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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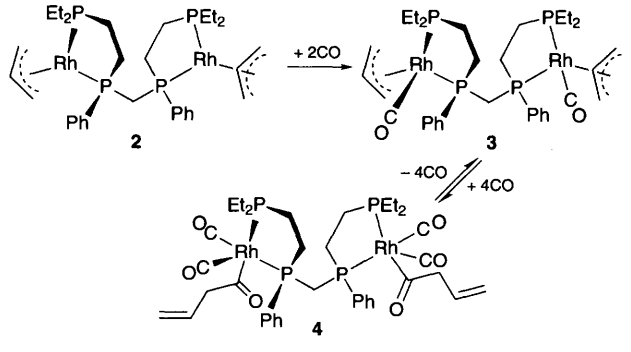
The X-ray structure of an unsymmetrical tetraphosphine bridged zwitterionic $Rh^{-I}Rh^{I}$ dinuclear tetracarbonyl complex is reported along with the facile CO addition equilibrium to form an Rh^{0} tetraphosphine pentacarbonyl bimetallic species; both of these are poor hydroformylation catalysts due 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*-$[Rh_2(ndb)_2L][BF_4]_2$ **1** [nbd = norbornadiene, L = $(Et_2PCH_2CH_2)PhPCH_2PPh(CH_2CH_2PEt_2)$], which is a precursor for a highly active and regioselective hydroformylation catalyst for alk-1-enes.[1,2] The initially proposed mechanism[1] for this novel catalyst assumed the presence of the netural Rh^{I} hydrido–carbonyl bimetallic complex *rac*-$[Rh_2H_2(CO)_4L]$, in direct analogy with monometallic hydroformylation catalysts that have the generic formula $[RhH(CO)_2(P_2)]$ [P_2 = 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*-$[Rh_2H_2(\mu\text{-}CO)_2(CO)_2L]^{2+}$.[4] In keeping with this observation, we have found that if one starts with a neutral dinuclear precursor, *e.g.* *rac*-$[Rh_2(\eta^3\text{-allyl})_2L]$ **2**, one accesses a different oxidation state manifold and a very poor bimetallic hydroformylation catalyst is generated.

rac-$[Rh_2(\eta^3\text{-allyl})_2L]$ **2** is prepared from the reaction of 20 equiv. of (allyl)MgCl with 1 equiv. of *rac*-$[Rh_2(nbd)_2L][BF_4]_2$, **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 H_2–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 × 10^3 Pa)]. This is in marked contrast to dicationic **1** which generates a highly active and regioselective catalyst (90 °C, 90 psi H_2–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*-$[Rh_2(\eta^3\text{-allyl})_2(CO)_2L]$ **3**, which has a symmetrical ^{31}P NMR and a single terminal CO band at 1930 cm^{-1}.§ With excess CO, the bis-acyl *rac*-$[Rh_2(COC_3H_5)_2(CO)_4L]$ **4**, is the only product initially formed, presumably going through an η^1-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 H_2–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*-$[Rh_2(\mu\text{-}CO)(CO)_3(\eta^3 : \eta^1\text{-}L)]$ **5** (Fig. 1).

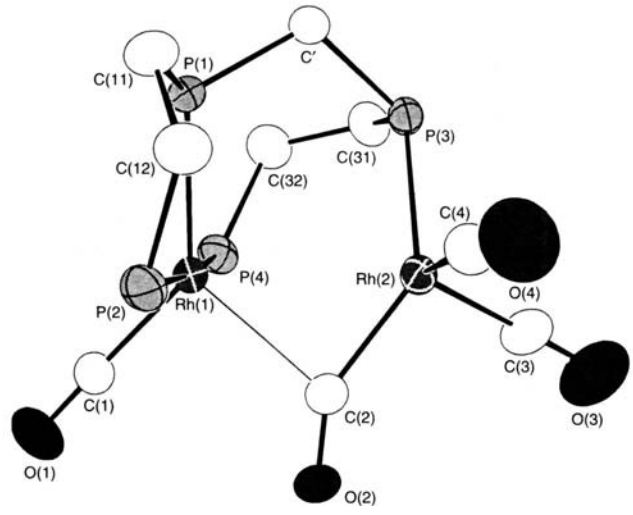


Fig. 1 ORTEP plot of **5** with the phosphine phenyl and ethyl groups omitted for clarity. Selected bond lengths (Å) and angles (°): Rh(1)···Rh(2) 2.9250(3), Rh(1)–P(1) 2.3565(7), Rh(1)–P(2) 2.3080(8), Rh(1)–P(4) 2.3157(8), Rh(1)–C(1) 1.858(3), Rh(1)–C(2) 2.340(3), Rh(2)–P(3) 2.3253(7), Rh(2)–C(2) 1.932(3), 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 −I 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 $[Rh(CO)_3(PR_3)]^-$ complexes.[7] Electron counting with these +I and −I 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) Å in **5** is 0.2 Å longer than a typical Rh^0–Rh^0 single bond of 2.7 Å.

