

**LETTERS TO NATURE**

18. von Dassow, G., Schmidt, J. E. & Kimmel, D. *Genes Dev.* **7**, 355-366 (1993).  
 19. Gont, L. K., Steinbeisser, H., Blumberg, B. & DeRobertis, E. M. *Development* **119**, 991-1004 (1993).  
 20. Ang, S.-L. & Rossant, J. *Cell* **78**, 561-574 (1994).  
 21. Weinstein, D. C. et al. *Cell* **78**, 575-588 (1994).  
 22. Stachel, S. E., Grunwald, D. J. & Myers, P. Z. *Development* **117**, 1261-1274 (1993).  
 23. Schulte-Merker, S., Van Eeden, F. J. M., Halpern, M. E., Kimmel, C. B. & Nüsslein-Volhard, C. *Development* **120**, 1009-1015 (1994).  
 24. Chesley, P. J. *exp. Zool.* **70**, 429-435 (1935).  
 25. Hatta, K., Kimmel, C. B., Ho, R. K. & Walker, C. *Nature* **350**, 339-341 (1991).  
 26. Solnica-Krezel, L., Schier, A. F. & Driever, W. *Genetics* **136**, 1401-1420 (1994).  
 27. Mullins, M. C., Hammerschmidt, M., Hafter, P. & Nüsslein-Volhard, C. *Curr. Biol.* **4**, 189-202 (1994).  
 28. Henion, P. D. et al. *Dev. Genet.* (in the press).  
 29. Hatta, K. *Neuron* **9**, 629-642 (1992).  
 30. Smith, J. C. & Watt, F. M. *Differentiation* **29**, 109-115 (1985).  
 31. Yamada, T., Pfaff, S., Edlund, T. & Jessell, T. M. *Cell* **73**, 673-686 (1993).  
 32. Echeleard, Y. et al. *Cell* **75**, 1417-1430 (1993).  
 33. Roelink, H. et al. *Cell* **76**, 761-775 (1994).  
 34. Krauss, S., Concordet, J.-P. & Ingham, P. W. *Cell* **75**, 1431 (1993).  
 35. Dessain, S. & McGinnis, W. *Adv. dev. Biol.* **2**, 1-54 (1993).  
 36. Helde, K. A. & Grunwald, D. J. *Dev. Biol.* **159**, 418-426 (1993).  
 37. Stein, S. & Kessel, M. *Mech. Dev.* **49**, 37-48 (1995).  
 38. Dalton, D., Chadwick, R. & McGinnis, W. *Genes Dev.* **3**, 1940-1956 (1989).  
 39. Simeone, A. et al. *EMBO J.* **11**, 2541-2550 (1992).  
 40. Postlethwait, J. E. et al. *Science* **264**, 699-703 (1994).

41. Williams, J. G. K., Kubelik, A. R., Livak, K. J., Rafalski, J. A. & Tingey, S. V. *Nucleic Acids Res.* **18**, 6531-6536 (1990).  
 42. Oppenheimer, J. M. *J. exp. Zool.* **140**, 247-268 (1959).  
 43. Ho, R. K. *Semin. dev. Biol.* **3**, 53-64 (1992).  
 44. Halpern, M. E. et al. *Development* **121**, 4257-4264 (1995).  
 45. Yan, Y.-L., Hatta, K., Riggleman, B. & Postlethwait, J. H. *Dev. Dyn.* **203**, 363-376 (1995).  
 46. Thisse, C., Thisse, B., Schilling, T. F. & Postlethwait, J. H. *Development* **119**, 1203-1215 (1993).  
 47. Kimmel, C. B., Ballard, W. W., Kimmel, S. R., Ullmann, B. & Schilling, T. F. *Dev. Dyn.* **203**, 253-310 (1995).  
 48. Trevarrow, B., Marks, D. & Kimmel, C. B. *Neuron* **4**, 669-679 (1990).  
 49. Pike, S. H., Melancon, E. F. & Eisen, J. S. *Development* **144**, 825-831 (1992).  
 50. Eisen, J. S., Pike, S. H. & Debu, B. *Neuron* **2**, 1097-1104 (1989).  
 51. Michelmore, R. W., Paran, I. & Kesseli, R. V. *Proc. natn. Acad. Sci. U.S.A.* **88**, 9828-9832 (1991).

