# Nitrogen–Carbon and Nitrogen–Hydrogen Bond Formation by Insertion of a Diazoalkane into Metal–Carbon and Metal–Hydrogen Bonds

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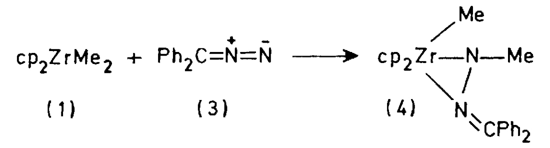
Diphenyldiazomethane reacts with [cp$_2$ZrMe$_2$] and [cp$_2$Zr(H)(Cl)] (cp = $\eta^5$-C$_5$H$_5$) inserting into zirconium–carbon and zirconium–hydrogen bonds; the resulting hydrazonido(1 – )-type ligands are $\eta^2$-*N,N'*-bonded to zirconium in [cp$_2$Zr(Me)(Ph$_2$C=N–NMe)] and in [cp$_2$Zr(Cl)(Ph$_2$C=N–NH)], respectively.

Diazoalkanes, which are highly versatile reagents in organometallic chemistry[1] as sources of carbenes and N$_2$, simulate the dinitrogen molecule in bonding to metals.[2] Moreover, they may undergo metal-promoted elementary transformations leading to species which are closely related to those expected to form from N$_2$.[3]

Early transition metals play a special role in this chemistry because of their ability to bind N$_2$[4] and carbene-related species.[5] Bis(cyclopentadienyl)-titanium(II) and -vanadium(II) derivatives have been found to be able either to co-ordinate diazoalkanes in their intact form or to promote the reaction of a diazoalkane with carbon monoxide.[6] The present report concerns the reaction of diphenyldiazomethane with the zirconium complexes, [cp$_2$ZrMe$_2$], (**1**),[7] and [cp$_2$Zr(H)(Cl)], (**2**)[8] (cp = $\eta^5$-C$_5$H$_5$), which are able to insert small molecules into the zirconium–carbon and into the zirconium–hydrogen bonds, respectively.



(1)

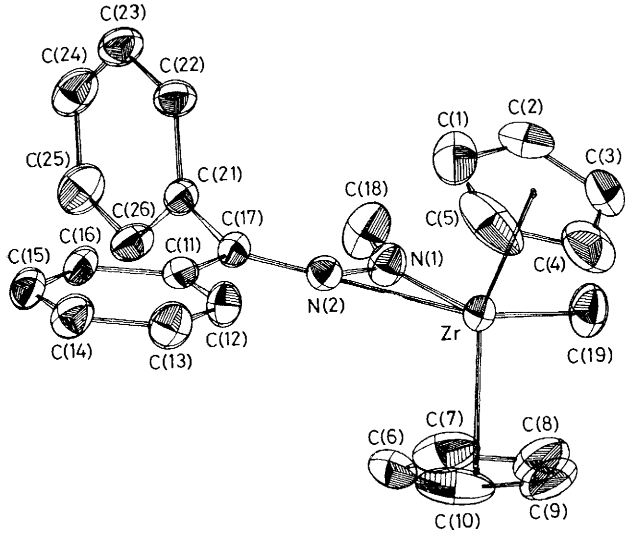
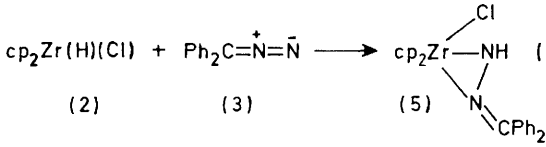


**Figure 1.** An ORTEP diagram of complex (**4**), [cp$_2$Zr(Me)(MeN–N=CPh$_2$)]. Bond distances: Zr–N(1), 2.103(3); Zr–N(2), 2.283(3); Zr–C(19), 2.357(6); C(18)–N(1), 1.446(6); N(1)–N(2), 1.338(4); C(17)–N(2), 1.307(4) Å. Bond angles: cp1–Zr–cp2, 128.8(3); C(19)–Zr–N(2), 115.4(2)°.

A toluene solution of (**1**) reacted at room temperature with neat diphenyldiazomethane, (**3**), producing a solution from which white crystals of (**4**) were obtained in good yield.‡ Reaction (1) led to the formation of an $\eta^2$-*N,N'*-methylhydrazonido(1 – ) ligand, bonded to zirconium, by the migration of a methyl group from the metal to the terminal nitrogen atom of the diazo-molecule.

