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ORGANOZIRCONIUM DINITROGEN COMPLEXES $[Zr(\eta\text{-}C_5H_4R')_2(\eta^2\text{-}N_2)R]$ AND $[\{Zr(\eta\text{-}C_5H_5)_2R\}_2N_2][R = (Me_3Si)_2CH, R' = H$ OR $Me]$ *

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Summary

Sodium-amalgam reduction of the complexes $[Zr(\eta\text{-}C_5H_4R')_2(Cl)R]$ $[R = (Me_3Si)_2CH$, $R' = H$ or Me) (I) under dinitrogen smoothly produces the brown Zr^{III} dinitrogen complexes $[Zr(\eta\text{-}C_5H_4R')_2(N_2)R]$ (II), characterised by analysis and spectroscopy, whereas with a more bulky substituent in the cyclopentadienyl ligand (R' = i-Pr, t-Bu, or Me_3Si) or a less bulky alkyl group at Zr (e.g., $R = Me_3SiCH_2$) no incorporation of N_2 was observed under ambient conditions although a Zr^{III} signal was observed in the ESR spectrum [g_{av}, ca. 1.992; $a(^{91}Zr)$, ca. 1.7 mT]. Evidence for "side-on" (η^2-) bound dinitrogen in II is based on (i) the appearance in their ESR spectra of a 1/2/3/2/1 quintet due to coupling to two equivalent ^{14}N atoms, or a 1/2/1 triplet for the $^{15}N_2$ isotopomers, which persists down to ca. −80°C, (ii) the frozen (−140°C) solid *Q*-band ESR spectra, which rule out a dimeric structure, and (iii) the absence of a clear IR band in the $\nu(N_2)$ region. The unusually low ^{91}Zr (ca. 0.4 mT) and high ^{14}N hyperfine coupling, together with a high g_{av} (ca. 2.004) are suggestive of significant unpaired electron delocalisation onto the N_2 ligand and relatively low spin density at the metal, as is also indicated by their facile protonation to yield N_2H_4 in modest yield upon treatment with concentrated HCl or HBr. The complexes II readily lose dinitrogen to give the purple diamagnetic complexes $[\{Zr(\eta\text{-}C_5H_4R')_2R\}_2(N_2)]$ (III). These results provide a further demonstration that the bulky alkyl ligand $(Me_3Si)_2CH^-$ may stabilise, for steric reasons, unusual metal complexes.

Introduction

There is at present considerable interest in the nature of metal—dinitrogen interactions and their implications to the mode of action of iron and molyb-

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* Dedicated to Professor J. Chatt on the occasion of his sixty-fifth birthday.
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denum in, for example, nitrogenase [1]. This activity has produced a wealth of transition-metal dinitrogen complexes, containing both "end-on" (η^1) and "end-on bridging" (μ-η^1) dinitrogen ligands, the physical properties of which have been studied in detail. Recently a gradual shift in emphasis has taken place away from Group VIII metal dinitrogen complexes to those of the earlier transition-metals, particularly those of Group VI metals, where the ligating dinitrogen is seemingly more reactive [1].

We now report the synthesis, characterisation, spectroscopic properties, and some preliminary chemical reactions of Zr^{III} dinitrogen complexes of the type $[Zr(\eta\text{-}C_5H_4R')_2(N_2)R]$ ($R = (Me_3Si)_2CH$, $R' = H$ or Me) containing the ligating dinitrogen in the rare "side-on" (η^2-) bonding mode, stabilised, we believe, by the bulky alkyl group $(Me_3Si)_2CH^-$ (see ref. 2 for earlier results on metal complexes derived from this ligand). Additional features of interest relate to (a) the role of substituents R and R' upon the sodium-amalgam reduction in tetrahydrofuran (THF) at 20°C under 1 atm of N_2 of the complexes $[Zr(\eta\text{-}C_5H_4R')_2(Cl)R'']$ ($R'' = (Me_3Si)_2CH$ or Me_3SiCH_2; $R' = H$, Me, i-Pr, t-Bu, or Me_3Si) [3], and (b) the new diamagnetic complex $[\{Zr(\eta\text{-}C_5H_5)_2R\}_2N_2]$ ($R = (Me_3Si)_2CH$). Some preliminary data have been published [4].

Results

The principal starting Zr^{IV} substrates for the present studies have the formula $[Zr(\eta\text{-}C_5H_4R')_2(Cl)R]$ ($R = (Me_3Si)_2CH$). The parent compound ($R' = H$) has been described [5], while the monosubstituted cyclopentadienyl derivatives (R' = Me, i-Pr, t-Bu, or Me_3Si) will be reported elsewhere, together with the crystal and molecular structures of the two most hindered compounds (R' = t-Bu or Me_3Si) [3]. Other potential substrates examined were $[Ti(\eta\text{-}C_5H_5)_2R]$ [5] and $[Zr(\eta\text{-}C_5H_5)_2(Cl)R'']$ ($R'' = Me_3SiCH_2$ or Me_3CCH_2) [6].

