Contribution from the Istituto di Chimica Generale, Unversità di Pisa, 56100 Pisa, Italy, and Istituto di Strutturistica Chimica,
Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, 43100 Parma, Italy

Insertion of CO_2-like Molecules into Zirconium–Carbon Bonds: Reactivity of Dialkylbis(cyclopentadienyl)zirconium(IV) with Diphenylketene, Aryl Isocyanates, and *p*-Tolylcarbodiimide

S. GAMBAROTTA,[†] S. STROLOGO,[†] C. FLORIANI,*[†] A. CHIESI-VILLA,[‡] and C. GUASTINI[‡]

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Diphenylketene, aryl isocyanates, and *p*-tolylcarbodiimide insert into Zr–C bonds of $(cp)_2ZrR_2$ (cp = η^5-C_5H_5; R = Me (I), $PhCH_2$ (II), Ph (III)). The insertion of the >C=O unit of diphenylketene into the Zr–R bond gives $\{(cp)_2Zr(R)[O-C(R)=CPh_2]\}$ complexes (II), which, because of the presence of a vacant coordination site on the metal, add a further molecule of diphenylketene to form $\{(cp)_2Zr[O-C(R)=CPh_2]_2\}$. The structures of both kinds of complexes were confirmed by an X-ray analysis on $\{(cp)_2Zr(Me)[O-C(Me)=CPh_2]\}$ (IV) and $\{(cp)_2Zr[O-C(Me)=CPh_2]_2\}$ (V). The vinyl–oxo ligand has normal structure characteristics, and the C=C bond does not interact with the metal. Reaction of isocyanates (ArNCO) with complexes (I–III) led to the formation of an imido ligand bonding the metal in a bidentate fashion, {(cp)$_2$Zr(R)[O⌐C(R)⌐NAr]}. The X-ray analysis on {(cp)$_2$Zr(Me)[O⌐C(Me)⌐NPh]} (VIII) is reported. The insertion of a second molecule of ArNCO is prevented by the absence of a free coordination site on the metal in complexes VI–VIII. Analogous results have been obtained by reacting complexes I–III with *p*-tolylcarbodiimide, as shown by the isolation of {(cp)$_2$Zr(R)[*p*-MeC$_6$H$_4$N⌐C(R)⌐NC$_6$H$_4$Me-*p*]} (XI). Insertion of the CO_2-like molecule into the Zr–R bond occurs according to the following sequence: Me > Ph >> $PhCH_2$. Moreover, the occurrence of the reaction does strongly depend on the nature of the heterocumulene in the order $Ph_2C=C=O$ > PhN=C=O > *p*-$MeC_6H_4N=C=NC_6H_4Me$-*p* >> CO_2. This order suggests that an important factor determining the insertion of the CO_2-like molecule can be polarization of the cumulene structure, thus making carbon dioxide the most difficult to insert. Crystallographic details for $\{(cp)_2Zr(Me)[O-C(Me)=CPh_2]\}$: space group $Pca2_1$ (orthorhombic); $a = 25.814$ (6), $b = 8.646$ (2), $c = 9.851$ (6) Å; $V = 2198.6$ (9) Å^3; $Z = 4$; $D_{calcd} = 1.35$ g cm^{-3}. The final R factor was 0.033 for 1792 observed reflections. Crystallographic details for $\{(cp)_2Zr[O-C(Me)=CPh_2]_2\}$: space group $P\bar{1}$ (triclinic); $a = 15.817$ (2), $b = 18.705$ (3), $c = 12.965$ (2) Å; $\alpha = 104.81$ (2), $\beta = 98.16$ (2), $\gamma = 113.98$ (2)°; $V = 3254.3$ (8) Å^3; $Z = 4$; $D_{calcd} = 1.31$ g cm^{-3}. The final R factor was 0.051 for 4693 observed reflections. Crystallographic details for {(cp)$_2$Zr(Me)[O⌐C(Me)⌐NPh]}: space group $P2_1/n$* (monoclinic); $a = 11.582$ (2), $b = 12.039$ (2), $c = 12.243$ (2) Å; $\beta = 95.73$ (2)°; $V = 1698.6$ (5) Å^3; $Z = 4$; $D_{calcd} = 1.45$ g cm^{-3}. The final R factor was 0.041 for 2238 observed reflections.

