Inorg. Chem. **1983**, *22*, 2029–2034

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Hydrazonato Ligands from the Insertion of Diazoalkanes into Zirconium–Carbon and Zirconium–Hydrogen Bonds

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Received July 9, 1982

Diazoalkanes, $R_2C{=}N{=}N$ (R = Ph, CO_2Et), insert into zirconium–carbon and zirconium–hydrogen bonds reacting with $(cp)_2ZrR_2$ (cp = η^5-C_5H_5, R = Me, CH_2Ph) and $[(cp)_2Zr(H)Cl]_n$ to form hydrazonato(1−) ligands η^2-N,N′ bonded to zirconium. The occurrence of this reaction is independent of the nature of the alkyl group bonded to the zirconium atom and of the substituent at the diazoalkane molecule. In spite of the high oxophilicity of zirconium, diethyl diazomalonate reacting with $(cp)_2Zr(CH_2Ph)_2$ gave an η^2-hydrazonato ligand, whose COOEt substituents do not interact with the metal atom. The X-ray analysis was carried out on the three complexes $(cp)_2Zr(X)(\eta^2\text{-}R_2C{=}N^*{-}N{-}Y)$ (X = Me, Y = Me, R = Ph; X = Y = $PhCH_2$, R = COOEt; X = Cl, Y = H, R = Ph). The hydrazonato ligand shows similar structural parameters in the three complexes, namely, Zr–N* bond distances ranging from 2.25 (1) to 2.283(3) Å, Zr–N distances ranging from 2.103 (3) to 2.21 (1) Å, N*–N bond distance having a significant double-bond character ranging from 1.30 (2) to 1.338 (4) Å, and the C=N* bond distance being slightly longer than expected for a double bond, falling in the range 1.308 (4)–1.32 (2) Å. The η^2 bonding mode of the hydrazonato ligand causes a significant lengthening of the Zr–X bond distance (Zr–Me, 2.357 (6); Zr–CH_2Ph, 2.37 (1); Zr–Cl, 2.549 (5) Å). No infrared band was observed for the C=N group above 1600 cm^{-1}, in agreement with the structural parameters cited above showing an electronic delocalization all over the C–N–N unit. Activation of diazoalkanes by metals does form species that are closely related to those expected from metal-assisted transformations of dinitrogen. Crystallographic details for $(cp)_2Zr(Ph_2C{=}N{-}NMe)(Me)$: space group $P2_1/c$ (monoclinic); a = 10.115 (3), b = 8.114 (2), c = 25.508 (6) Å; β = 93.35 (6)°; Z = 4; D_{calcd} = 1.361 g cm^{-3}. The final R factor was 0.037 for 3036 observed reflections. Crystallographic details for $(cp)_2Zr[(EtOOC)_2C{=}N{-}NCH_2Ph](PhCH_2)$: space group $P2_1/c$; a = 17.405 (3), b = 9.718 (1), c = 16.805 (3) Å; β = 100.10 (3)°; Z = 4; D_{calcd} = 1.401 g cm^{-3}. The final R factor was 0.051 for 1318 observed reflections. Crystallographic details for $(cp)_2Zr(Ph_2C{=}N{-}NH)(Cl)$: space group $C2/c$ (monoclinic); a = 27.667 (3), b = 8.766 (1), c = 19.389 (2) Å; β = 123.57 (3)°; Z = 8; D_{calcd} = 1.53 g cm^{-3}. The final R factor was 0.058 for 1023 observed reflections.

Introduction

Functionalization of organic substrates promoted by metal complexes occurs very often by the so-called "insertion reaction".[1] It can be statistically observed that there is some sort of "compatibility" between the nature of the migrating group and that of the insertable molecule. The growing of a carbon chain is viewed to occur via the insertion of C_1 and C_2 units such as >C=C<, CO, and CO_2 into a metal–carbon σ bond.[1] Metal-bonded carbon ligands can migrate to a large number of unsaturated units, including those not containing carbon. Insertion, however, of a dinitrogen molecule into metal–carbon and metal–hydrogen bonds has never been reported,[2a] while the insertion of the N_2 function of a diazoalkane molecule is a rather rare process.[2b–d]

In order to get some insight into this problem, we studied the reaction of diazolkanes with complexes having as a migrating ligand an alkyl or a hydrido group, namely, $(cp)_2ZrR_2$[3] (cp = η^5-C_5H_5) and $[(cp)_2Zr(H)Cl]_n$.[4] Both kinds of complexes have been found to be useful models in the insertion reaction with carbon monoxide. $(cp)_2ZrR_2$ complexes led to the identification of the first η^2-C,O metal-bonded acyl groups;[5] $[(cp)_2Zr(H)Cl]_n$ reacted with carbon monoxide to form an oxymethylene group bridging two zirconium atoms.[6] Their reactivity with organic functional groups resembling CO and CO_2 was recently explored.[7] Moreover, bis(pentamethylcyclopentadienyl)zirconium(II)[8a] and dicyclopentadienylalkylzirconium(III)[8b] complexes have been found to form well-defined dinitrogen complexes.