A smooth reaction occurs at ambient temperature between the monoalkylzirconium(IV) metallocenes $[Zr(\eta\text{-}C_5H_4R')_2(Cl)R]$ (I: $R = (Me_3Si)CH$, $R' = H$ or Me) and sodium amalgam in THF under dinitrogen to give (after 1—2 h) a dark-brown solution according to eq. 1. These solutions are exceedingly

$$\underset{\text{(I)}}{[Zr(\eta\text{-}C_5H_4R')_2(Cl)R]} \xrightarrow[N_2/20^\circ C]{\text{Na-Hg/THF}} \text{dark-brown solution} \qquad (1)$$

sensitive to both dioxygen and moisture, rapidly turning colourless (via purple and yellow intermediates) on exposure to air.

ESR investigation of the THF solutions (transferred via stainless steel tubes under dinitrogen) gave the intense ESR signals shown in Fig. 1 consisting predominantly of a central 1/2/3/2/1 quintet flanked by low intensity satellites. Computer simulation of the ESR spectra showed that they could only be fitted to the interaction of one Zr^{III} nucleus (^{91}Zr, $I = 5/2$, 11.23%) with two magnetically equivalent nitrogen nuclei (^{14}N, $I = 1$, 99.63%), coordinated, we believe, as "side-on" (η^2) dinitrogen. No hyperfine coupling to the α-CH of the alkyl groups was observed. The ESR parameters that gave the best fit to the observed

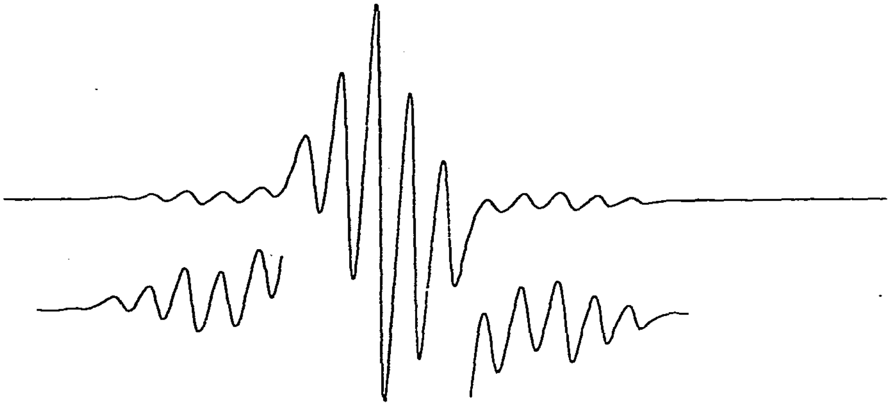


Fig. 1. The ESR solution spectrum of $[Zr(\eta\text{-}C_5H_4R')_2(\eta^2\text{-}N_2)R]$ ($R = (Me_3Si)_2CH$; $R' = H$ (IIa), or Me (IIb)) in THF at 20°C (inset X5) at 9.15 Gc.

spectra are given in Table 1.

When the reduction was performed under $^{15}N_2$, the spectrum showed instead a central 1/2/1 triplet consistent with coupling to two equivalent ^{15}N ($I = 1/2$) nuclei (Table 1), and the observed ratio of $a(^{15}N)/a(^{14}N)$ confirms the assignment (Found 1.3; calcd. 1.4).

Attempts to obtain crystalline material from the THF solution for $R' = H$ by various routes and solvents inevitably gave a diamagnetic purple material. However, slow crystallisation from THF/n-C_6H_{12} at —30°C gave a moderately good yield of reasonably well-formed flaky dark-brown crystals. Although these did diffract X-rays, a single crystal suitable for a complete structural study has not yet been obtained. Microanalytical data shown in Table 2 suggest that the product of the reduction is the complex $[Zr(\eta\text{-}C_5H_5)_2(N_2)R]$ (IIa) formed according to eq. 2.

$$[Zr(\eta\text{-}C_5H_4R')_2(Cl)\,CH(SiMe_3)_2] \xrightarrow[N_2/20^\circ C]{Na\text{-}Hg/THF} [Zr(\eta\text{-}C_5H_4R')_2(N_2)CH(SiMe_3)_2]_2 \quad (2)$$

(Ia, $R' = H$; Ib, $R' = Me$) (IIa, $R' = H$; IIb, $R' = Me$)

The infrared spectra of complexes II (KBr discs) showed the vibrations expected for $(\eta\text{-}C_5H_4R')^-$ and $(Me_3Si)_2CH^-$ ligands, but no absorption in the range

TABLE 1

ESR PARAMETERS FOR THE COMPLEXES $[Zr(\eta\text{-}C_5H_4R')_2(N_2)CH(SiMe_3)_2]$ ($R' = H$ or Me) IN THF AT 20°C

Complex	g-value	a(Zr) [a]	a(N) [a]	Structure
$[Zr(\eta\text{-}C_5H_5)_2(^{14}N_2)CH(SiMe_3)_2]$	2.0037	0.85	0.366	1/2/3/2/1 quintet
$[Zr(\eta\text{-}C_5H_5)_2(^{15}N_2)CH(SiMe_3)_2]$	2.004	[b]	0.450	1/2/1 triplet
$[Zr(\eta\text{-}C_5H_4Me)_2(^{14}N_2)CH(SiMe_3)_2]$	2.0041	0.80	0.350	1/2/3/2/1 quintet

[a] Coupling constants in mT. [b] Spectrum too weak for accurate simulation.