Introduction

Insertion of a small molecule or an organic functional group into a metal–carbon bond represents a fundamental step for any metal-promoted functionalization of a hydrocarbon residue.[1] To this purpose, we can anticipate that the reaction of carbon dioxide with σ-bonded organo–transition-metal compounds together with the subsequent evolution of the products represent key steps in the eventual exploitation of CO_2 in the catalytic synthesis of organic molecules.[2] To date, however, there has been no systematic investigation of this area of CO_2.[2-4] The accumulated information in this field of the reactions of CO_2 with σ-bonded organometallic compounds indicates that not all compounds react with CO_2.[2] When the reaction with CO_2 does occur, the product is in the majority of cases the corresponding carboxylate.[3,4] In some instances, the presence at the metal center of a second organic ligand (alkyl, aryl) permits the evolution of the metallocarboxylate, forming an organic product, albeit in a stoichiometric process.[5] These reactions have an important role in the exploitation of carbon dioxide in the synthesis of organic molecules,[6] and the key problem is how to make them catalytic.

The mechanism of carboxylation reactions is rather obscure,[4] and apparently, the concept of CO_2 insertion is an oversimplification of the actual processes that take place. In some instances, the reaction seems to proceed by the interaction of a stabilized carbanion with free CO_2 and not by a prior "coordination" of CO_2. The necessity for prior coordination or activation by a metal center, the interaction mode, and the eventual evolution of the carboxylate product are domains of large interest.

In order to answer some of the above-mentioned questions, we describe a study on the interaction of CO_2-like molecules, namely diphenylketene, isocyanates, and *p*-tolylcarbodiimide, with dialkylbis(cyclopentadienyl)zirconium(IV) complexes, $(cp)_2ZrR_2$ (cp = η^5-C_5H_5; R = Me, $PhCH_2$, Ph), which have been used in modeling studies concerning the insertion of carbon monoxide into a metal–carbon bond.[7] Titanium– and zirconium–alkyl complexes have been found to insert carbon dioxide into the M–C σ bonds. Tetrabenzyltitanium and -zirconium react readily with CO_2.[8] Similarly, dimethyltitanocene gives the expected titanocene diacetate with CO_2.[9] Insertion of CO_2 has been found to occur with a benzyne intermediate formed from $(cp)_2TiPh_2$ by a thermal reaction.[3,10] Moreover, [$(cp)_2$TiR] (R = alkyl, allyl, alkenyl) complexes insert CO_2 and some CO_2-like molecules to form the corresponding carboxylato-type complexes.[11] A study examining

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[†] Università di Pisa.

[‡] Università di Parma.

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the factors affecting the insertion of CO_2 and CO_2-like molecules into the metal–carbon bond has never been produced.

Experimental Section

All the reactions described were carried out under an atmosphere of purified nitrogen. Solvents were purified by standard methods. Dialkylbis(cyclopentadienyl)zirconium(IV) complexes, $(cp)_2ZrR_2$ (cp = η^5-C_5H_5; R = Me,[12] $PhCH_2$,[7] Ph[12]) were prepared as previously reported. Phenyl isocyanate, p-tolylcarbodiimide, and 1-naphthylisocyanate are commercially available compounds, which have been recrystallized or distilled before use. Diphenylketene, DPK, was prepared as in the literature.[13a] IR spectra were recorded with a Perkin-Elmer 283 spectrophotometer. ^1H NMR spectra were taken with Varian E-360 (60 MHz) apparatus. Carbon dioxide was high-purity (99.99%) oxygen-free gas.

Reaction of $(cp)_2ZrR_2$ (R = Me, $PhCH_2$, Ph) with Diphenylketene. A toluene solution (30 mL) of $(cp)_2ZrMe_2$ (2.29 g, 9.08 mmol) was reacted with neat diphenylketene, DPK (1.76 g, 9.08 mmol). When it stood for 2 days at room temperature, the original yellow-orange solution turned to colorless. By addition of n-hexane (30 mL) to the concentrated solution, white needles of $\{(cp)_2Zr(Me)[O{-}C(Me){=}CPh_2]\}$ (IV) formed (50.2%). Anal. Calcd for $C_{26}H_{26}OZr$: C, 70.11; H, 5.89. Found: C, 70.43; H, 5.85. IR spectrum (Nujol): $\nu(C{=}C)$ at 1605 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.10 (m, Ph, 10 H), 5.86 (s, cp, 10 H), 1.77 (s, Me, 3 H), 0.07 (s, Me, 3 H).