The present paper describes the insertion of diazoalkanes into zirconium–carbon and zirconium–hydrogen bonds using $(cp)_2ZrR_2$ (R = Me, $PhCH_2$) and $[(cp)_2Zr(H)Cl]_n$ complexes. The reaction proved to be an alkylation and hydrogenation of the >C=N=N unit to form the hydrazonato(1−) ligand, which is found η^2-N,N′ bonded to the metal. Related ligands are expected to form from metal-promoted transformations of dinitrogen. Part of this work was recently communicated.[9]

Experimental Section

All the operations were carried out under an atmosphere of purified argon. Solvents were purified as described in the literature. IR spectra were recorded with a Perkin-Elmer 283 spectrophotometer. ^1H NMR

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0020-1669/83/1322-2029$01.50/0

Table I. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes II, III, and V

	complex II, $C_{25}H_{26}N_2Zr$	complex III, $C_{31}H_{34}N_2O_4Zr$	complex V, $C_{23}H_{21}ClN_2Zr$
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ [C_{2h}^5, No. 14]	$P2_1/c$ [C_{2h}^5, No. 14]	$C2/c$ [C_{2h}^6, No. 15]
a, Å	10.115 (3)	17.405 (3)	27.667 (3)
b, Å	8.114 (2)	9.718 (1)	8.766 (1)
c, Å	26.508 (6)	16.805 (3)	19.389 (2)
α, deg	90	90	90
β, deg	93.35 (6)	100.10 (3)	123.57 (3)
γ, deg	90	90	90
V, Å^3	2171.9	2798.4	3918.1
Z	4	4	8
D_{calcd}, g cm^{-3}	1.36	1.40	1.53
mol wt	445.7	589.8	452.1
cryst dimens, mm	0.43 × 0.18 × 0.66	0.24 × 0.11 × 0.40	0.27 × 0.10 × 0.43
linear abs, cm^{-1}	5.08	4.22	6.98
A^a	1.18–1.75	1.10–1.33	1.13–1.65
diffractometer	Siemens AED		
scan type	$\theta/2\theta$		
scan speed, deg min^{-1}	3–12		
scan width, deg^b	$(\theta - 0.5°)$–$[\theta + (0.5 + \Delta\theta)]$		
radiation	Nb-filtered Mo Kα (λ = 0.7107 Å)		
2θ range, deg	5–58	5–44	5–44
std reflcn^c	241	602	911
unique total data	5770	3576	2222
unique obsd data ($I > 2\sigma$)	3036	1318	1023
no. of variables	253	241	202

^{a} A minimum and maximum for absorption correction factor. ^{b} $\Delta\theta = [(\lambda_{\alpha_2} - \lambda_{\alpha_1})/\lambda] \tan\theta$. ^{c} These were measured after every 50 refections; no significant changes in intensity were observed.

spectra were taken with a E-360 (60 MHz) Varian apparatus. The syntheses of $[(cp)_2Zr(H)Cl]_n$,[10] $(cp)_2ZrMe_2$,[3] $(cp)_2Zr(CH_2Ph)_2$,[11] $Ph_2C{=}N{=}N$,[12] and $(COOEt)_2C{=}N{=}N$[13] have been performed as reported in the literature. The reported synthesis for $[(cp)_2Zr(H)Cl]_n$ gives the zirconium complex containing NaCl.[10]

Reaction of $[(cp)_2Zr(H)Cl]_n$ with Diphenyldiazomethane. Freshly prepared diphenyldiazomethane (0.70 mL, 3.60 mmol) was added to a THF stirred suspension (50 mL) of $[(cp)_2Zr(H)Cl]_n$ (1.10 g, 3.60 mmol) on the basis of the hydrogen content.[10] The color of the suspension changed from violet (the color of diphenyldiazomethane) to light yellow, and the solid dissolved in 10 min, giving a solution from which a solid crystallized. The zirconium complex reacted in a 1:1 molar ratio with Ph_2CN_2, as checked by the IR spectrum. The suspension was heated to dissolve the complex and filtered when hot, in order to remove NaCl. The resulting solution gave on standing overnight light yellow crystals (0.65 g, 40.0%) of $(cp)_2Zr(Cl)(Ph_2C{=}N{-}NH)$. Anal. Calcd for $C_{23}H_{21}N_2ClZr$: C, 61.12; H, 4.65; N, 6.20; Cl, 7.86. Found: C, 61.26; H, 4.68; N, 6.15; Cl, 8.00. ^1H NMR spectrum (τ, $CDCl_3$): 4.28 (10 H, s, cp); 3.13 (11 H, m, Ph and NH). IR (cm^{-1}, Nujol): ν_{N-H} 3310. The N-H assignment is tentative, since it, usually, shows a broad resonance.[2b]

Reaction of $(cp)_2ZrMe_2$ with Diphenyldiazomethane. A toluene solution (50 mL) of $(cp)_2ZrMe_2$ (2.27 g, 9.04 mmol) was reacted with neat diphenyldiazomethane (2.0 g, 10.31 mmol) at room temperature. A slight excess of diazo compound was evident in the IR spectrum of the solution. The solution was concentrated and then treated with *n*-hexane (50 mL). The resulting solution cooled at −20 °C gave on standing overnight white needles of $(cp)_2Zr(Me)(Ph_2C{=}N{-}NMe)$ (2.30 g, 57.2%). Anal. Calcd for $C_{25}H_{26}N_2Zr$: C, 67.41; H, 5.84; N, 6.29. Found: C, 67.86; H, 5.90; N, 6.32. ^1H NMR spectrum (τ, $CDCl_3$): 2.70 (10 H, m, Ph); 4.17 (10 H, s, cp); 7.62 (3 H, s, Me); 10.0 (3 H, s, Me). The IR spectrum (Nujol) does not show any band above 1600 cm^{-1}. A strong C=N band falls at 1515 cm^{-1}.