TABLE 2

ANALYTICAL AND OTHER DATA FOR THE ZIRCONIUM DINITROGEN COMPLEXES ISOLATED

Complex	Analysis (Found (calcd.) (%))			Colour	M.p. (°C)
	C	H	N		
$[Zr(\eta\text{-}C_5H_5)_2(N_2)CH(SiMe_3)_2]$ (IIa)	49.8 (49.8)	7.10 (7.11)	6.85 (6.2)	Dark-brown	175—180 (dec.)
$[\{Zr(\eta\text{-}C_5H_5)_2CH(SiMe_3)_2\}_2(N_2)]$ (IIIa)	51.9 (51.8)	7.35 (7.90)	3.55 (3.56)	Purple	

2400—1500 cm^{-1} which is typically diagnostic of "end-on" ligated dinitrogen [7], and is consistent with the view that complexes II contain side-on bonded dinitrogen.

Redissolving pure crystalline complex IIa in THF gave an identical ESR spectrum to that of the in situ reduction product. Cooling the solution in the cavity of an ESR spectrometer produced no dramatic change in the spectrum (apart from a slight loss in signal intensity and some line broadening) until ca. —80°C when the solution began to freeze and resolution was lost. Examination of the frozen solution (—140°C) at 9.5 Gc gave a broad spectrum with a slight shoulder (Fig. 2), whilst at 35.5 Gc two *g* values were apparent with signs of a third (Fig. 3).

A series of small scale experiments revealed the sensitivity of this reduction, to give a Zr^{III} "side-on" bonded dinitrogen complex, to the nature of the metal and its inner coordination sphere. Thus, reduction (i) according to eq. 1 of $[Zr(\eta\text{-}C_5H_5)_2(Cl)R'']$ ($R'' = CH_2SiMe_3$ or CH_2CMe_3) or $[Zr(\eta\text{-}C_5H_4R')_2(Cl)R]$ (R' = Et, i-Pr, t-Bu, or $SiMe_3$); or (ii) $[Zr(\eta\text{-}C_5H_5)_2(Cl)R]$ (Ia) by sodium naphthalide, or the electron-rich olefin $(EtNCH_2CH_2NC=)_2$, in THF under dinitrogen gave for both (i) and (ii) strong ESR spectra typical of Zr^{III} (*g* ca. 1.992), but showing no coordinated dinitrogen, whilst reduction of complex Ia in either diethyl ether (no ESR spectrum) or dioxane (complex ESR spectrum) gave un-

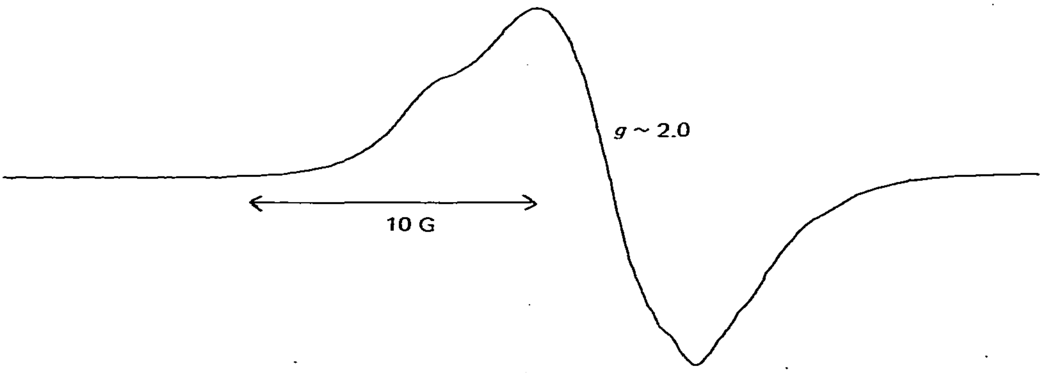


Fig. 2. The ESR frozen (—140°C) solution spectrum of $[Zr(\eta\text{-}C_5H_5)_2(\eta^2\text{-}N_2)R]$ (R = $(Me_3Si)_2CH$ (IIa)) at 9.5 Gc.