When the reaction was carried out with a DPK/Zr molar ratio of 2 for 4 days, the disappearance of all DPK was observed in the IR spectrum. By the procedure described above $\{(cp)_2Zr[O{-}C(Me){=}CPh_2]_2\}$ (V) was isolated as white crystals (60.3%). Anal. Calcd for $C_{40}H_{36}O_2Zr$: C, 75.07; H, 5.67. Found: C, 75.09; H, 5.56. IR spectrum (Nujol): $\nu(C{=}C)$ at 1610 cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 7.20 (m, Ph, 20 H), 5.88 (s, cp, 10 H), 1.92 (s, Me, 6 H).

DPK reacted with $(cp)_2Zr(CH_2Ph)_2$ in a 1:1 molar ratio, forming $\{(cp)_2Zr(CH_2Ph)[O{-}C(CH_2Ph){=}CPh_2]\}$ (VI) (44.1%). The reaction is significantly slower (10 days at room temperature) than for complex I. Anal. Calcd for $C_{38}H_{34}OZr$: C, 76.38; H, 5.69. Found: C, 76.07; H, 5.73. IR spectrum (Nujol): $\nu(C{=}C)$ at 1610 cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 7.00 (m, Ph, 20 H), 5.53 (s, cp, 10 H), 3.53 (s, CH_2, 2 H), 2.03 (s, CH_2, 2 H).

The reaction of $(cp)_2ZrPh_2$ with DPK is very slow at room temperature. By the procedure reported above, a toluene solution of $(cp)_2ZrPh_2$ was reacted with DPK at 100 °C for 5 days. $\{(cp)_2Zr[O{-}C(Ph){=}CPh_2]_2\}$ (VII) was recovered as a microcrystalline orange solid (50.7%). ^1H NMR spectrum ($CDCl_3$): δ 7.08 (bm, Ph, 30 H), 5.81 (s, cp, 10 H). Anal. Calcd for $C_{50}H_{40}O_2Zr$: C, 78.63; H, 5.24. Found: C, 77.58; H, 5.04.

Reaction of $(cp)_2ZrR_2$ (R = Me, $PhCH_2$, Ph) with RNCO (R = Ph, 1-Naphthyl, C_6H_{11}). Phenyl isocyanate (0.50 mL, 4.69 mmol) was added to a toluene (50 mL) solution of $(cp)_2ZrMe_2$ (1.11 g, 4.41 mmol). The resulting colorless solution was heated to 100 °C for 36 h until complete disappearance of PhNCO, checked by the IR spectrum. The concentrated solution gave on standing overnight orange crystals of $\{(cp)_2Zr(Me)[O\overset{\cdots}{-}C(Me)\overset{\cdots}{-}NPh]\}$ (VIII) (41.5%). Anal. Calcd for $C_{19}H_{21}NOZr$: C, 61.62; H, 5.67; N, 3.78. Found: C, 61.39; H, 5.71; N, 3.49. ^1H NMR ($CDCl_3$): δ 7.00 (m, Ph, 6 H); 5.96 (s, cp, 10 H); 1.70 (s, Me, 3 H); –0.33 (s, Me, 3 H). IR (Nujol): $\nu(C{-}N)$ at 1660 cm^{-1} (m–s). The reaction of $(cp)_2ZrMe_2$ with 1-naphthylisocyanate was significantly slower (3 days). The reaction gave $\{(cp)_2Zr(Me)[O\overset{\cdots}{-}C(Me)\overset{\cdots}{-}NC_{10}H_7]\}$ (IX) as a light brown crystalline solid (51.5%). Anal. Calcd for $C_{23}H_{23}NOZr$: C, 65.57; H, 64.81; N, 3.33. Found: C, 64.81; H, 5.44; N, 3.09. ^1H NMR spectrum ($CDCl_3$): δ 7.50 (m, naphthyl, 7 H), 6.10 (s, cp, 10 H), 1.60 (s, Me, 3 H), –0.48 (s, Me, 3 H). IR (Nujol): $\nu(C{-}N)$ at 1655 cm^{-1} (m–s).

No reaction with RNCO (R = Ph, 1-naphthyl, C_6H_{11}) was observed with $(cp)_2Zr(PhCH_2)_2$, though it was refluxed for 3 days.