The $^{31}P\{^1H\}$ 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. $^{31}P\{^1H\}$ 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 $[Rh_2(\mu\text{-}CO)(CO)_4L]$ **6**.†† The presence of a CO-based equilibrium between these two species has been confirmed by a two-dimensional $^{31}P\{^1H\}$ NOESY study.

Both **5** and **6** are somewhat related to $[Rh_2(\mu\text{-}CO)(CO)_2(dppm)_2]$, 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. $^{31}P\{^1H\}$ 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 H_2–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 *rac*-$[Rh_2H_2(\mu\text{-}CO)_2(CO)_2L]^{2+}$ 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 that initially proposed.[1]

Footnotes

† *rac*-$[Rh_2(nbd)_2L][BF_4]_2$ (2.06 g, 2.0 mmol) in 20 ml of thf was cooled to −25 °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. $^{31}P\{^1H\}$ 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 $C_{31}H_{50}P_4Rh_2$: 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. $^{31}P\{^1H\}$ NMR ([$^2H_8$]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); $^{31}P\{^1H\}$ NMR ([$^2H_8$]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). $^{13}C\{^1H\}$ NMR ([$^2H_8$]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, $RhC(O)CH^{\alpha}{}_2CH^{\beta} = CH\gamma_2$ 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, $C_{31}H_{50}P_4Rh_2$, monoclinic, space group $P2_1/n$ (no. 14), a = 12.4850(6), b = 17.7854(9), c = 14.7921(5) Å, β = 91.70(1)°, U = 3283.2(5) Å^3, Z = 4, D_c = 1.58 g cm^{-3}, μ(Mo-Kα) = 12.12 cm^{-1}. Data collection information: CAD4 diffractometer, Mo-Kα 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); $^{31}P\{^1H\}$ NMR ([$^2H_8$]toluene, 1 atm CO, H_3PO_4 ref., δ/ppm 65.6 (dddd, P^1, $^1J_{PRh}$ 95.5, $^2J_{P1P2}$ 25.8, $^4J_{P1P3}$ 10.4 Hz, $^2J_{P1P4}$ 327.5 Hz), 53.1 (ddd, P^2, $^1J_{PRh}$ 118.8, $^2J_{P2P3}$ 217.2, $^2J_{P2P4}$ 43.7 Hz), 35.7 (ddm, P^3, $^1J_{PRh}$ 139.6, $^3J_{P3P4}$ 10.4 Hz), 21.6 (ddd, P^4, $^1J_{PRh}$ 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); $^{31}P\{^1H\}$ NMR ([$^2H_8$]thf, 1 atm CO, H_3PO_4 ref., δ/ppm) 67.9 (ddd, P_{ext}, $^1J_{PRh}$ 133.8, J_{PP} 36.6, 15.9 Hz), 46.1 (dm, P_{int}, $^1J_{PRh}$ 133.1 Hz, J_{PP} is a second-order pattern).

References

1 M. E. Broussard, B. Juma, S. G. Train, W. J. Peng, S. A. Laneman and G. G. Stanley, *Science*, 1993, **260**, 1784.
2 G. Süss-Fink, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 67.
3 B. Cornils, in *New Syntheses with Carbon Monoxide*, ed. J. Falbe, Springer-Verlag, Berlin, 1980; G. G. Stanley, in *Encyclopedia of Inorganic Chemistry*, ed. R. B. King, Wiley, New York, 1995.
4 R. D. Matthews, D. K. Howell, W. J. Peng, S. G. Train, W. D. Treleaven and G. G. Stanley, *Angew. Chem.*, 1996, **108**, 2402.
5 G. Yagupsky, C. K. Brown and G. Wilkinson, *J. Chem. Soc. A.*, 1970, 1392.
6 C. Bianchini, A. Meli, M. Peruzzini and F. Vizza, *Organometallics*, 1990, **9**, 226.
7 A. S. C. Chan, H.-S. Shieh and J. R. Hill, *J. Organomet. Chem.*, 1985, **279**, 171.
8 C. P. Kubiak and R. Eisenberg, *J. Am. Chem. Soc.*, 1980, **102**, 3637.
9 R. Crabtree and H. Felkin, *J. Mol. Catal.*, 1979, **5**, 75.
10 G. Consiglio and F. Rama, *J. Mol. Catal.*, 1991, **66**, 1.

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March 1997

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April 1997

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16th Conference on Coordination Chemistry
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35th National Organic Symposium
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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.oscs.montana.edu
www http://euch6f.chem.emory.edu/bozeman.hml

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 Orgamometallic Chemistry
Prague, Czech Republic August 31-September 5
Contact: J Schraml, FECHEM, Institute of Chemical Process Fundamentals ASCR, 16502 Prague 6-Suchdol, 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, Universita 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.

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†*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 fur 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
Conact: Professor Shinji Murai, Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan.
Tel +81 6 879 7397. Fax +71 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. Venizian 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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