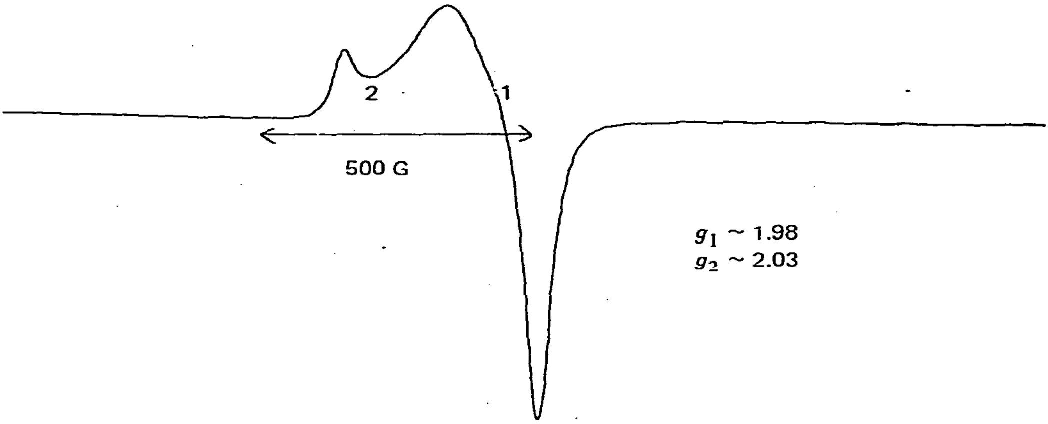


Fig. 3. The ESR frozen (—140°C) solution spectrum of $[Zr(\eta\text{-}C_5H_5)_2(\eta^2\text{-}N_2)R]$ (R = $(Me_3Si)_2CH$ (IIa)), at 34.4 Gc.

identified products. Uptake of dinitrogen was not found for $[Ti(\eta\text{-}C_5H_5)_2\{CH(SiMe_3)_3\}]$.

Addition of PEt_3 to a THF solution of complex IIa did not displace the bound dinitrogen, as judged by ESR spectroscopy. Recrystallisation of pure IIa from toluene (decomposition occurs in $CHCl_3$ or CH_2Cl_2) produced a purple crystalline diamagnetic complex formulated as $[\{Zr(\eta\text{-}C_5H_5)_2R\}_2(N_2)]$ (IIIa) on the basis of analytical data (Table 2), the ^1H NMR spectrum, and the absence of bands assignable to $\nu(N{\equiv}N)$ in its IR spectrum. Accordingly, we propose the structure shown in Fig. 4, which is similar to that of the known aryldicyclopentadienyltitanium(III) complexes which likewise show no clear $\nu(N_2)$ absorption [8].

Complex IIIa was also formed when solid complex IIa was stored under vacuum (ca. 20°C/10^{-3} mmHg), as evident from the colour changes, the original dark-brown crystals becoming increasingly purple.

Reaction of complex IIa with aqueous hydrochloric or hydrobromic acid produced only a low yield (ca. 25%) of hydrazine, together with traces of ammonia, and dinitrogen. ^1H NMR examination of the metal product in the HBr experiment indicated that $[Zr(\eta\text{-}C_5H_5)_2Br_2]$ had formed [9]. At present the yield of hydrazine is no more than a qualitative indication; the experimental procedure (vacuum line technique with an initial sequence of freeze-thaw cycles prior to

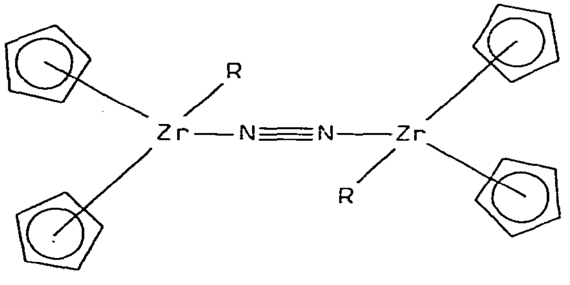


Fig. 4. Proposed structure for IIIa (R = $(Me_3Si)_2CH$).

TABLE 3

OTHER DINITROGEN COMPLEXES OF TITANIUM AND ZIRCONIUM (based on a table by J. Chatt, J.R. Dilworth and R.L. Richards [1])