The reaction of $(cp)_2ZrPh_2$ with $C_6H_{11}NCO$ (1:1 molar ratio) was carried out at 100 °C for 48 h in toluene. $\{(cp)_2Zr(Ph)[O\overset{\cdots}{-}C(Ph)\overset{\cdots}{-}NC_6H_{11}]\}$ was recovered as orange crystals (45.7%). Anal. Calcd for $C_{29}H_{31}NOZr$: C, 69.53; H, 6.24; N, 2.80. Found: C, 69.24; H, 6.35; N, 2.58. ^1H NMR ($CDCl_3$): δ 6.89 (m, 10 H, Ph), 6.10 (s, 10 H, cp), 1.49 (m, 10 H, C_6H_{11}).

Reaction of $(cp)_2ZrR_2$ (R = Me, $PhCH_2$, Ph) with p-Tolylcarbodiimide. A toluene solution of $(cp)_2ZrMe_2$ (1.04 g, 4.15 mmol) and p-tolylcarbodiimide, p-TCD (0.93 g, 4.19 mmol), was refluxed for 4 days until p-TCD disappeared, as checked with the IR spectrum. The concentrated solution kept standing for 10 days gave brown crystals of $\{(cp)_2Zr(Me)[p\text{-}MeC_6H_4N\overset{\cdots}{-}C(Me)\overset{\cdots}{-}NC_6H_4Me\text{-}p]\}$ (XI) (0.88 g, 44.8%). Anal. Calcd for $C_{27}H_{30}N_2Zr$: C, 68.50; H, 6.51; N, 5.65. Found: C, 68.52; H, 6.51; N, 5.65. IR spectrum (Nujol): no band above 1550 cm^{-1} is observed. ^1H NMR spectrum ($CDCl_3$): δ 7.00 (m, Ph, 8 H); 5.80 (s, 10 H, cp); 2.33 (s, Me, 3 H), 2.37 (s, Me, 3 H), 1.56 (s, Me, 3 H), –0.47 (s, Me, 3 H).

No reaction was observed with use of $(cp)_2Zr(PhCH_2)_2$ under the same conditions. A toluene solution of $(cp)_2ZrPh_2$ (1.47 g, 3.92 mmol) was reacted with p-tolylcarbodiimide (0.90 g, 4.05 mmol) for 36 h at 100 °C. $\{(cp)_2Zr(Ph)[p\text{-}MeC_6H_4N\overset{\cdots}{-}C(Ph)\overset{\cdots}{-}NC_6H_4Me\text{-}p]\}$ was recovered as an orange crystalline solid (60.5%). Anal. Calcd for $C_{37}H_{34}N_2Zr$: C, 74.37; H, 5.70; N, 4.69. Found: C, 74.53; H, 5.25; N, 4.78. ^1H NMR spectrum ($CDCl_3$): δ 6.92 (Ph, m, 18 H), 5.90 (s, cp, 10 H), 2.18 (s, Me, 3 H), 2.08 (s, Me, 3 H). IR spectrum (Nujol): $\nu(C{-}N)$ at 1575 cm^{-1}.

Reaction of $(cp)_2ZrR_2$ (R = Me, $PhCH_2$, Ph) with Carbon Dioxide. Toluene solutions of complexes I–III did not react at room temperature under an atmosphere of carbon dioxide.

A toluene solution of $(cp)_2ZrMe_2$ (2.67 g, 10.6 mmol) was pressurized in an autoclave under a pressure of 50 atm of CO_2. The autoclave was heated to 80 °C for 24 h. A red-maroon powder was recovered. This solid is insoluble in the most common solvents. The IR spectrum (poly(trichlorofluoroethylene)) showed a broad band at 1510–1455 cm^{-1}, which can be assigned to an acetato group symmetrically bonded, either bridging or bidentate.[13b] The hydrolysis, carried out with use of 15% H_2SO_4, gave CH_3COOH (7.5 mmol) and methane (6.2 mmol).

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 complex IV to be orthorhombic with systematic absences consistent with the space groups *Pbcm* (or *Pca*2_1). The lack of any systematic absences indicated the crystals of complex V to be triclinic. A crystal of complex (VIII) was mounted in a random orientation on a Philips PW 1100 diffractometer; the reduced cell quoted was obtained with use of TRACER.[14] 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 $2\theta > 30°$ for all the complexes.

