## Organozirconium(III)—Dinitrogen Complexes: Evidence for $(\eta^2-N_2)$ —metal Bonding in $[Zr(\eta-C_5H_5)_2(N_2)(R)]$ [R = Me<sub>3</sub>Si)<sub>2</sub>CH]<sup>†</sup>

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Summary Reduction of  $[Zr(\eta-C_5H_5)_2(Cl)R]$  [R =  $(Me_3Si)_2-CH]$  with Na–Hg in tetrahydrofuran (THF) under  $^{14}N_2$  affords brown, paramagnetic, air-sensitive, crystalline  $\dagger$  No reprints available.

 $[Zr(\eta-C_5H_5)_2(^{14}N_2)R]$ , which in THF shows an e.s.r. 1:2:3:2:1 quintet due to coupling  $[a(^{14}N)=0.375 \text{ mT}]$  with two equivalent  $^{14}N$  atoms [or a 1:2:1 triplet for the

 $^{15}\rm{N}_2\text{-}isotopomer,}~\alpha(^{15}\rm{N})=0.45~mT],$  and no i.r. absorption in the  $2400-1500~\rm{cm}^{-1}$  region; one half of the  $\rm{N}_2$  is gradually lost at  $ca.~20~^{\circ}\rm{C}$  and  $10^{-3}~\rm{mmHg}$  to yield purple crystals (from PhMe) of  $[\{Zr(\eta\text{-}C_5H_5)_2R\}_2N_2].$ 

We report (a) the first  $Zr^{III}$ —dinitrogen complex  $[Zr(\eta-C_5H_5)_2(N_2)(R)]$  [ $R=(Me_3Si)_2CH]$  (1), a brown, air-sensitive, crystalline, paramagnetic material [from tetrahydrofuran (THF)–n-C $_6H_{14}$ ] under ambient conditions; (b) e.s.r. spectroscopic data on  $[Zr(\eta-C_5H_5)_2(^{14}N_2)R]$  (Figure) and its  $^{15}N_2$  isotopomer which are suggestive of a sideways-bound ( $N_2$ ) molecule, consistent also with the failure to observe an i.r. band in the  $\nu(N_2)$  region, and (c) the conversion of (1) into the diamagnetic  $[\{Zr(\eta-C_5H_5)_2R\}_2\mu-(N_2)]$  (2). Satisfactory analytical data have been obtained for complexes (1) and (2), which are stable indefinitely when stored in the solid state at 0° C in a dinitrogen atmosphere; reaction of aqueous hydrochloric acid with complex (1) provides a low yield (<20%) of hydrazine, traces of ammonia, and dinitrogen.

Reduction of the pale-yellow  $[Zr(\eta-C_5H_5)_2(Cl)R]^1$  in THF solution under a dinitrogen atmosphere using sodium-amalgam proceeds smoothly during ca. 2 h at 20 °C to give a yellow-brown solution which, upon addition of  $n-C_6H_{14}$  and cooling to -30 °C, furnishes in moderate (after recrystallisation) yield, flaky dark-brown crystals of  $[Zr(\eta-C_5-H_5)_2(N_2)R]$  (1) (Scheme). Similar experiments using the

$$[Zr(\eta - C_5H_5)_2(Ci)R] \xrightarrow{i} [Zr(\eta - C_5H_5)_2(N_2)R]$$

$$(1)$$

$$[\{Zr(\eta - C_5H_5)_2R\}_2\mu - (N_2)]$$

$$(2)$$

Scheme. i, Na-Hg, THF,  $\rm N_2,~20~^{\circ}C\,;~ii,~(a)~10^{-3}~mmHg~(b)$  crystallisation from PhMe.

less bulky neopentyl or trimethylsilyl² analogues of the starting materials  $[Zr(\eta\text{-}C_5H_5)_2(Cl)R]$   $(R=Me_3CCH_2)$  or  $Me_3SiCH_2)$  did not lead to  $N_2$  incorporation into a product. Reduction of  $[Zr(\eta\text{-}C_5H_5)_2(Cl)R]$  in  $OEt_2$  or dioxan did not yield a tractable product. The reduction under argon at  $20^{\circ}$  C of  $[Zr(\eta\text{-}C_5H_5)_2(Cl)R]$  using (i) an electron-rich olefin

[EtNCH<sub>2</sub>CH<sub>2</sub>N(Et)C–]<sub>2</sub> in THF, PhMe, or OEt<sub>2</sub> and u.v. irradiation, (ii) Na–Hg in THF, or (iii) Na–Hg in THF in the presence of PEt<sub>3</sub> gave in each case a Zr<sup>III</sup> signal in the e.s.r. spectrum (g=1.992). Using procedure (i), a particularly strong signal was observed with a(Zr)=1.667 mT; soluble, persistent Zr<sup>III</sup> complexes are as yet unknown. In none of (i)—(iii) was a characterisable material isolated. Complex (1) rapidly turns purple and then yellow upon exposure to the atmosphere.