Reaction of $(cp)_2Zr(CH_2Ph)_2$ with Diphenyldiazomethane. A toluene solution (20 mL) of $(cp)_2Zr(CH_2Ph)_2$ (0.922 g, 2.29 mmol) was reacted with neat diphenyldiazomethane (0.50 mL, 2.55 mmol). The solution on standing for 3 h turned from deep red to light red. The addition of *n*-hexane (30 mL) promoted the crystallization as light yellow needles of $(cp)_2Zr(Ph_2C{=}N{-}NCH_2Ph)(CH_2Ph)$ (1.20 g, 78.8%). Anal. Calcd for $C_{37}H_{34}N_2Zr$: C, 74.37; H, 5.70; N, 4.69. Found: C, 74.58; H, 5.75; N, 4.54. The solid was washed with *n*-hexane and dried in vacuo. ^1H NMR (τ, $CDCl_3$): 7.67 (2 H, s, CH_2); 5.63 (2 H, s, CH_2); 4.20 (10 H, s, cp); two broad multiplets centered at 2.77 and 2.53 (20 H, Ph).

Reaction of $(cp)_2Zr(CH_2Ph)_2$ with Diethyl Diazomalonate. A toluene solution (30 mL) of $(cp)_2Zr(CH_2Ph)_2$ (1.95 g, 4.84 mmol) was treated with neat diethyl diazomalonate (0.75 mL, 4.80 mmol). No significant change in color was observed after 2 days. *n*-Hexane (30 mL) was added, and the solution kept in the dark for 2 weeks gave yellow crystals (0.58 g, 20.3%). Anal. Calcd for $C_{31}H_{34}N_2O_2Zr$: C, 63.15; H, 5.77; N, 4.75. Found: C, 63.37; H, 5.80; N, 4.81. ^1H NMR spectrum (τ, $CDCl_3$): 8.77 (6 H, 2 t, Me); 7.77 (2 H, s, CH_2Ph); 6.07 (2 H, q, CH_2Me); 5.67 (2 H, q, CH_2Me); 5.28 (2 H, s, CH_2Ph); 4.06 (10 H, s, cp); 2.80 (10 H, m, Ph). The IR spectrum (Nujol) shows a strong broad band for the carbonylic functions centered at 1710 cm^{-1}.

X-ray Crystallography. The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. Extensive preliminary investigations employing rotation and Weissenberg photographs showed the crystals of the three complexes to be monoclinic with systematic absences consistent with the space groups $P2_1/c$ for II and III and $C2/c$ (or Cc) for V. Crystal data and details of the parameters associated with data collections are given in Table I. Lattice constants came from a least-squares refinement of the 2θ values for 20 reflections having 2θ > 30° for the three complexes.

Data were collected at room temperature on a single-crystal diffractometer. For intensities and background the profile measurement technique was used.[14] The structure amplitudes were obtained after the usual Lorentz and polarization reduction,[15] and the absolute scale was established by the Wilson method.[16] No correction for absorption was applied.

The function minimized during the least-squares refinement was $\sum w|\Delta F|^2$. The weighting scheme used was $w = k/[\sigma^2(F_o^2)]$; *k* is redetermined after each structure factor calculation and refined by

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Table II. Fractional Atomic Coordinates ($\times 10^4$) for Complex II

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Zr	2701 (1)	1741 (1)	1644 (1)	C18	−699 (5)	1296 (7)	1652 (2)
N1	676 (3)	1170 (4)	1536 (1)	C19	1822 (5)	3656 (6)	2203 (2)
N2	1175 (3)	180 (3)	1191 (1)	C11	1415 (3)	−1813 (4)	532 (1)
C1	3129 (10)	−1112 (7)	1985 (3)	C12	2797 (4)	−1706 (5)	530 (1)
C2	2739 (7)	−227 (8)	2389 (2)	C13	3481 (4)	−2520 (6)	172 (2)
C3	3699 (7)	922 (8)	2503 (2)	C14	2839 (4)	−3482 (5)	−193 (2)
C4	4689 (6)	871 (9)	2189 (2)	C15	1492 (5)	−3588 (5)	−202 (2)
C5	4358 (9)	−489 (11)	1854 (2)	C16	782 (4)	−2787 (5)	158 (1)
C6	3017 (8)	2720 (9)	750 (2)	C21	−773 (4)	−1526 (4)	938 (1)
C7	4238 (7)	2354 (8)	947 (3)	C22	−1023 (4)	−2888 (5)	1233 (1)
C8	4558 (7)	3471 (10)	1327 (3)	C23	−2314 (5)	−3499 (5)	1250 (2)
C9	3579 (11)	4476 (7)	1374 (3)	C24	−3338 (4)	−2750 (6)	982 (2)
C10	2536 (7)	4069 (11)	1010 (4)	C25	−3103 (4)	−1400 (6)	689 (2)
C17	625 (3)	−961 (4)	901 (1)	C26	−1827 (4)	−794 (5)	657 (2)