Data were collected at room temperature on single-crystal four-circle diffractometers. For intensities and background, individual reflection profiles were analyzed as described by Lehmann and Larsen[15] for complexes IV and V; the "three-point" technique was used for complex VIII. The structure amplitudes were obtained after the usual Lorentz and polarization reduction,[16] and the absolute scale was established by the Wilson method.[17] 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 $w = k/[\sigma^2(F_o) + |g|(F_o^2)]$; k is redetermined after each structure factor calculation and refined by 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 18 for Zr, from ref 19 for O, C, and N, and from ref 20 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary.

Residual R and weighted residual R_w indices were defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. The

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

	IV	V	VIII
	$C_{26}H_{26}OZr$	$C_{40}H_{36}O_2Zr$	$C_{19}H_{21}NOZr$
cryst syst	orthorhombic	triclinic	monoclinic
space group	$Pca2_1$ [C_{2v}^5, no. 29]	$P\bar{1}$ [C_i^1, no. 2]	$P2_1/n$[a]
a, Å	25.814 (6)	15.817 (2)	11.582 (2)
b, Å	8.646 (2)	18.705 (3)	12.039 (2)
c, Å	9.851 (2)	12.965 (2)	12.243 (2)
α, deg	90	104.81 (2)	90
β, deg	90	98.16 (2)	95.73 (2)
γ, deg	90	113.98 (2)	90
V, Å^3	2198.6 (9)	3254.3 (8)	1698.6 (5)
Z	4	4	4
D_{calcd}, g cm^{-3}	1.35	1.31	1.45
mol wt	445.7	639.9	370.6
cryst dimens, mm	0.45 × 0.18 × 0.71	0.45 × 0.06 × 0.75	0.27 × 0.37 × 0.72
linear abs coeff, cm^{-1}	5.03	3.63	6.37
diffractometer	Siemens AED		Philips PW 1100
scan type	$\theta/2\theta$		$\omega/2\theta$
scan speed	3–12°/min		0.075°/s
scan width, deg	$(\theta - 0.5) - [\theta + (0.5 + \Delta\theta)]$ $(\Delta\theta = (\lambda_{\alpha_2} - \lambda_{\alpha_1})/\lambda \tan\theta)$		1.50
radiation	Nb-filtered Mo Kα (λ = 0.7107 Å)		graphite-monochromated Mo Kα (λ = 0.7107 Å)
2θ range, deg	6–58	5–46	6–53
reflcns measd	hkl	$\pm h,\pm k,l$	$\pm h,k,l$
std reflcns	802[b]	$5\bar{5}2$[b]	404[c]
unique total data	2547	7285	3495
criterion for obsn	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 3\sigma(I)$
unique obsd data	1792	4963	2238
no. of variables	210	564	199

[a] A nonstandard setting of C_{2h}^5 [No. 14]. Coordinates of equivalent positions are as follows: x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$. [b] 1 every 50 reflections; no significant changes. [c] 1 every 1 h; no significant changes.

Table II. Fractional Atomic Coordinates ×10^4 for Complex IV

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Zr	−4189 (0)	−2256 (1)	−5000 (0)	C9	−3601 (3)	−2432 (6)	−7052 (8)
O1	−3732 (1)	−3690 (4)	−4000 (4)	C10	−3346 (3)	−1443 (6)	−6115 (8)
C17	−3393 (2)	−4017 (5)	−1812 (6)	C11	−3214 (1)	−2372	−1735 (4)
C18	−3631 (2)	−4575 (6)	−2914 (6)	C12	−2917 (1)	−1693 (3)	−2758 (4)
C19	−3807 (3)	−6204 (7)	−3111 (7)	C13	−2771 (1)	−144 (3)	−2655 (4)
C20	−4663 (3)	−4138 (9)	−6061 (10)	C14	−2920 (1)	725 (3)	−1528 (4)
C1	−4969 (2)	−2408 (6)	−3448 (7)	C15	−3217 (1)	46 (3)	−505 (4)
C2	−5079 (2)	−1257 (6)	−4435 (7)	C16	−3363 (3)	−1502 (3)	−608 (4)
C3	−4731 (2)	−7 (6)	−4229 (7)	C21	−3307 (1)	−4946 (4)	−561 (4)
C4	−4406 (2)	−384 (6)	−3115 (7)	C22	−3719 (1)	−5660 (4)	108 (4)
C5	−4553 (2)	−1869 (6)	−2633 (7)	C23	−3631 (1)	−6462 (4)	1316 (4)
C6	−3653 (3)	−92 (6)	−5955 (8)	C24	−3132 (1)	−6550 (4)	1853 (4)
C7	−4097 (3)	−246 (6)	−6793 (8)	C25	−2721 (1)	−5836 (4)	1184 (4)
C8	−4065 (3)	−1692 (6)	−7471 (8)	C26	−2808 (1)	−5034 (4)	−23 (4)

"goodness of fit" parameter (GOF) was determined by the equation $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO is the number of observed reflections and NV is the number of variables refined.