The e.s.r. spectrum of complex (1) in THF solution shows (Figure) a central 1:2:3:2:1 quintet with satellites shown to arise from coupling with the  $^{91}$ Zr nucleus ( $I=^{5}/_{2}$ ; natural abundance,  $11\cdot2\%$ ). The quintet structure shows that the unpaired electron is also coupled with two equivalent  $^{14}$ N (I=1) nuclei and the fairly high hyperfine constant

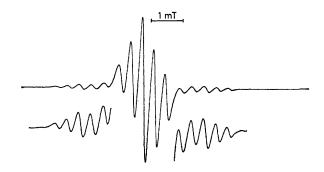


Figure. The e.s.r. spectrum of  $[Zr(\eta-C_6H_5)_2(^{14}N_2)R]$  [ $R=(Me_3Si)_2CH]$  (1) in THF at 20 °C (inset  $\times$  5); upon cooling, the splitting pattern was maintained down to ca.-80 °C whereafter the sample solidified.

[ $a(^{14}\mathrm{N})=0.375~\mathrm{mT}$ ] shows that there is substantial spin density on the N<sub>2</sub> ligand. Consistent with this, the g value of 2.0037 is significantly higher than expected for a  $d^1$  complex,  $^3$  and the  $^{91}\mathrm{Zr}$  hyperfine coupling constant is low [ $a(^{91}\mathrm{Zr})=0.85~\mathrm{mT}$ ].  $^{91}\mathrm{Zr}$  coupling does not appear to have previously been reported for a  $\mathrm{Zr^{111}}$  complex; however, Myatt<sup>4</sup> finds that the e.s.r. spectrum of [ $\mathrm{Zr}(\eta-\mathrm{C_5H_5})_2(\mathrm{PPh_2})_2$ ] at high sensitivity shows  $g_{\mathrm{av}}=1.988$ ,  $a(^{91}\mathrm{Zr})=2.25~\mathrm{mT}$ , and  $a(^{31}\mathrm{P})=1.16~\mathrm{mT}$ . The experimental e.s.r. spectrum shown in the Figure was reproduced almost exactly by computer simulation using the quoted values for  $a(^{14}\mathrm{N})$  and  $a(^{91}\mathrm{Zr})$ .

When the reduction of  $[Zr(\eta-C_5H_5)_2(Cl)R]$  was performed under  $^{15}N_2$ , the e.s.r. spectrum showed a central 1:2:1 triplet, consistent with coupling  $[a(^{15}N)=0.45 \text{ mT}]$  with two equivalent  $^{15}N$  ( $I=\frac{1}{2}$ ) nuclei. The i.r. spectrum of complex (1) shows bands arising from vibrational modes expected from  $C_5H_5^-$  and  $R^-$  ligands, but no absorption in the range  $2400-1500 \text{ cm}^{-1}$  which is characteristic (strong band) of end-on ligated dinitrogen.<sup>5</sup> The Raman spectrum was not recorded because of the photolability of the complex.

The e.s.r. and i.r. data are best accommodated by structure (1a). Alternatives are (i) the dimeric structure (1b), or (ii) a rapid zirconyl oscillation between the two nitrogen atoms

$$\begin{array}{c|c}
R & N \equiv N \\
\hline
Zr & N \equiv N
\end{array}$$

$$\begin{array}{c|c}
R & Zr & N \equiv N
\end{array}$$

$$\begin{array}{c|c}
R & Zr & N \equiv N
\end{array}$$

$$\begin{array}{c|c}
R & (1c)
\end{array}$$

of an end-on bonded  $N_2$ -complex (1c), whence structure (1a) represents the transition state. Structure (1b) is unlikely because it might be expected to require diamagnetism and for steric reasons.

There is currently no precedent for a simple sidewaysbound N<sub>2</sub> complex, although there are X-ray data for  $\label{eq:continuity} [\,\{\mathrm{Ni}(\mathrm{LiPh})_3\}_2\mu - (\eta^2 - \mathrm{N_2})(\mathrm{OEt_2})_2]^{7a} \quad \text{ and } \quad [\,\{\mathrm{Ph}[\mathrm{Na}(\mathrm{OEt_2})_2]_2 - (\eta^2 - \mathrm{Ne})(\mathrm{OEt_2})_2]_2 - (\eta^2 - \mathrm{Ne})(\mathrm{OEt_2})_2]_2 - (\eta^2 - \mathrm{Ne})(\mathrm{OEt_2})_2]_2 - (\eta^2 - \mathrm{Ne})(\mathrm{OEt_2})_2 - (\eta^2$  $(NiPh_2)_2N_2NaLi_6(OEt)_4(OEt_2)$ <sub>2</sub>]<sup>7b</sup> in each of which a  $\eta^2-N_2$ 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<sup>-3</sup> mmHg, it became increasingly purple. Crystallisation from PhMe yielded the purple diamagnetic [ $\{Zr(\eta-C_5H_5)_2R\}_2(N_2)$ ], 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.<sup>8</sup> Zirconium(II)-dinitrogen complexes have been reported.9 We find no N2 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<sub>3</sub>Si)<sub>2</sub>CH<sup>-</sup> may stabilise for steric reasons unusual or unusually-bonded co-ligands.

$$\begin{array}{c|c}
R \\
\downarrow \\
Zr - N \equiv N - Zr \\
R
\end{array}$$
(2a)

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