ACKNOWLEDGEMENTS. We thank P. Hafter and C. Nüsslein-Volhard for providing *fh<sup>h241</sup>* and *fh<sup>m229</sup>* DNA samples; W. McGinnis for sharing the *90Bre* sequence; A. Schier, A. Ruiz | Altaba and our colleagues in Eugene for discussions and comments on the manuscript; S. Wilson and P. Ingham for sharing unpublished results; B. Riggleman, P. Ingham and S. Schulte-Merker for probes and antibodies; R. BreMiller and M. McDowell for technical assistance; and E. Trevarrow, S. Foster and E. Lawson for help with fish care. This work was supported by a Jane Coffin Childs Memorial Fund Fellowship to W.S.T., a Royal Society Visiting Fellowship to B.T., a Centennial Fellowship from the MRC of Canada to M.E.H., a March of Dimes grant to D.K., NIH grants to C.B.K. and J.H.P., and grants from the Wellcome Trust and the Nuffield Foundation to T.J.

**LETTERS TO NATURE**

**Dynamical evidence for a black hole in the eclipsing X-ray nova GRO J1655 - 40**

**Charles D. Bailyn\***, **Jerome A. Orosz\***,  
**Jeffrey E. McClintock†** & **Ronald A. Remillard‡**

\* Department of Astronomy, Yale University, PO Box 208101, New Haven, Connecticut 06520, USA

† Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02138, USA

‡ MIT Center for Space Research, Rm 37-595, Cambridge, Massachusetts 02139, USA

**X-RAY novae are binary systems in which a compact object accretes gas from a companion star. In several cases there is good evidence that the compact object is a black hole<sup>1-5</sup>. The best evidence for the presence of a black hole comes from measuring the orbital velocity of the companion star and thereby determining the minimum mass of the compact object; when this mass exceeds the maximum mass for a neutron star ( $\lesssim 3$  solar masses<sup>6</sup>), a black hole seems the only remaining possibility. The unusual X-ray nova GRO J1655 - 40 (refs 7-10) is unique because it emits superluminal radio jets, suggesting that it is a low-luminosity counterpart to active galactic nuclei<sup>7,9</sup>, which are thought to be powered by accretion onto a massive black hole. Here we report observations of the optical counterpart<sup>10</sup> of GRO J1655 - 40, which show that the system undergoes periodic eclipses; the edge-on geometry thus implied allows a determination of the companion star's true velocity. The mass of the compact object derived from the velocity curve is at least  $3.16 \pm 0.15$  solar masses, which strongly supports its identification as a black hole.**

We made photometric measurements of GRO J1655 - 40 on 18-25 March and 5-24 April 1995 with the 0.9-m telescope and CCD imager at the Cerro Tololo Interamerican Observatory (CTIO), and on 28 March to 2 April 1995 with the CTIO 1.5-m telescope and CCD imager (all dates are given in UT). The magnitude of the source was in the range of  $16.2 \leq V \leq 16.9$  during this time, about a magnitude brighter than the quiescent value of 17.3 (ref. 7). Spectra were obtained with the Ritchey-Chretien spectrograph on the CTIO 4-m telescope on the nights of 30 April and 2-4 May 1995. On 3 May 1995, during our spectroscopy run, M. Postman obtained five photometric measurements of the source with the CTIO 1.5-m telescope.

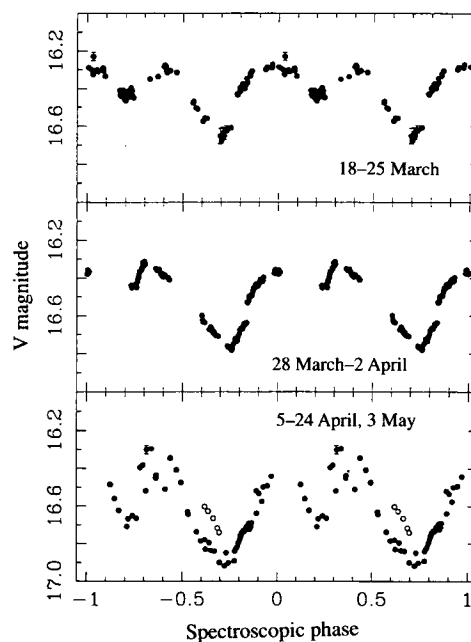


FIG. 1 Lightcurves of GRO J1655-40, folded on a period of 2.612 days. The depth of the eclipses is seen to be increasing and approaching the pre-outburst magnitude level of  $V=17.3$ . Open symbols on the bottom plot are data from 3 May. Error bars smaller than the symbols have been suppressed.