During the refinement the cp and Ph rings of complexes IV and V were treated as rigid regular pentagons (C–C = 1.42 Å) and hexagons (C–C = 1.39 Å), respectively.

Final atomic coordinates are listed in Tables II–IV, SI, and SII, and thermal parameters are given in Table SIII–V.[21a]

Structure Solution and Refinement for Complex IV. The 1792 reflections with $I > 2\sigma(I)$ were used in the structure solution and refinement. The structure was solved by the heavy-atom method. The initial assumption of space group $Pca2_1$, based on E statistics calculated as a function of sin θ, resulted in a satisfactory solution and refinement of the structure ($\langle|E^2 - 1|\rangle$ is equal to 0.75, near the theoretical value accepted for noncentrosymmetric structures, 0.74). All the non-hydrogen atoms were refined anisotropically by full-matrix least squares down to R = 0.039. At this point a difference map revealed all the hydrogen atoms, which were introduced as fixed contributors in the successive refinement with isotropic B fixed at 7.8 Å^2. Refinement stopped at R = 0.034 and R_w = 0.036. Since the space group is *polar*, the chirality of the crystal was tested by inverting all coordinates ($x, y, z \rightarrow -x, -y, -z$) and refining to convergence again. The resulting values (R = 0.033, R_w = 0.035) indicate that the "inverted" structure should be accepted. The previous data were then discarded.

In the final cycle refinement no parameter shifted by more than 0.4 times its standard deviation. The overdetermination ratio was 1792:210 ≃ 8.5, and GOF = 0.95. The values for k and g were 0.2994 and 0.003 05, respectively. In the final difference map there was no peak greater than 0.4 e Å^{-3}.

Structure Solution and Refinement for Complex V. The structure was solved by heavy-atom methods starting from a three-dimensional Patterson map, which gave the approximate coordinates of the two independent zirconium atoms. Refinement was by blocked (two blocks) full-matrix least squares. Owing to the limitations of the local version of SHELX ($N_{iso} + 2N_{aniso}$ = 160; N_{iso} is the number of isotropic atoms, N_{aniso} is the number of anisotropic atoms), 16 phenyl carbon atoms were refined isotropically, while all the other non-hydrogen atoms were refined anisotropically. In the final difference map the only significant peaks were in the region geometrically feasible for hydrogen atoms. Due to the limitations of the program used, their coordinates could not be introduced in calculations. The final R factor was 0.051. Unit weights were used. In the last cycle no parameter shifted by more than 0.3 times its standard deviation. The overdetermination ratio was 4963:564 ≃ 8.8.

Structure Solution and Refinement for Complex VIII. The structure was solved by the heavy-atom method and refined anisotropically by full-matrix least squares without constraints down to the final R and R_w values of 0.041 and 0.044, respectively (GOF = 1.00). All the hydrogen atoms were located in a difference map and introduced in the last three cycles of refinement as fixed contributors (isotropic B fixed at 7.8 Å^2).

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(21) (a) See paragraph at the end of paper regarding supplementary material. (b) Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 349–355.