Table III. Fractional Atomic Coordinates ($\times 10^4$) for Complex III

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Zr	2366 (1)	1053 (1)	616 (1)	C19	1913 (7)	1894 (13)	−707 (8)
O1	3280 (5)	988 (11)	2863 (5)	C27	3626 (8)	2030 (14)	2821 (8)
O2	4192 (5)	2515 (9)	3395 (6)	C28	4355 (8)	1659 (15)	4099 (9)
O3	4484 (6)	4466 (10)	1734 (6)	C29	5085 (8)	2162 (15)	4618 (9)
O4	3812 (5)	5193 (10)	2676 (6)	C30	3999 (9)	4309 (14)	2137 (10)
N1	2782 (6)	3194 (12)	790 (7)	C31	4255 (10)	6478 (15)	2754 (10)
N2	3042 (6)	2583 (11)	1471 (7)	C32	3829 (10)	7498 (15)	3173 (10)
C1	3787 (5)	455 (10)	615 (8)	C11	1527 (5)	968 (8)	−1403 (5)
C2	3518 (5)	−440 (10)	1176 (8)	C12	1986 (5)	233 (8)	−1857 (5)
C3	2954 (5)	−1338 (10)	736 (8)	C13	1635 (5)	−643 (8)	−2473 (5)
C4	2874 (5)	−998 (10)	−96 (8)	C14	825 (5)	−783 (8)	−2635 (5)
C5	3389 (5)	110 (10)	−171 (8)	C15	366 (5)	−48 (8)	−2181 (5)
C6	1549 (11)	−352 (21)	1384 (20)	C16	717 (5)	828 (8)	−1565 (5)
C7	1103 (11)	−158 (21)	600 (20)	C21	2203 (4)	5222 (9)	71 (5)
C8	897 (11)	1255 (21)	514 (20)	C22	2296 (4)	5582 (9)	−710 (5)
C9	1217 (11)	1935 (21)	1246 (20)	C23	1674 (4)	6158 (9)	−1243 (5)
C10	1620 (11)	942 (21)	1783 (20)	C24	959 (4)	6374 (9)	−994 (5)
C17	3502 (7)	3012 (14)	2130 (8)	C25	867 (4)	6014 (9)	−213 (5)
C18	2875 (8)	4680 (15)	670 (9)	C26	1489 (4)	5438 (9)	320 (5)

Table IV. Fractional Atomic Coordinates ($\times 10^4$) for Complex V

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Zr	1680 (1)	3067 (2)	2941 (1)	C17	1146 (6)	4379 (21)	914 (9)
Cl	2022 (2)	344 (6)	3430 (3)	C11	1078 (4)	3490 (14)	214 (5)
N1	1548 (5)	2289 (18)	1812 (8)	C12	1567 (4)	3031 (14)	230 (5)
N2	1359 (5)	3682 (18)	1629 (9)	C13	1504 (4)	2190 (14)	−426 (5)
C1	2700 (7)	3803 (22)	3388 (15)	C14	951 (4)	1809 (14)	−1099 (5)
C2	2370 (7)	5167 (22)	3085 (15)	C15	462 (4)	2268 (14)	−1116 (5)
C3	2195 (7)	5572 (22)	3626 (15)	C16	526 (4)	3109 (14)	−459 (5)
C4	2418 (7)	4458 (22)	4263 (15)	C21	977 (4)	6034 (10)	810 (6)
C5	2730 (7)	3364 (22)	4116 (15)	C22	740 (4)	6730 (10)	40 (6)
C6	716 (5)	1996 (16)	2612 (10)	C23	600 (4)	8279 (10)	−55 (6)
C7	588 (5)	3436 (16)	2213 (10)	C24	698 (4)	9130 (10)	618 (6)
C8	850 (5)	4580 (16)	2834 (10)	C25	935 (4)	8433 (10)	1388 (6)
C9	1141 (5)	3847 (16)	3618 (10)	C26	1075 (4)	6885 (10)	1483 (6)
C10	1058 (5)	2250 (16)	3481 (10)				

fitting $(|F_o| - |F_c|)^2$ to $[\sigma^2(F_o) + |g|(F_o^2)]/k$. The value for g was that giving the smallest variation of the mean values of $w(|F_o| - |F_c|)^2$ as a function of the magnitude of F_o. Anomalous scattering corrections were included in all structure factor calculations. Scattering factors for neutral atoms were taken from ref 17 for Zr, from ref 18 for Cl, O, N, and C, and from ref 19 for H.

Residual R and weighted residual R_{wF} indices were defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. The "goodness of fit" parameter was determined by equation $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO is the number of observed reflections and NV is the number of variables refined.

The hydrogen atoms, either located or calculated, were included in fixed positions prior to final refinement with the isotropic thermal parameter, B, fixed at 6.3 Å^2.

Final atomic coordinates are listed in Tables II–IV and SI–SIII, and thermal parameters are given in Tables SIV–SVI.[20]

Structure Solution and Refinement for Complex II. The 3036 reflections with $I > 2\sigma(I)$ were used in the structure solution and refinement. The structure was solved by the heavy-atom method and refined to final R and R_w value of 3.7% and 4.1%, respectively. In the initial stages the Ph and cp rings were considered as rigid groups.[15] In the final refinement all constraints were removed and all non-hydrogen atoms were allowed to vary anisotropically. Refinement was continued until shifts in all parameters were less than 0.3 times the standard deviation in the respective parameter. The hydrogen

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(18) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321–4.

(19) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–87.

(20) See paragraph at the end of the paper regarding supplementary material.

atoms were located from successive difference-Fourier syntheses. In the final difference map there were no peaks above the general background. The NO:NV ratio was 3036:253 ≃ 12.0:1. The values for *k* and *g* were 0.3472 and 0.004489, respectively, and the goodness of fit was 0.90.

