28006 Madrid, Spain. Tel +34 1 5616800. Fax +34 1 5645557. E-mail pcarmona@pinarl.csic.es

Faraday Discussion 107, Interaction of Acoustic Waves with Thin Films and Interfaces

Leicester, UK September 8-10
Contact: Professor A R Hillman, Department of Chemistry, University of Leicester, UK LE1 7RH.

30th Colloquium Spectroscopicum Internationale 1997 (CSI)

Melbourne, Australia September 21-26
Contact: The Meeting Planners, 108 Church Street, Hawthorn, Victoria 3122, Australia. Tel +61 (3) 981 93700. Fax +61 (3) 981 95978.

3rd World Congress on Oxidation Catalysis

San Diego, USA September 21-26
Contact: A M Gaffney, ARCO Chemical Co, 3801 W Chester Pike, Newton Square, PA 19073-2387, USA. Tel +1 (610) 3592771. Fax +1 (610) 3592778. E-mail cvxamg@arco.com

October 1997**7th International Symposium on Catalyst Deactivation**

Cancun, Mexico October 5-8
Contact: G A Fuentes, Area de Ingenieria Quimica, University A Metropolitana-Iztapalapa, AP 55-534, 09340 Mexico, DF Mexico. Fax +52 (5) 7244900. E-mail gfuentes@xanum.uam.mx or C H Bartolomew, Chemical Engineering Department, Brigham Young University, 350 CB, Provo, UT 84602, USA. Fax +1 (801) 3787799. E-mail bartc@et.byu.edu

9th International Symposium on Chiral Discrimination (ISCD-97)

Nagoya, Japan October 27-30
Contact: Professor Yoshio Okamoto, Department of Applied Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan. Fax +81 52 789 3188.

November 1997**7th International Kyoto Conference on New Aspects of Organic Chemistry**

Kyoto, Japan November 10-14
Contact: Professor Shinji Murai, Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan. Tel +81 6 879 7397. Fax +81 6 879 7396. E-mail ikcoc@chem.eng.osaka-u.ac.jp

5th Chemical Congress of North America

Cancun, Mexico November 11-15
Contact: C Pruitt, Conference Manager, American Chemical Society, 1155 Sixteenth Street, N.W. Washington, D.C. 20036, USA. Tel +1 202 872 4397. Fax +1 202 872 6128. E-mail cpp91@acs.org

March 1998**Spring ACS Meeting**

Dallas, USA March 29-April 2
Contact: ACS Meetings, 1155-16th St., N.W., Washington DC 20036-4899, USA. Tel +1 202 872 4396. Fax +1 202 872 6128. E-mail natlmtgs@acs.org

June 1998**XXIII International Symposium on Macrocyclic Chemistry**

Turtle Bay, USA June 7-12
Contact: Jonathan L Sessler, Department of Chemistry and Biochemistry, The University of Texas, Austin, Texas 78712-1167, USA. Fax +1 512 471 8696. E-mail sessler@mail.utexas.edu or Eiichi Kimura, Institute of Pharmaceutical Sciences, Hiroshima University School of Medicine, Kasumi 1-2-3, Minami-ku, Hiroshima 734, Japan. Fax +81 82 257 5324. E-mail ekimura@ve.ipc.hiroshima-u.ac.jp

26th National Medicinal Chemistry Symposium

Richmond, USA June 13-19
Contact: D J Abraham, Virginia Commonwealth University, Department of Medicinal Chemistry, 410 North 12th St, PO Box 581, Richmond, Va 23298, USA. Tel +1 (804) 828 8483. Fax +1 (804) 828 7436.

12th International Conference on Organic Synthesis

Venice, Italy June 28-July 2
Contact: Professor C Scolastico, Dip.to di Chimica Organica e Industriale, Università di Milano, Via G. Venezian 21, I-20133 Milano, Italy.

August 1998**9th International Conference on Pesticide Chemistry**

London, UK August 2-7
Contact: RSC†

The Conference Diaries from other RSC journals can be found on the RSC World Wide Web pages at <http://chemistry.rsc.org/rsc/>

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