Table III. Fractional Atomic Coordinates $\times10^4$ for Complex V

	molecule A			molecule B		
atom	x/a	y/b	z/c	x/a	y/b	z/c
Zr	4316 (1)	3299 (0)	5111 (1)	420 (1)	769 (0)	8127 (1)
O1	5741 (4)	3787 (3)	5317 (4)	1599 (4)	711 (3)	8771 (5)
O2	4231 (4)	4213 (3)	6221 (4)	138 (4)	1285 (3)	9494 (5)
C11	4041 (5)	4487 (5)	7186 (6)	122 (6)	1922 (5)	10247 (6)
C12	3158 (5)	4402 (5)	7206 (6)	−706 (6)	1972 (5)	10217 (7)
C13	4915 (6)	4894 (6)	8184 (7)	1086 (6)	2508 (5)	11100 (7)
C17	6971 (6)	3387 (5)	5541 (7)	3134 (6)	998 (5)	8539 (7)
C18	6575 (5)	3876 (5)	5913 (6)	2572 (6)	1145 (5)	9138 (7)
C19	6999 (6)	4603 (5)	7006 (7)	2920 (7)	1769 (6)	10323 (7)
C1	3645 (5)	1775 (4)	4814 (4)	467 (9)	1158 (4)	6411 (5)
C2	4586 (5)	2144 (4)	5542 (4)	1440 (9)	1473 (4)	7015 (5)
C3	4606 (5)	2662 (4)	6568 (4)	1639 (9)	2119 (4)	8015 (5)
C4	3677 (5)	2613 (4)	6475 (4)	788 (9)	2204 (4)	8029 (5)
C5	3083 (5)	2065 (4)	5391 (4)	64 (9)	1611 (4)	7037 (5)
C6	4023 (5)	2813 (5)	3024 (5)	−287 (4)	−724 (4)	6773 (5)
C7	3101 (5)	2573 (5)	3216 (5)	−975 (4)	−436 (4)	6564 (5)
C8	3031 (5)	3310 (5)	3713 (5)	−1325 (4)	−317 (4)	7511 (5)
C9	3909 (5)	4005 (5)	3828 (5)	−852 (4)	−531 (4)	8306 (5)
C10	4522 (5)	3698 (5)	3402 (5)	−211 (4)	−782 (4)	7850 (5)
C23	863 (3)	2911 (3)	4896 (4)	−3067 (3)	−18 (3)	8779 (4)
C24	814 (3)	3408 (3)	4274 (4)	−3405 (3)	128 (3)	7840 (4)
C25	1540 (3)	4226 (3)	4589 (4)	−2858 (3)	864 (3)	7663 (4)
C26	2315 (3)	4548 (3)	5527 (4)	−1974 (3)	1454 (3)	8425 (4)
C33	1940 (4)	5179 (4)	9209 (4)	−1488 (4)	3165 (3)	12368 (5)
C34	2142 (4)	4905 (4)	10074 (4)	−827 (4)	3988 (3)	12561 (5)
C35	2702 (4)	4488 (4)	10024 (4)	−134 (4)	4157 (3)	11979 (5)
C36	3059 (4)	4345 (4)	9110 (4)	−103 (4)	3503 (3)	11203 (5)
C43	9460 (4)	3603 (4)	6597 (4)	5822 (3)	1658 (3)	9313 (5)
C44	9454 (4)	3563 (4)	7656 (4)	6218 (3)	2523 (3)	9614 (5)
C45	8641 (4)	3462 (4)	8027 (4)	5616 (3)	2897 (3)	9568 (5)
C46	7833 (4)	3400 (4)	7339 (4)	4618 (3)	2406 (3)	9221 (5)
C53	5939 (4)	2314 (3)	2406 (4)	1763 (4)	−1147 (3)	6311 (4)
C54	5860 (4)	1524 (3)	2280 (4)	2051 (4)	−985 (3)	5392 (4)
C55	6139 (4)	1342 (3)	3210 (4)	2690 (4)	−176 (3)	5491 (4)
C56	6497 (4)	1949 (3)	4265 (4)	3042 (4)	470 (3)	6510 (4)
C21	2364 (3)	4051 (3)	6149 (4)	−1636 (3)	1308 (3)	9364 (4)
C22	1638 (3)	3232 (3)	5834 (4)	−2183 (3)	572 (3)	9541 (4)
C31	2856 (4)	4619 (4)	8246 (4)	−764 (4)	2680 (3)	11009 (5)
C32	2297 (4)	5036 (4)	8295 (4)	−1457 (4)	2511 (3)	11592 (5)
C41	7839 (4)	3440 (4)	6281 (4)	4222 (3)	1541 (3)	8920 (5)
C42	8652 (4)	3542 (4)	5909 (4)	4824 (3)	1167 (3)	8966 (5)
C51	6576 (4)	2739 (3)	4391 (4)	2754 (4)	309 (3)	7430 (4)
C52	6297 (4)	2922 (3)	3461 (4)	2115 (4)	−500 (3)	7330 (4)