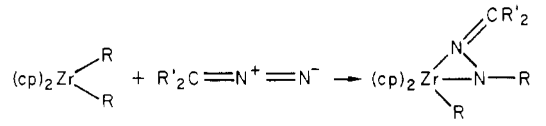
Structure Solution and Refinement for Complex III. The structure was solved by the heavy-atom method, starting from a three-dimensional Patterson map, which gave the approximate coordinates for the zirconium atom. The remaining non-hydrogen atoms were located from a series of difference-Fourier syntheses, each being phased by an increasing number of atoms. Full-matrix least-squares refinement of the scale factor and positional and anisotropic thermal parameters for all non-hydrogen atoms (except for the phenyl carbon atoms, which were refined isotropically) led to final convergence with R_F = 5.1%, R_{wF} = 5.2%, and GOF = 1.23 for 1318 observed reflections. The hydrogen atoms of methyl and ethyl groups were located in a difference-Fourier map. All the others were introduced in calculated positions. The NO:NV ratio was 1318:241 = 5.5:1. In the final cycle no parameter shifted by more than 0.5 times its standard deviation, and the values of *k* and *g* were 0.5130 and 0.003574, respectively. A final difference-Fourier synthesis showed no unexpected features with no peaks above the general background. During all of the refinement the cp and Ph rings were treated as rigid bodies.[15]

Structure Solution and Refinement for Complex V. *E* statistics calculated as a function of sin *θ* marginally favor the centric case, $\langle |E^2 - 1| \rangle$ being equal to 0.90 (~0.97 is the theoretical value accepted for centrosymmetric structures). The space group *C*2/*c* was then assumed and was confirmed by the successful solution and refinement of the crystal structure. The structure was solved by the heavy-atom method, starting from a three-dimensional Patterson map, which gave the approximate coordinates for the zirconium and chlorine atoms. The remaining non-hydrogen atoms were located from the subsequent difference-Fourier synthesis. Full-matrix least-squares refinement of the scale factor and positional and anisotropic thermal parameters for all the non-hydrogen atoms led to final convergence with R_F = 5.8%, R_{wF} = 6.0, and GOF = 1.06 for 1023 observed data. Thirteen hydrogen atoms of the cp and Ph rings were located in a difference-Fourier map; all the others (except for that originally bonded to zirconium, which was not located) were put in calculated positions. The NO:NV ratio was 1023:202 = 5.1:1.

In the final cycle no parameter shifted by more than 0.2 times its standard deviation, and the values for *k* and *g* were 0.4211 and 0.006830, respectively. A final difference-Fourier synthesis showed four peaks of height 0.5–0.8 e Å^{-3} at ~1.2 Å from zirconium, no other peak being greater than 0.3 e Å^{-3}. During all of the refinement the cp and Ph rings were treated as rigid bodies.[15]

Results and Discussion

Dialkylzirconocenes, $(cp)_2ZrR_2$ (cp = η^5-C_5H_5; R = Me, $PhCH_2$) reacted with diazoalkanes at room temperature and in toluene solution, as exemplified in reaction 1. One of the alkyl groups originally bonded to zirconium migrated to the terminal nitrogen of the diazo molecule to produce a hydrazonato(1−) ligand, which resulted in η^2-N,N′ bonding to the zirconium atom in the final complexes I–III. The ^{1}H NMR spectrum showed the nonequivalence of the two R and the two R′ groups in complexes I–III. The IR spectrum did not reveal any $\nu_{C=N}$ band above 1600 cm^{-1}. All these spectroscopic data are in agreement with the structural parameters deduced from an X-ray analysis on complexes II and III. We can add that complexes I–III did not insert a further molecule of diazoalkane as expected from the η^2 bonding mode of the hydrazonato ligand filling all the coordination sites around zirconium, so as to prevent any precoordination of a further diazoalkane molecule.



$$(cp)_2ZrR_2 + R'_2C{=}N^+{=}N^- \longrightarrow (cp)_2Zr(R)[\eta^2\text{-}N(R)N{=}CR'_2] \qquad (1)$$

R = Me, $PhCH_2$
R′ = Ph, COOEt

I: R = $PhCH_2$; R′ = Ph
II: R = Me; R′ = Ph
III: R = $PhCH_2$; R′ = COOEt

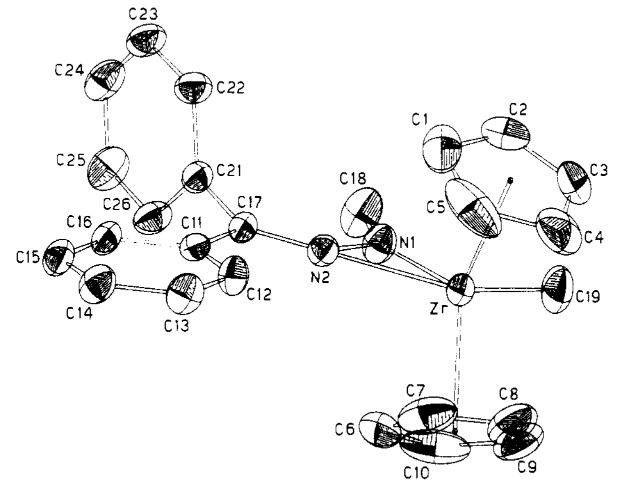


Figure 1. ORTEP drawing for complex II (30% probability ellipsoids).

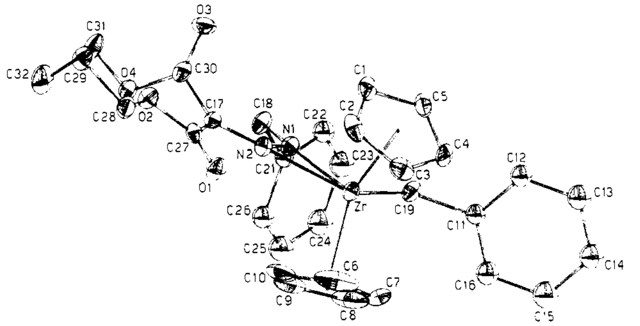
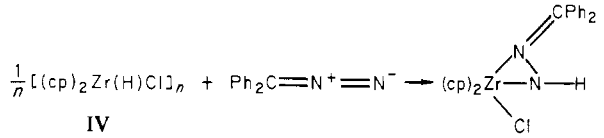


Figure 2. ORTEP drawing for complex III (20% probability ellipsoids).