The structure proposed for (**4**) is supported by an *X*-ray analysis.§ Figure 1 shows an ORTEP diagram of the complex (**4**) with the most relevant bond distances and angles. The hydrazonido(1 – ) ligand is $\eta^2$-bonded to zirconium with Zr–N(1) significantly shorter than Zr–N(2). The N(1)–N(2) bond distance closely approximates to that of a single bond, while C(17)–N(2) has a high double bond character. C(19) is 0.189(5) Å out of the plane defined by Zr, N(1), and N(2). In spite of a different genesis, there is a close analogy between the $\eta^2$-hydrazonido(1 – )-ligand present in (**4**) and some $\eta^2$-hydrazido-ligands which are plausible intermediates in metal-promoted nitrogen transformations.[3,9] In this context, the bonding modes of nitrogen hydrides bound to a transition metal are of considerable importance in understanding nitrogen-fixation intermediates.

A tetrahydrofuran suspension of (**2**) reacted with diphenyldiazomethane giving a light yellow solution from which crystals of complex (**5**) were recovered in a good yield [reaction (2)]. Analytical and spectroscopic determinations, including a preliminary *X*-ray analysis confirmed the structure proposed for (**5**).¶



(2)

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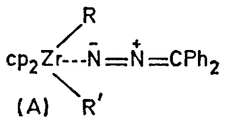
† Visiting from the Laboratoire de Chimie de Coordination du CNRS, Toulouse, France.

‡ Satisfactory elemental analytical data were obtained. $^1$H n.m.r. spectrum ($\tau$, CDCl$_3$): 2.70 (10 H, m, Ph), 4.17 (10 H, s, cp), 7.62 (3 H, s, Me), and 10.0 (3 H, s, Me).

§ *Crystal data:* C$_{25}$H$_{26}$N$_2$Zr, $M$ = 445.7, monoclinic, space group $P2_1/c$, $a$ = 10.115(3), $b$ = 8.114(2), $c$ = 26.508(6) Å, $\beta$ = 93.35(6)°, $U$ = 2172(1) Å$^3$, $Z$ = 4, $D_c$ = 1.363 g cm$^{-3}$, $F(000)$ = 920 electrons, Mo-$K_\alpha$ radiation ($\lambda$ = 0.71069 Å), $\mu$(Mo-$K_\alpha$) = 5.08 cm$^{-1}$. The structure was solved by conventional heavy atom methods (Patterson and Fourier) and refined by full-matrix least squares. All calculations were carried out using the SHELX-76 program. For 3036 unique observed structure amplitudes [$I > 2\sigma(I)$] collected at room temperature on a Siemens AED diffractometer in the range $5 < 2\theta < 58°$ the current $R$ is 0.037.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¶ Satisfactory elemental analytical data were obtained. $^1$H n.m.r. spectrum ($\tau$, CDCl$_3$): 3.14 (11 H, m, Ph and NH) and 4.29 (10 H, s, cp); $\nu_{N-H}$(Nujol) 3320 cm$^{-1}$.



(A)

R = R′ = Me; R = H, R′ = Cl.

Both reactions (1) and (2) can be viewed as occurring through a preliminary step (A) in which the diazoalkane molecule coordinates to the electrophilic zirconium(IV) using the more basic terminal nitrogen atom, to which the methyl or hydrido-ligand can then migrate. Migration of a ligand to metal-bonded dinitrogen has never been clearly identified[3,10] in any model complex containing ligated $N_2$ together with $\sigma$-bonded alkyl[11] or hydrido-groups.[3] The alkylation of the diazoalkane molecule occurs, very probably, by an intramolecular process, involving a metal-bonded carbanion rather than through an attack by a free radical-like species, as reported for $N_2$.[3] Moreover, the ($N_2$) unit depicted in (A) simulates a bridging dinitrogen highly polarized by the intervention of a Lewis acid [zirconium(IV)] and of an electron-rich centre (:$CR_2$ moiety), while only terminal metal-bonded $N_2$ can be alkylated.[3] Nevertheless, reactions of diazoalkanes with complexes having inserting ligands may suggest novel methods for forming N–C and N–H bonds from $N_2$ itself, and they give rise to some structural models of species formally derived from $N_2$.

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