Complex	Colour	$\nu(N\equiv N)$ [a] (cm^{-1})	Preparation	Comments	Ref.
$[\{Ti(\eta\text{-}C_5H_5)_2Pr\text{-}i\}_2(N_2)]$	Dark-blue		$[\{Ti(\eta\text{-}C_5H_2)_2Cl\}_2]$ + 2 i-PrMgCl + N_2 in OEt_2 at −80°C	No elemental aanlyses reported. N_2 measured after reaction with HCl/MeOH	32
$[Ti(\eta\text{-}C_5H_5)_2(N_2)MgCl]$	Dark-blue	1255(1215)	$[\{Ti(\eta\text{-}C_5H_5)_2Pr\text{-}i\}_2N_2]$ + i-PrMgCl in OEt_2	Paramagnetic, μ_{eff} 1.1 BM/Ti; mode of attachment of Mg unknown	31
$[\{Ti(\eta\text{-}C_5H_5)_2\}_2(N_2)]$	Dark-blue	1280(1240)	$[\{Ti(\eta\text{-}C_5H_5)_2Cl\}_2]$ + 2 MeMgI + N_2 in OEt_2 at −70°C	Paramagnetic, μ_{eff} (300 K) 1.45 BM; stable at 20°C	30
$[\{Ti(\eta\text{-}C_5H_5)_2R\}_2(N_2)]$ (R = C_6H_5, o-, m-, p-MeC_6H_4, 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, C_6F_5, $C_6H_5CH_2$)	Dark-blue		$[Ti(\eta\text{-}C_5H_5)_2R]$ + N_2 in toluene at −20°C in 47—60% yield.	Complexes indefinitely stable in solid state under N_2 at −20°C	28, 29
				Mechanism of reduction	25
$[\{Ti(\eta\text{-}C_5H_5)_2(C_6H_4Me\text{-}p)\}N_2]$				X-ray	14
$[\{Ti(\eta\text{-}C_5H_5)_2\}_2(N_2)]$	Dark-blue		"$[Ti(\eta\text{-}C_5H_5)_2]$" + N_2 in toluene at −80°C	No elemental analyses. N_2 measured after decomposition at −20°C	27
$[\{Ti_2(\eta\text{-}C_5H_5)_3(C_5H_4)\}_2(N_2)]$	Dark-blue		$[(\eta\text{-}C_5H_5)_2$-$Ti\text{-}\mu\text{-}(\eta^1:\eta^5\text{-}C_5H_4)Ti(\eta\text{-}C_5H_5)]$ in ether at −35°C + N_2	Decomposition at 20°C in toluene; over 3 *d* with loss of N_2	26
$[\{Ti(\eta\text{-}C_5Me_5)_2\}_2(N_2)]$	Blue-black needles		$[\{Ti(\eta\text{-}C_5Me_5)_2\}_2]$ + N_2 in pentane at 20°C	Paramagnetic, μ 2.18 BM/Ti. X-ray structure	14, 15
$[\{Ti(\eta\text{-}C_5Me_5)_2(N_2)\}_2(N_2)]$	Blue-purple	2023h, 2056h (−65°C)	$[\{Ti(\eta\text{-}C_5Me_5)_2\}_2]$ + N_2 in toluene at −80°C	Complex unstable above −80°C in toluene	14
$[\{Zr(\eta\text{-}C_5Me_5)_2\}_2(N_2)_3]$	Red-purple	2041, 2006, 1556 (1972, 1937, 1515)	$[Zr(\eta\text{-}C_5Me_5)_2Cl_2]$ + Na/Hg + N_2 in toluene/in HCl 20°C/48 h, 30—40% yield	X-ray crystal structure. Reactions. Variable temperature ^1H and ^{15}N NMR	16—18 24
$[\{Zr(\eta\text{-}C_5Me_5)_2L\}_2N_2]$ (L = CO or PF_3)	Green	1682m (L = CO) 1655vw (L = PF_3)	$[\{Zr(\eta\text{-}C_5Me_5)_2N_2\}N_2]$ + L	Variable temperature ^1H NMR	24

[a] $^{15}N_2$ values in parentheses; those labelled 'h' in hexane solution.

introduction of acid) makes it inevitable that complex IIa was partly converted to IIIa prior to acidification, as also revealed by colour changes.

Discussion

Sodium amalgam in THF under dinitrogen smoothly reduces the monoalkylzirconium(IV) metallocenes (Ia or Ib) to the dinitrogenzirconium(III) complexes (IIa or IIb) (containing "side-on" bonded dinitrogen) according to Scheme 1.

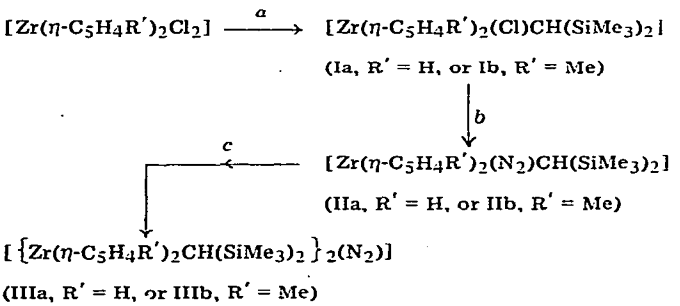
There is currently no clear precedent for a mononuclear sideways-bound dinitrogenmetal complex. X-Ray data for $[\{Ni(LiPh)_3\}_2\text{-}\mu\text{-}(\eta^2\text{-}N_2)(OEt_2)_2]$ [10] and $[\{Ph[Na(OEt)_2]_2(NiPh_2)_2N_2NaLi_6(OEt)_4(OEt_2)\}_2]$ [11] show that in each compound there is a η^2-N_2 bridge between the two nickel atoms, and, interestingly, $\nu(N{\equiv}N)$ was not located. The proposal has been made that in the complex *trans*-$[Rh(Cl)(N_2)(P(Pr\text{-}i)_3)_2]$ the dinitrogen ligand is η^2-bonded [12]. In this molecule, a medium intensity IR band observed at 2100 cm^{-1} was attributed to $\nu(N_2)$, but nevertheless the authors sought support for their structural proposal from X-ray data; this has now been reassessed and a terminal η^1-N_2 arrangement is established [13].

Table 3 lists other well-characterised dinitrogen complexes of zirconium and, for comparison, of titanium. The Table is based on a summary given by Chatt, Dilworth and Richards [1], with up-dating.