The easy insertion of diazoalkanes into a Zr–C bond prompted us to extend such a reaction to the Zr–H bond. It is well-known that the hydrido species has a migrating ability, at least in the case of carbon monoxide, which is rather unique and different from the case for carbon ligands.[1e,6,21] The complex chosen for this reaction was $[(cp)_2Zr(H)Cl]_n$ (IV)[4]



$$\frac{1}{n}[(cp)_2Zr(H)Cl]_n + Ph_2C{=}N^+{=}N^- \longrightarrow (cp)_2Zr(Cl)[\eta^2\text{-}N(H)N{=}CPh_2] \qquad (2)$$

IV

V

because of the presence on the metal of only one inserting group. The reaction of IV with diphenyldiazomethane was carried out in THF to produce light yellow crystals of complex V. The IR spectrum does not show any C=N band above 1600 cm^{-1}, which indicates an electronic delocalization over the C–N–N unit; the N–H group displays a sharp and strong band at 3310 cm^{-1}. The η^2-N,N′ bonding mode of the hydrazonato ligand in complexes II, III, and V and the other structural features are disclosed by the results of the corresponding X-ray analyses.

Figures 1–3 show ORTEP views of the molecular structures of complexes II–V, respectively. The most relevant bond distances and angles are listed in Table V. The geometries of the $(cp)_2Zr$ unit in the three complexes are very similar (Table V) with the cp–Zr distances ranging from 2.22 (2) to 2.25 (2) Å and with the angle cp1–Zr–cp2 varying from 126.4 (7) to 129.9 (6)°.[22] The bent $(cp)_2Zr$ unit makes an equatorial

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[21] Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121–7.

[22] Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767–75. Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Floriani, C.; Fachinetti, G.; Chiesi-Villa, A. *Inorg. Chem.* **1980**, *19*, 3812–7. Hunter, W. E.; Atwood, J. L.; Fachinetti, G.; Floriani, C. *J. Organomet. Chem.* **1981**, *204*, 67–74.

Table V. Selected Bond Distances (Å) and Angles (deg) for Complexes II, III, and V[a,b]

Complexes II, III, and V

	II	III	V		II	III	V
Zr-N1	2.103 (3)	2.21 (1)	2.12 (2)	N1-N2	1.338 (4)	1.30 (2)	1.30 (2)
Zr-N2	2.283 (3)	2.25 (1)	2.25 (2)	N1-C18	1.446 (6)	1.47 (2)	
Zr-X	2.357 (6)	2.37 (1)	2.549 (5)	N2-C17	1.307 (4)	1.31 (2)	1.32 (2)
Zr-Cp1	2.236 (7)	2.24 (1)	2.24 (2)	C17-C11	1.471 (5)		1.48 (2)
Zr-Cp2	2.242 (8)	2.22 (2)	2.25 (2)	C17-C21	1.495 (5)		1.50 (2)
Cp1-Zr-Cp2	128.8 (3)	129.9 (6)	126.4 (7)	Zr-N1-N2	79.8 (2)	75.0 (7)	78.1 (9)
X-Zr-Cp2	101.4 (2)	103.4 (6)	102.7 (4)	Zr-N1-C18	153.8 (3)	161.7 (9)	
X-Zr-Cp1	101.4 (2)	103.8 (4)	104.0 (6)	N2-N1-C18	126.4 (3)	122.7 (11)	
N2-Zr-Cp2	105.7 (2)	104.1 (7)	102.9 (6)	Zr-N2-C17	162.6 (3)	156.9 (9)	165.5 (13)
N2-Zr-Cp1	104.7 (2)	101.3 (4)	103.7 (7)	Zr-N2-N1	65.0 (2)	71.2 (7)	67.5 (9)
N2-Zr-X	115.4 (2)	114.9 (4)	118.6 (4)	N1-N2-C17	131.5 (3)	131.6 (12)	127.0 (15)
N1-Zr-Cp2	117.8 (2)	111.7 (6)	115.1 (6)	C11-C17-N2	119.7 (3)		118.4 (14)
N1-Zr-Cp1	110.9 (2)	113.5 (4)	113.2 (8)	C11-C17-C21	116.9 (3)		120.8 (11)
N1-Zr-X	80.3 (2)	81.2 (4)	84.2 (4)	N2-C17-C21	123.4 (3)		120.9 (13)
N1-Zr-N2	35.2 (1)	33.9 (4)	34.4 (6)				

Complex III

C19-C11	1.53 (1)	C27-O1	1.19 (2)	C30-O3	1.18 (2)
C18-C21	1.50 (2)	C27-O2	1.34 (2)	C30-O4	1.33 (2)
C17-C27	1.49 (2)	O2-C28	1.43 (2)	O4-C31	1.46 (2)
C17-C30	1.53 (2)	C28-C29	1.49 (2)	C31-C32	1.49 (2)
Zr-C19-C11	122.8 (8)	N2-C17-C27	115.9 (12)	N2-C17-C30	121.9 (12)
C19-C11-C12	120.1 (8)	C17-C27-O1	126.0 (12)	C17-C30-O3	124.2 (13)
C19-C11-C16	119.9 (8)	C17-C27-O2	108.9 (11)	C17-C30-O4	109.5 (13)
N1-C18-C21	110.2 (10)	O1-C27-O2	125.1 (12)	O3-C30-O4	126.3 (13)
C18-C21-C22	121.0 (8)	C27-O2-C28	113.9 (10)	C30-O4-C31	115.1 (11)
C18-C21-C26	118.9 (9)	O2-C28-C29	108.5 (11)	O4-C31-C32	108.2 (13)
C27-C17-C30	121.2 (12)				

[a] X = C19 for II and III; X = Cl for V. [b] Cp1 and Cp2 are referred to the centroids of the rings C1···C5 and C6···C10, respectively.