As the photometric data were obtained, it became clear that the lightcurve showed eclipses, as previous data had suggested<sup>10</sup>, and was periodic on a timescale of  $\lesssim 3$  days. Unfortunately, only one compelling fiducial point fell within our observing windows, namely a sharp minimum on 2 April (UT) at heliocentric Julian day (HJD)  $2,449,809.70 \pm 0.02$ . A variety of different periods near 2.6 days could be derived by invoking night-to-night variations of  $\leq 0.1$  magnitudes in the overall brightness of the source, which are common in such sources during decay from outburst<sup>11,12</sup>. However the overall lightcurve shape was similar for all possible periods, consisting of a broad triangular primary minimum, and a shorter secondary minimum displaced by about 0.5 in phase from the primary minimum. This lightcurve is similar to that of the eclipsing X-ray binary CAL87 (ref. 13). Cycle-

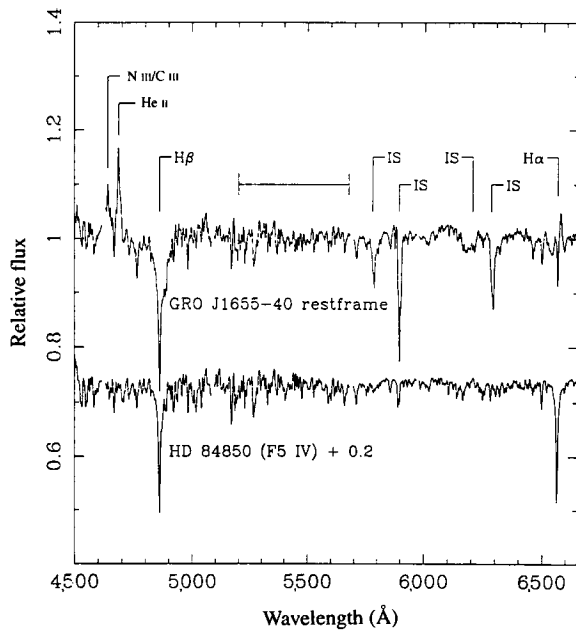


FIG. 2 Top spectrum is the sum of all our data of GRO J1655-40 after each individual spectrum was shifted to the rest frame. Bottom spectrum is of our radial velocity template, HD84850, a F5 subgiant. The combination of the Loral  $1,000 \times 3,000$  pixel detector and the KPGL3 grating gave a wavelength range of 3,850–7,150 Å and a pixel scale of 1.1 Å per pixel. Both spectra have been normalized to a polynomial fit to the continuum. To facilitate comparison with the GRO J1655-40 spectrum, a constant has been added to the template spectrum, so that the absorption lines are of similar depth. The horizontal bar indicates the cross-correlation region, which avoids emission lines, interstellar lines (marked 'IS'), and bad columns of the CCD detector.

to-cycle variations in lightcurve shape as well as a gradual increase in the depth of the primary minimum were superposed on this basic lightcurve shape (Fig. 1).

It seems likely that an eclipse of a large accretion disk by the secondary star is responsible for the primary minimum, and an eclipse of the secondary star by the disk is responsible for the secondary minimum. This conclusion is strengthened by the fact that the source became redder during primary minimum and bluer during secondary minimum, as would be expected given a hot disk and a cooler star. The simultaneous spectroscopic and photometric data obtained on 3 May also strongly support this interpretation (see below). Furthermore, the fraction of the light contributed by the secondary star decreased during the secondary minimum. The implication that the system is close to edge-on is supported by models of the radio jets (ref. 10), which predicts an orbital inclination of  $i = 85^\circ$ . Such edge-on systems allow the use of the powerful tool of eclipse mapping<sup>14</sup>, in which a detailed picture of the disk can be built up by modelling the lightcurve. Although the combination of incomplete data on any one orbit and clear orbit-to-orbit variability makes such detailed modelling difficult with our current data, the application of this technique to GRO J1655-40 promises to greatly increase our understanding of accretion processes and jet production near black holes.