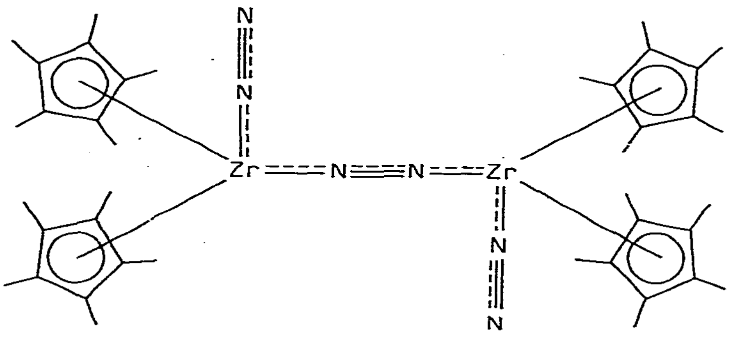
The complex $[Ti(\eta\text{-}C_5Me_5)_2(N_2)]$ was originally proposed to have both "end-on" and "side-on" dinitrogen ligands in equilibrium on the basis of ^{15}N NMR [14]. However, subsequent experiments have indicated that it is better formulated as $[\{Ti(\eta\text{-}C_5Me_5)_2(N_2)\}_2(N_2)]$ [15] similar to its better characterised zirconium analogue formed by sodium amalgam reduction of $[Zr(\eta\text{-}C_5Me_5)_2Cl_2]$ under dinitrogen [16]. The crystal and molecular structure of this complex has been determined [17]: there are two terminal and one bridging dinitrogen ligands present in the molecule (IV). Solution IR bands at 1556 cm^{-1} and 2006/2041 cm^{-1} were assigned to the bridging and terminal dinitrogen ligands, respectively [18].

SCHEME 1

PREPARATION OF ALKYL(DICYCLOPENTADIENYL)ZIRCONIUM DINITROGEN COMPLEXES



[a] $LiCH(SiMe_3)_2$, OEt_2, 20°C. [b] Na-Hg, THF, N_2, 20°C. [c] PhMe or vacuum.



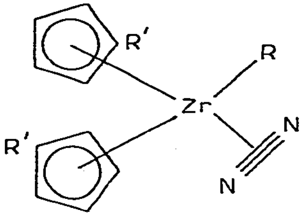
(IV)

Compounds II are of interest not merely as dinitrogen complexes but also as examples of well-characterised Zr^{III} species. Until 1978 the only other characterised Zr^{III} species was $[Zr(\eta\text{-}C_5H_5)_2(PPh_2)_2]^-$ [19]. However, we have recently reported [20] the synthesis and ESR parameters of a number of Zr^{III} complexes of the type $[Zr(\eta\text{-}C_5H_4R')_2R''_2]^-$ (R′ = H, Me, or i-Pr; R″ = Me, $PhCH_2$, Me_2CCH_2, Me_3SiCH_2, or Ph_2CH), which typically have g_{av} values in the range 1.984—1.993 and ^{91}Zr isotropic coupling constants of 1.75—2.35 mT. We attribute the high g_{av} value of complexes IIa and IIb, together with the low ^{91}Zr coupling constants, to extensive spin delocalisation out on to the dinitrogen ligand. For a d^1 metal complex a g_{av} value significantly less than for the free electron (2.0032) is expected. For complexes II, on the contrary, a somewhat higher value is found (ca. 2.004). This indicates that these complexes are to some extent nitrogen- rather than zirconium-centred free radicals, which is entirely consistent with the low $a(^{91}Zr)$ (ca. 0.8 mT) and (presumably) high $a(^{14}N)$. Further support for the view that the dinitrogen ligand is relatively electron-rich comes from its facile protonation (see below).

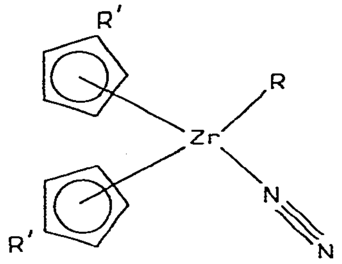
We now turn to the question of the mode of attachment of the dinitrogen ligand to the metal. There are four pertinent items of data which must be accommodated: (i) the magnetic equivalence of the two N atoms, even down to −80°C, (ii) the absence of an electronic triplet structure in the frozen solution ESR spectrum, (iii) the failure to observe an IR band clearly attributable to $\nu(N_2)$, and (iv) the influence of changes in the structure of the substrate $[Zr(\eta\text{-}C_5H_4R')_2(Cl)R]$ (i.e., variations in R and R′) on the facility for N_2 uptake upon reduction. Structure V is consistent with each of (i)—(iv). Alternatives which should be considered are (a) the η^1-bonded complex VI, (b) a modification of VI whereby there is a rapid fluxional process, as shown in eq. 3, with structure V then representing a transition state, and (c) the dimeric structure VII.

$$[Zr(\eta\text{-}C_5H_4R')_2(R)(N_A{\equiv}N_B)] \rightleftharpoons [Zr(\eta\text{-}C_5H_4R')_2(R)(N_B{\equiv}N_A)] \qquad (3)$$