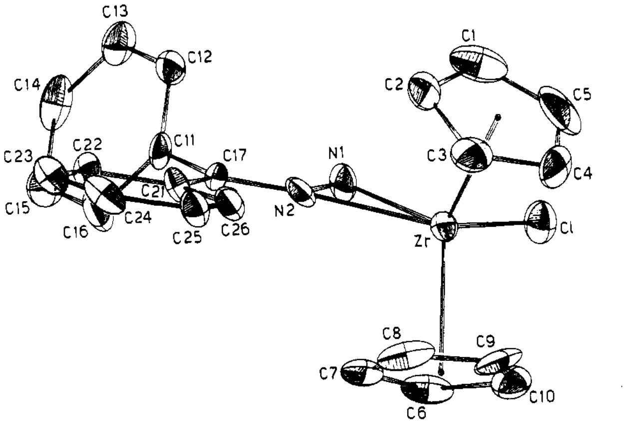

Figure 3. ORTEP drawing for complex V (30% probability ellipsoids).

cavity where the atoms of the skeleton of the hydrazonato ligand and the alkyl carbon or halogen are located. The dihedral angles between the equatorial best plane (Zr, N1, N2, X) and the Zr, cp1, cp2 plane are 90.4 (2), 90.7 (6), and 90.7 (9)° for II (X = C19), III (X = C19), and V (X = Cl), respectively. Most of the other structural parameters are very close. The only highly significant differences concern the lengthening of the Zr–N1 distance and the narrowing of the N1–Zr–cp2 angle in III with respect to those in II and V (Zr–N(1), 2.21 (1) Å in III vs. 2.103 (3) and 2.12 (2) Å in II and (V); Nil–Zr–cp2, 111.7 (6)° in III vs. 117.8 (2) and 115.1 (10)° in II and V). This can be attributed to steric hindrance between the cyclopentadienyl rings and the phenyl rings at C18 and C19, which are not present in II and III. The Zr, N1, N2, C17 atoms are perfectly coplanar in V and show small departure from planarity in II and III; the greatest deviation, is observed for N2: 0.044 (3) and 0.031 (11) Å in II and III, respectively. The C19 and Cl atoms deviate from that plane 0.090 (5), 0.236 (13), and 0.127 (6) Å in II, III, and V, respectively. The values of the N1–N2 and C17–N2 distances[23] (Table V) clearly indicate a rather high double-bond character for both bonds and suggest an electronic delocalization over the C–N–N unit in agreement with the IR spectra (theoretical values: C(sp^2)–N(sp^2) = 1.26 Å, N(sp^2)–N(sp^2) = 1.45 Å). This is further supported by the structural parameters concerning a bridging η^1-hydrazonato(1–) ligand. A longer N–N bond distance (1.388 (35) Å) and a shorter C=N bond distance (1.269 (35) Å) have been observed.[2b] All the other structural parameters are as expected (Table V).

The η^2 bonding mode of the hydrazonato group is very strong since even in the presence of oxygen donor ligands (complex III) no competition was observed either in the solid state or in solution between N* and the oxygen atoms. The ^{1}H NMR spectrum shows two ethyl groups as due only to the stereochemical difference of the two CO_2Et groups. The η^2 bonding mode of the N–N unit may explain the lack of the insertion of a further molecule of diazoalkane, even under drastic condtiions. Such a reaction requires as a prerequisite a vacant coordination site on the metal to precoordinate the diazoalkane molecule. This observation was further confirmed by the fact that complexes I–III, notwithstanding the fact that they have a Zr–alkyl bond, did not insert carbon monoxide. We would like to call attention to other significant aspects of reactions 1 and 2.

Relatively few reactions have been so far reported between metal–hydrido and metal–alkyl compounds with diazoalkanes.[24] In all cases, however, the reaction can be described as occurring through a 1,3-addition of the M–R or M–H

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(23) For a comparison of N–N and C–N bond distances in related ligands see ref 24 and the following: (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 1918–24. (b) Nakamura, A.; Yoshida, T.; Cowie, M.; Otsuka, S.; Ibers, J. A. *Ibid.* **1977**, *99*, 2108–17. Schramm, R. D.; Ibers, J. A. *Inorg. Chem.* **1980**, *19*, 2441–8. (c) Bart, J. C. J.; Bassi, I. W.; Cerruti, G. F.; Calcaterra, M. *Gazz. Chim. Ital.* **1980**, *110*, 423–36.

(24) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800–12. Lappert, M. F.; Poland, J. S. *Adv. Organomet. Chem.* **1970**, *9*, 397–435.

moiety to the C=N=N unit of the diazoalkane molecule, so as to generate an alkyldiazenido complex. This result can be exemplified as

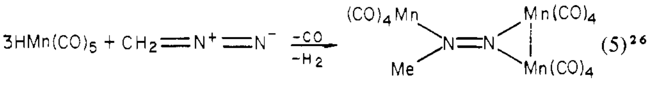
$$L_nM{-}H + R_2C{=}N^+{=}N^- \rightarrow L_nM{-}N{=}N{-}CHR_2 \quad (3)$$

Herrmann reported the most significant examples of such a reaction:

$$HM(CO)_3cp + R_2C{=}N{=}N \rightarrow cp(CO)_3M{-}N{=}N{-}CHR_2 \quad (4)^{25}$$