The spectra of GRO J1655-40 had less prominent Balmer emission lines and stronger high-excitation lines (for example, He II 4,686 Å and N III/C III 4,640–4,650 Å) than X-ray novae in quiescence<sup>13</sup>, presumably because the outburst was still underway. Nevertheless, it was immediately apparent from the individual spectra that a stellar F-type absorption spectrum was present (see Fig. 2). We used the FXCOR routine in the software package IRAF to cross-correlate the spectra of GRO J1655-40 against that of HD84850, a sixth magnitude F5 subgiant of known radial velocity. The range of wavelengths over which the

cross-correlation was performed is also shown in Fig. 2. We obtained highly significant cross-correlation peaks and radial velocities from each of our 73 spectra, with  $r$ -values<sup>15</sup> of at least 7 in all cases. Cross-correlating with other template spectra and wavelength regions yielded similar results.

We fitted a sine curve to the velocity data from 30 April and 3 and 4 May using standard  $\chi^2$  minimization techniques. The best-fit sinusoid had a period of  $2.601 \pm 0.027$  days, an epoch of maximum radial velocity of HJD  $2,449,839.083 \pm 0.003$  and a semi-amplitude  $K = 227.2 \pm 3.5$  km s<sup>-1</sup> (Fig. 3). The observed period is compatible with the  $3 \pm 0.2$  day periodicity derived from the wiggles seen in the radio jets<sup>9</sup>. Because we had four nine-hour-long spans of data over five nights, aliases of this period are ruled out. Cross-correlating our 34 radial velocity templates with each other reveals discrepancies of up to 40 km s<sup>-1</sup> between our observations and the velocities listed in the SIMBAD data base. Therefore we have averaged results from all of our templates to determine the systemic velocity  $\gamma = -150 \pm 19$  km s<sup>-1</sup>, where the error is dominated by systematic effects. Correcting for the Sun's motion and differential galactic rotation results in a radial velocity of  $-114 \pm 19$  km s<sup>-1</sup> for this object<sup>16</sup>. Unfortunately there are currently only upper limits on the proper motion of the source<sup>10</sup>.

The large value of  $\gamma$  is unexpected: previous dynamically confirmed black-hole candidates have much smaller values of  $\gamma$  (refs 1-4). Neutron-star systems often have large peculiar velocities, presumably imparted by kicks during an asymmetric collapse, but black holes are not expected to show such behaviour. A detailed consideration of the implications of the high  $\gamma$  value of GRO 1655-40 is given in ref. 16. The most satisfactory explanation seems to be that the black hole in this system did not form as a result of a prompt collapse, but via an intermediate neutron-star stage.

The period ( $P$ ) and semi-amplitude ( $K$ ) of the velocity curve result in the following value for the mass function:

$$f(m) = \frac{M_1^3 \sin^3(i)}{(M_1 + M_2)^2} = \frac{PK^3}{2\pi G} = 3.16 \pm 0.15 M_\odot$$

where  $M_1$  is the mass of the compact object,  $M_2$  is the mass of the secondary star,  $i$  is the inclination of the orbit to the line of sight, and  $M_\odot$  is the mass of the Sun. An inspection of the above equation reveals that the mass function represents the minimum possible mass of the compact object. The maximum stable mass

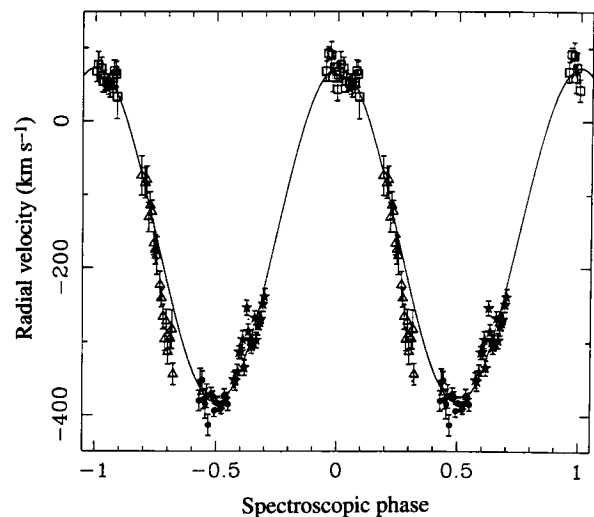


FIG. 3 Radial velocity curve of GRO J1655-40. Filled circles indicate data taken on 30 April; triangles, stars and squares indicate data from 2, 3 and 4 May respectively. Exposure times were typically 1,200 seconds. Errors are derived from fitting a gaussian function to the cross-correlation peak.

of a neutron star is  $3M_{\odot}$  for all causal equations of state<sup>5</sup>, and below  $2.5M_{\odot}$  for most plausible equations of state<sup>17</sup>. Thus, in the absence of exotic matter and/or non-einsteinian gravity, a mass function above  $3M_{\odot}$  requires the compact object to be a black hole.

