

Organozirconium(III)–Dinitrogen Complexes: Evidence for (η^2 -N₂)–metal Bonding in [Zr(η -C₅H₅)₂(N₂)(R)] [R = Me₃Si)₂CH]†

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Summary Reduction of [Zr(η -C₅H₅)₂(Cl)R] [R = (Me₃Si)₂-CH] with Na–Hg in tetrahydrofuran (THF) under ¹⁴N₂ affords brown, paramagnetic, air-sensitive, crystalline

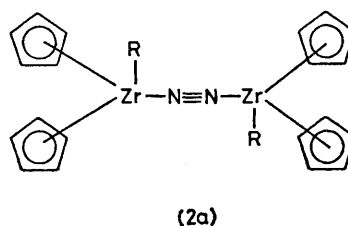
[Zr(η -C₅H₅)₂(¹⁴N₂)R], which in THF shows an e.s.r. 1:2:3:2:1 quintet due to coupling [$a(^{14}\text{N}) = 0.375$ mT] with two equivalent ¹⁴N atoms [or a 1:2:1 triplet for the

† No reprints available.

There is currently no precedent for a simple sideways-bound N_2 complex,⁶ although there are X-ray data for $[\{Ni(LiPh)_3\}_2\mu-(\eta^2-N_2)(OEt)_2]$ ^{7a} and $[\{Ph[Na(OEt)_2]_2(NiPh_2)_2N_2NaLi_6(OEt)_4(OEt_2)_2\}]$ ^{7b} in each of which a η^2-N_2 ligand bridges the two nickel atoms; $\nu(N-N)$ was not located.^{7c} Attempts to date to obtain molecular weights on complex (1) were unsuccessful; dissolution in aromatic solvent led to formation of (2), and THF is not a convenient medium for cryoscopy.

When solid (1) was kept at ca. 20 °C at 10^{-3} mmHg, it became increasingly purple. Crystallisation from PhMe yielded the purple diamagnetic $[Zr(\eta-C_5H_5)_2R(N_2)]$, with no band obviously due to $\nu(N_2)$. Structure (2a) is accordingly proposed and is similar to the known arylbis(cyclopentadienyl)titanium(III) complexes which also show no clear $\nu(N_2)$ absorption.⁸ Zirconium(II)-dinitrogen complexes have been reported.⁹ We find no N_2 uptake by $[Ti(\eta-C_5H_5)_2\{CH(SiMe_3)_2\}]$.¹

These results on Zr-dinitrogen complexes demonstrate *inter alia* that the bulky ligand $(Me_3Si)_2CH^-$ may stabilise for steric reasons unusual or unusually-bonded co-ligands.



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¹ J. L. Atwood, G. K. Barker, J. Holton, W. E. Hunter, M. F. Lappert, and R. Pearce, *J. Amer. Chem. Soc.*, 1977, **99**, 6645.

² M. R. Collier, M. F. Lappert, and R. Pearce, *J.C.S. Dalton*, 1973, 445.

³ Cf. B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 136.

⁴ J. Myatt, unpublished work.

⁵ Cf. D. Sellmann, *Angew. Chem. Internat. Edn.*, 1974, **13**, 639.

⁶ A recent paper provides evidence for a sideways bound N_2 ligand in a Rh^I complex: C. Bussetto, A. D'alfonso, F. Maspero, G. Perego, and A. Zazzeta, *J. C. S. Dalton*, 1977, 1828.

⁷ (a) C. Krüger and Yi-Hung Tsay, *ibid.*, 1973, **12**, 998; (b) K. Jonas, D. J. Brauer, C. Krüger, P. J. Roberts, and Yi-Hung Tsay, *J. Amer. Chem. Soc.*, 1976, **98**, 74; (c) K. Jonas, *Angew. Chem. Internat. Edn.*, 1973, **12**, 997.

⁸ J. H. Teuben, *J. Organometallic Chem.*, 1973, **57**, 159.

⁹ R. D. Senners, J. M. Manriquez, R. E. Marsh, and J. E. Bercaw, *J. Amer. Chem. Soc.*, 1976, **98**, 8351, and refs. therein.