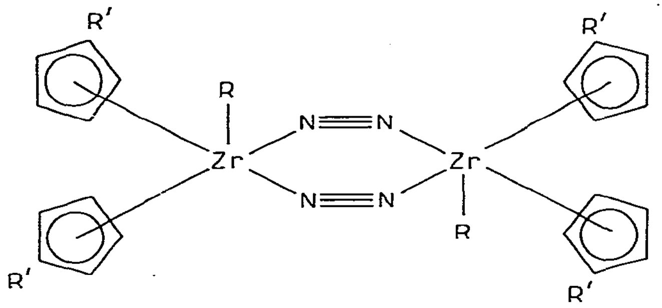
Against (a) or (b) is item (iii), while in order to reconcile item (i) with formula VI it would be necessary to make the unlikely assumption that the coupling of the α- and β-nitrogen atoms would be essentially equivalent. In order for (b) to become tenable the improbable supposition would have to be made that $\Delta G^{\ddagger}$ for site exchange at −80°C is < ca. 5 kJ mol^{-1}. Alternative (c) seems implausible



(V)



(VI)



(VII)

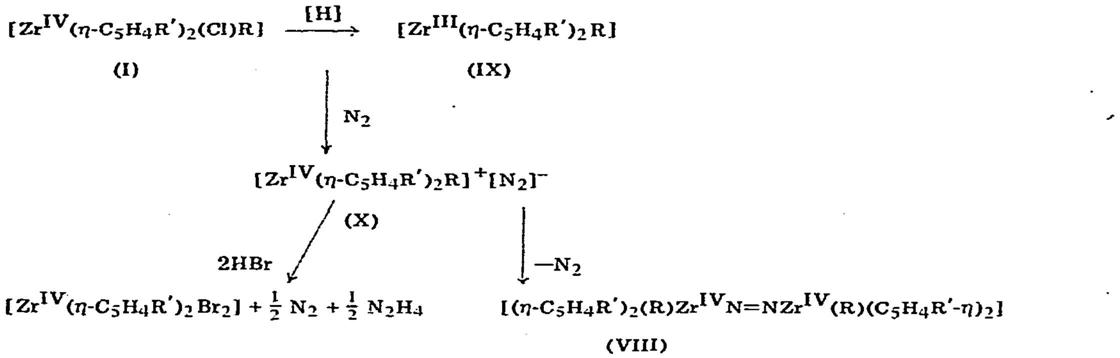
both for steric grounds and inconsistency with item (ii); thus, by analogy with the d^1 vanadyl(IV) tartrates [21] a triplet signal would be expected to be observed in the frozen solution ESR spectrum. (Attempts to obtain molecular weights by cryoscopy proved unsuccessful; either, in C_6H_6 because of interaction with solvent, or THF because suitable equipment was not available.)

This leaves structure V as the most satisfactory solution. The sensitivity of the formation of compounds $[Zr(\eta\text{-}C_5H_4R')_2(N_2)R]$ to steric effects in the precursors I has some analogy with the sensitivity of an active site in a metalloenzyme to substrate binding. X-Ray data on $[Zr(\eta\text{-}C_5H_4R')_2(Cl)R]$ (I, R = $(Me_3Si)_2CH$, R' = t-Bu or Me_3Si), show that a large substituent in the cyclopentadienyl ring causes significant compression at the zirconium centre [3], and therefore may prevent dinitrogen binding.

The proposal that the dinitrogen ligand in complexes II is η^2-bonded is consistent with MO calculations on binding of a diatomic ligand in an early transition-metal complex [22].

Compounds II are easily converted into the diamagnetic complexes III containing, we believe, a bridging "end-on" dinitrogen (see IIIa), similar to the known aryldicyclopentadienyltitanium(III) complexes (see Table 3). The diamagnetism of compounds III is attributed to either (i) the back-bonding from each Zr atom into the same π^*-orbital of the bridging dinitrogen ligand, as proposed for the aryldicyclopentadienyltitanium(III) complexes [23], or (ii) a Zr^{IV} formulation (VIII), featuring the diazenido ligand (see Scheme 2). There is ESR

SCHEME 2.
STRUCTURAL PROPOSALS RELATING TO METAL OXIDATION STATE CHANGES FOR SOME REACTIONS.



evidence for the proposed Zr^{III} intermediate IX if R′ is a bulky group such as i-Pr, t-Bu, or Me_3Si; this aspect is still under investigation.

In terms of structure VIII, the zirconium atoms have formal oxidation state +4. This proposal appears to us to have merit not only because it explains the diamagnetism of compounds III, but also because it offers a plausible basis to account for the metal oxidation changes which are involved in the sequence of reactions which forms the basis of the present study, as indicated in Scheme 2. We propose that initially the Zr^{IV} substrate I undergoes chlorine atom abstraction to give the highly-active neutral alkylzirconium(III) compound (IX), which then reduced N_2 to coordinated N_2^- in the cationic Zr^{IV} complexes (X), which may lose N_2 to yield the Zr^{IV} complexes (VIII) or be protonated by treatment with HBr to give the zirconium(IV) bromide, $[Zr(\eta\text{-}C_5H_4R')_2Br_2]$. A corrollary of this analysis reformulates the complexes II as resonance hybrids in which X are a contributing, and perhaps dominant, canonical form, although the ion pair has, of course, the geometrical form of V.