The emission lines varied in shape from night to night, which made it impossible to determine a velocity curve for the accretion disk. We were, however, able to study the characteristics of the secondary star by creating a summed spectrum in its rest frame. We also observed a number of bright stars of known spectral type. We determined limits on the spectral type of the secondary star by multiplying these reference spectra by a constant and subtracting them from the summed rest-frame spectrum of GRO J1655–40. Subtracting spectra of stars of type F3–F6 from GRO J1655–40 resulted in significantly smoother residuals than other types, and we conclude that the spectral type of the secondary star is within this range (Fig. 2). We were unable to determine a luminosity type in this way, but we note that a secondary star that fills its Roche lobe in a 2.6-day orbit must be somewhat larger than a mid-F main-sequence star. In the likely case that the secondary is no more massive than a main-sequence star of equivalent spectral type ( $M_2 \leq 1.5M_{\odot}$ ) and  $i \geq 80^\circ$ , the compact object would have a maximum mass of  $5.4 \pm 0.2M_{\odot}$ . The fraction of light from the secondary star was found to be  $\sim 40\%$ , except during the night of 2 May, when it was  $\sim 30\%$ . No change in spectral type was observed during our observations.

The steep slope of the velocity measurements on 2 May is incompatible with any sine curve which fits the other three nights of data. As we rotated the spectrograph slit from time to time each night to follow the parallactic angle<sup>18</sup>, we do not believe that a steady monotonic drift in our equipment (for example, in the placement of the star in the slit) is likely. This fact, combined with the smooth progression of the 2 May velocity data, suggests that the deviation from the predicted sinusoid is real. These deviations probably do not represent orbital motion of the secondary star, so we did not include the 2 May data in our determination of the parameters of the sinusoidal fit. These data are, however, shown in Fig. 3 for completeness.

Interestingly, the data deviate from the theoretical curve starting at approximately the predicted time of the middle of the secondary eclipse. This is a phase when a number of effects might come into play. First, X-ray heating, which is known to affect radial velocities<sup>19</sup>, is at a maximum. However, the lack of changes in the spectral type of the secondary star indicates that this effect must be much smaller in GRO J1655–40 than in Hercules X-1 (ref. 17). Alternatively, the eclipse of the secondary star by the accretion disk might mask part of the secondary star, resulting in an asymmetric contribution from the star's rotational velocity to the observed radial velocity. Although our moderate-resolution spectra do not significantly constrain the rotational velocity of the secondary star, the equatorial rotational velocity of a Roche lobe filling star in a 2.6-day orbit should be  $\geq 100 \text{ km s}^{-1}$ , significantly larger than the size of the velocity deviations. As the fraction of light contributed by the secondary star was demonstrably lower on 2 May than on other nights, such an effect is plausible.

We attempted to improve our spectroscopic ephemeris by including constraints imposed by the photometry. The photometric data taken on 3 May between spectroscopic phase 0.6 and 0.7 clearly show an ingress into a primary eclipse, implying that primary eclipse is at spectroscopic phase 0.75, as would be expected for an eclipse of the accretion disk. Applying this assumption to the primary minimum observed on 2 April leads to an orbital period of  $2.612 \pm 0.003$  days. As can be seen in Fig. 1, this period results in apparent phase offsets in the photometry obtained between 18 and 25 March. Indeed, no single period fits all the data; periods that align the top two panels of Fig. 1 result in sizeable misalignments with the spectroscopic phase. Given the phase problems with the photometric data, we caution against taking the 2.612-day period at face value. As the source

was brighter during 18–25 March epoch, we suggest that activity in the disk, such as hotspots<sup>20,21</sup> and superhumps<sup>11,22</sup>, may be responsible for the observed phase offset. Similarly, we note that the eclipse event observed in August 1994 (ref. 10) also cannot be aligned with our current data, so once again it appears that some combination of X-ray heating, hot spots and superhumps is distorting the lightcurve. When an orbital period sufficiently accurate to trace back to the beginning of the outburst becomes available, these issues may be resolvable.  $\square$

Received 12 June; accepted 28 September 1995.