VI

M = Mo, W; R = Ph, H, Me, SiMe$_3$



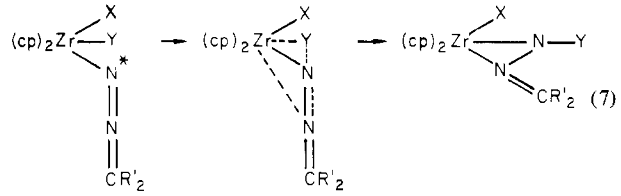
VII

Unlike reactions 4 and 5, reactions 1 and 2 formally represent the addition of the Zr–H and Zr–C fragments to the N=N= unit of a diazoalkane molecule. They exemplify the formation of a nitrogen–carbon and a nitrogen–hydrogen bond by the insertion of molecules resembling dinitrogen into metal–carbon and metal–hydrogen bonds. A very recent report[2b] describes the reaction of diazoalkanes with an Os–H unit in $[(CO)_{10}Os_3(\mu\text{-}H)_2]$, affording an η^1-hydrazonato(1–) ligand bridging two metal atoms with the terminal nitrogen:

$$[(CO)_{10}Os_3(\mu\text{-}H)_2] + R'R''C{=}N{=}N \rightarrow [(CO)_{10}Os_3(\mu\text{-}H)(\mu\text{-}NH{-}N{=}CR'R'')] \quad (6)$$

$R' = R'' = Ph$; $R' = Ph$, $R'' = Me$; $R' = H$, $R'' = Ph$; $R' = R'' = Me$

Diazoalkane can be considered as having its N–N unit highly polarized by an electron-rich center (the carbene moiety). Moreover, we can consider as a preliminary step in reactions 1 and 2, leading to the insertion of a diazoalkane molecule, the coordination of the diazoalkane molecule on the acidic zirconium center, as sketched in VIII. VIII may be



VIII

X = Y = R; X = Cl, Y = H

considered a plausible intermediate preceding the migration of the alkyl or hydrido group to the diazoalkane. The incoming ligand may labilize the M–C and M–H bonds, providing in close proximity an insertable group for the migrating ligand. The η^2 bonding mode is the consequence of the changed geometry around N*, when the Y group migrates to it in a concerted type process.

Acknowledgment. This work was supported by the CNR (Rome).

Registry No. I, 85650-33-5; II, 82942-37-8; III, 85650-32-4; IV, 37342-97-5; V, 82942-38-9; Cp_2ZrMe_2, 12636-72-5; $Cp_2Zr(CH_2Ph)_2$, 37206-41-0; $Ph_2C{=}N{=}N$, 883-40-9; $(EtOCO)_2C{=}N{=}N$, 5256-74-6.

Supplementary Material Available: Listings of observed and calculated structure factors, coordinates for hydrogen atoms (Tables SI–SIII), thermal parameters (Tables SIV–SVI), bond distances and angles (Table SVII), and equations of least-squares planes (Table SVIII) (50 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
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Nucleophilic Nitrosylations of Metal Carbonyls Using Bis(triphenylphosphine)nitrogen(1+) Nitrite

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Received October 18, 1982

Bis(triphenylphosphine)nitrogen(1+) nitrite (PPN(NO$_2$)) has been found to be very effective for converting metal carbonyls into nitrosyl carbonyl complexes. The reactions are conducted in dipolar aprotic solvents such as tetrahydrofuran (THF) or acetonitrile and characteristically give high yields with no side products. The reaction has been successfully applied to $Fe(CO)_5$, $[Mn(CO)_6]^+$, $[Mn(CO)_5(CH_3CN)]^+$, $[Fe(CO)_2(PPh_3)_2(NO)]^+$, $Mn(CO)_4(NO)$, $Mn_2(CO)_{10}$, $Co_2(CO)_8$, $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and $Ru_6C(CO)_{17}$ to generate CO$_2$, a two-electron donor ligand (L), and the product, resulting in replacement of CO and L with NO and a negative charge. A kinetic analysis of the reaction of Fe(CO)$_5$ and PPN(NO$_2$) in acetonitrile verifies that the reaction is first order in iron and nitrite with $k = 0.111 \pm 0.007$ M^{-1} s^{-1} at 26 ± 1 °C. The addition of a 10-fold excess of PPh$_3$ had no effect on the rate of the reaction. The new nitrosylcarbonylmetalate, $[Mn(CO)_2(NO)_2]^-$, was characterized by a single-crystal X-ray crystallographic study ($P2_1/a$ space group, $Z = 4$, $a = 21.890$ (5) Å, $b = 9.194$ (3) Å, $c = 17.495$ (3) Å, $\beta = 96.25$ (2)°), which shows that it has a tetrahedral geometry with disordered NO and CO ligands. Characterization of the new clusters $[Ru_3(CO)_{10}(NO)]^-$ and $[Os_3(CO)_{10}(NO)]^-$ establishes that the NO is bridging one edge of the metal triangle, while spectroscopic evidence suggests that $[Ru_6C(CO)_{15}(NO)]^-$ contains a terminal nitrosyl ligand. Nitrogen-15 magnetic resonance spectra of the bridging nitrosyls exhibit a 400 ppm downfield shift relative to the resonance of mononuclear nitrosyl carbonyl compounds. In some cases PPN(NO$_2$) simply substitutes a NO$_2^-$ for a carbonyl. This occurs with Co(CO)$_3$(NO) to give the new nitro nitrosyl product $[Co(NO_2)(CO)_2(NO)]^-$.

Introduction

Unlike carbon monoxide, nitric oxide is not one of the basic building blocks of the chemical industry. If anything, there has been much work devoted to develop efficient means to destroy NO. With this in mind, it is worth mentioning some of the reasons for the interest in the nitrosyl ligand. We can designate two categories of reactivity of metal nitrosyl complexes: those reactions directly involving the NO ligand and

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