Most attempts to activate relatively inert small molecules, such as N_2 or CO, via their transition-metal complexes have relied on electron removal from the ligand, e.g., via coordinated N_2H^+. Our study offers the alternative approach and has some analogy with Sellmann's efforts to treat dinitrogen complexes with nucleophiles [24]. Reactions with other small molecules are being investigated.

Our observation that compound IIa gives hydrazine on protonation is somewhat surprising in the light of the prior art, irrespective of whether the oxidation state of zirconium in IIa is designated to be +3 or +4. Many of the previously reported dinitrogen complexes of titanium and zirconium have been protonated to give hydrazine and/or ammonia. The complexity of the titanium systems has made the development of a unifying mechanism difficult; increased yields of ammonia and/or hydrazine have been achieved by pretreatment of the dinitrogen complexes with sodium or potassium naphthalide prior to protonation [25]. However, greater success has been achieved in the zirconium systems for which compounds are somewhat more stable [16—18]. Thus treatment of $[\{Zr(\eta\text{-}C_5H_5Me)_2(N_2)\}_2N_2]$ with anhydrous hydrogen chloride in toluene at −80°C gave hydrazine. It is notable that this type of binuclear complex (and the related titanium compound) but not higher oxidation state species such as

$[\{Ti(\eta\text{-}C_5H_5)_2R\}_2(N_2)]$ (R = alkyl or aryl), gave hydrazine. In the former, all four electrons needed to produce hydrazine from one dinitrogen molecule are available in the two zirconium(II) atoms; in the latter only two electrons are available and hydrazine formation was considered to be possible only by disproportionation of a diazene intermediate; such a mechanism seems plausible also for the case of protonation of compound IIa.

In a detailed investigation of the above zirconium(II) system it was found that terminal dinitrogen ligands are essential for hydrazine production [18]. Thus the titanium complex, $[\{Ti(\eta\text{-}C_5H_5Me)_2\}_2(N_2)]$ gave at best only a small yield of hydrazine whilst a quantitative yield of hydrazine was found for $[\{Ti(\eta\text{-}C_5H_5Me)_2(N_2)\}_2(N_2)]$ [15].

Apparently a more complicated situation arises when $C_5H_5^-$ is ligating the metal rather than $C_5Me_5^-$, since now apparently one $C_5H_5^-$ group may be lost during the reaction [26].

Experimental

All experiments were performed under purified dinitrogen, using Schlenk-type glassware. Solvents were purified by conventional methods and freed from dioxygen by repeated degassing and saturation with dinitrogen. Only typical preparations are described.

ESR spectra were recorded on a Varian E3 spectrometer with *g*-values measured relative to polycrystalline DPPH or (for the Q-band spectra) on a Varian E9 instrument.

Preparation of $[Zr(\eta\text{-}C_5H_5)_2(N_2)CH(SiMe_3)_2]$ *(IIa)*

To a stirred solution of $[Zr(\eta\text{-}C_5H_5)_2(Cl)CH(SiMe_3)_2]$ [5], (0.25 g) in THF (25 cm^3) an excess (0.2 mol) of sodium amalgam was added. Over a period of 2 h at ambient temperature the initial pale-yellow solution became dark-brown, after which time the brown solution was transferred by means of stainless steel tubes to a Schlenk tube. Addition of hexane (25 cm^3) and cooling to —30° C gave brown flaky crystals of the product.

Preparation of $[\{Zr(\eta\text{-}C_5H_5)_2CH(SiMe_3)_2\}_2(N_2)]$ *(IIIa)*

Recrystallisation of pure complex IIa from toluene at —30°C produced pure purple crystals of the product.

Protonation of $[Zr(\eta\text{-}C_5H_5)_2(N_2)CH(SiMe_3)_2]$ *(IIa)*

The experimental procedure was that of Chatt, Pearman, and Richards [34]. Using vacuum line procedures, a weighed sample (ca. 0.1—0.3 g) of complex IIa was cooled to —196° C and the flask was then evacuated to 10^{-3} mmHg. A sequence of five cycles of freeze-thawing was carried out. Dry and degassed THF was condensed into the flask at —196° C followed by a ca. 10-fold excess of gaseous HBr. The mixture was allowed to warm to room temperature and evolution of gas was noted, the volume of the non-condensible N_2 being monitored by use of a Töpler pump; the colour of the solution was discharged. Potassium hydroxide was added and the mixture distilled into 0.1 *M* sulphuric acid. Ammonia and hydrazine were estimated spectrophotometrically [34].

A number of runs, some using HBr and others HCl, were carried out. The results were somewhat erratic, dinitrogen evolution corresponded to ca. 30—40% and N_2H_4 ca. 25% based on Scheme 2.

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