1. McClintock, J. E. & Remillard, R. A. *Astrophys. J.* **308**, 110–122 (1986).
2. Casares, J., Charles, P. A. & Naylor, T. *Nature* **355**, 614–617 (1992).
3. Remillard, R. A., McClintock, J. E. & Bailyn, C. D. *Astrophys. J.* **390**, L145–L149 (1992).
4. Remillard, R. A., McClintock, J. E., Orosz, J. A. & Bailyn, C. D. *Astrophys. J.* (in the press).
5. Charles, P. A. & Casares, J. *IAU Circ. No.* 2498 (1995).
6. Chitre, D. M. & Hartle, J. B. *Astrophys. J.* **207**, 592–600 (1976).
7. Tingay, S. J. et al. *Nature* **374**, 141–143 (1995).
8. Harmon, B. A. et al. *Nature* **374**, 704–706 (1995).
9. Hjellming, R. M. & Rupen, M. P. *Nature* **375**, 464–468 (1995).
10. Bailyn, C. D. et al. *Nature* **374**, 701–703 (1995).
11. Bailyn, C. D. *Astrophys. J.* **381**, 298–305 (1992).
12. Callanan, P. J. et al. *Astrophys. J.* **441**, 785–799 (1995).
13. Cowley, A. P., Schmidtke, P. C., Crampton, D. & Hutchings, J. B. *Astrophys. J.* **350**, 288–294 (1990).
14. Horne, K. *Mon. Not. R. astr. Soc.* **213**, 129–141 (1985).
15. Tonry, J. & Davis, M. *Astr. J.* **84**, 1511–1525 (1979).
16. Brandt, W. N., Podsiadlowski, Ph. & Sigurdsson, S. *Mon. Not. R. astr. Soc.* (in the press).
17. Arnett, W. D. & Bowers, R. L. *Astrophys. J. Suppl. Ser.* **33**, 415–436 (1978).
18. Filippenko, A. V. *Publ. astr. Soc. Pacif.* **94**, 715–721 (1982).
19. Crampton, D. & Hutchings, J. B. *Astrophys. J.* **191**, 483–491 (1974).
20. Marsh, T. R., Robinson, E. L. & Woods, J. H. *Mon. Not. R. astr. Soc.* **206**, 137–154 (1994).
21. Orosz, J. A., Bailyn, C. D., Remillard, R. A., McClintock, J. E. & Foltz, C. B. *Astrophys. J.* **436**, 848–858 (1994).
22. Warner, B. in *Interacting Binary Stars* (eds Eggleton, P. P. & Pringle, J. E.) 367–392 (NATO ASI Ser., Reidel, Dordrecht, 1985).

ACKNOWLEDGEMENTS. The authors are Visiting Astronomers at the Cerro Tololo Interamerican Observatory, which is operated by A.U.R.A., Inc. under contract to the US NSF. We are grateful to S. Barnes, M. Schaefer and M. Postman for obtaining some of the photometric observations reported here. This research made use of the SIMBAD database, operated by the Centre de Données Stellaires in Strasbourg, France. This work was supported in part from the US NSF and NASA.

## Heterogeneous catalysts obtained by grafting metallocene complexes onto mesoporous silica

Thomas Maschmeyer, Fernando Rey, Gopinathan Sankar & John Meurig Thomas\*

Davy-Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London W1X 4BS, UK

THE synthesis of mesoporous siliceous solids with large-diameter channel apertures (25–100 Å) has greatly expanded the capabilities of heterogeneous catalysis<sup>1–7</sup>. The large apertures in such mesoporous silicas can, for example, be modified by framework substitution to create highly selective catalysts<sup>4,5</sup>. Here we show that direct grafting of an organometallic complex onto the inner walls of mesoporous silica MCM-41 (ref. 1) generates a shape-selective catalyst with a large concentration of accessible, well spaced and structurally well defined active sites. Specifically, attachment of a titanocene-derived catalyst precursor to the pore walls of MCM-41 produces a catalyst for the epoxidation of cyclohexene and more bulky cyclic alkenes.

There is currently great interest in titanium-containing zeolitic catalysts for selective oxidations. Titanium ions incorporated into the framework sites of silicalite I and II (that is, TS1 and TS2 respectively, introduced by the Enichem Company)<sup>8</sup> as well

\* To whom correspondence should be addressed.