Table IV. Fractional Atomic Coordinates $\times10^4$ for Complex VIII

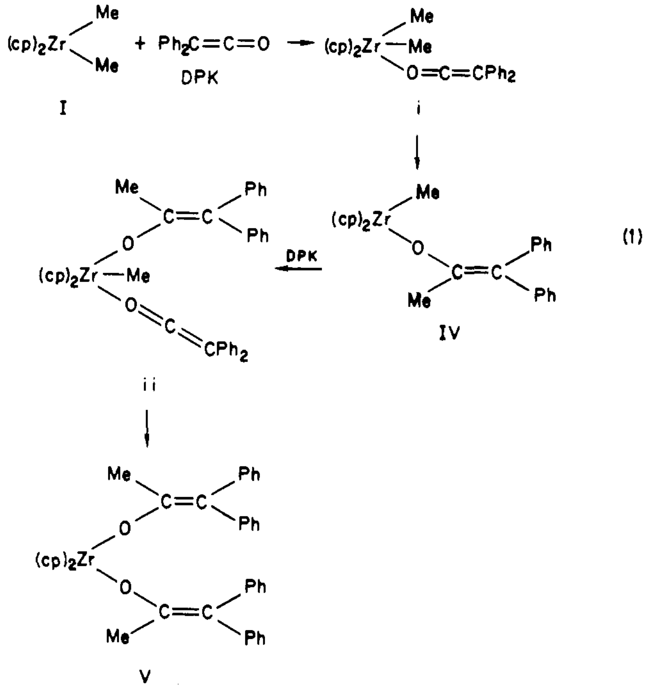
atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Zr	3090 (1)	1740 (1)	765 (1)	C8	1436 (7)	1102 (6)	−587 (7)
O1	3999 (3)	1852 (3)	−816 (3)	C9	964 (5)	1174 (7)	417 (9)
N1	3197 (4)	3345 (3)	−234 (3)	C10	1494 (7)	396 (6)	1105 (7)
C17	3701 (4)	2870 (4)	−1009 (4)	C11	2797 (4)	4473 (4)	−301 (4)
C1	4723 (5)	588 (5)	1646 (5)	C12	3426 (4)	5279 (4)	294 (4)
C2	5258 (5)	1535 (6)	1264 (5)	C13	3054 (5)	6379 (5)	253 (5)
C3	4934 (5)	2438 (5)	1873 (5)	C14	2046 (6)	6656 (4)	−371 (6)
C4	4209 (5)	2048 (5)	2633 (5)	C15	1401 (6)	5850 (6)	−965 (7)
C5	4072 (5)	914 (5)	2498 (5)	C16	1791 (5)	4760 (5)	−927 (5)
C6	2248 (6)	−201 (5)	550 (6)	C18	3968 (6)	3397 (5)	−2066 (5)
C7	2248 (5)	203 (6)	−490 (6)	C19	2041 (5)	3011 (5)	1696 (5)

In the final cycle no parameter shifted by more than 0.3 times its standard deviation. The overdetermination ratio was 2238:199 = 11.2. The values for k and g were 0.9269 and 0.001 98, respectively. In the final difference map there was no peaks above the general background.

Results and Discussion

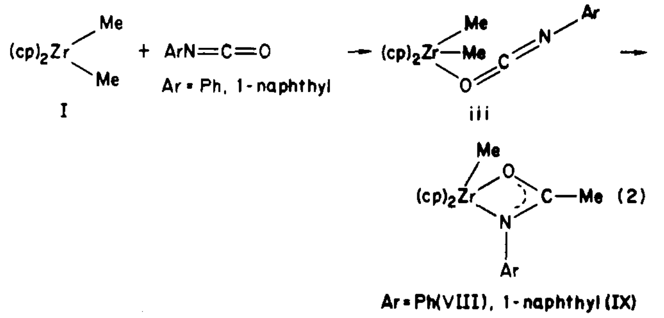
Toluene solutions of dialkylbis(cyclopentadienyl)zirconium(IV), $(cp)_2ZrR_2$ (R = Me (I), $PhCH_2$ (II), and Ph (III)),[10] have been reacted with heterocumulenes, namely diphenylketene, DPK and RNCO (R = Ph, 1-naphthyl, C_6H_{11}), which have features in common with carbon dioxide. Reaction of carbon dioxide with complexes I–III does not occur under ambient conditions, while under more drastic conditions only complex I was found to form a ill-defined product giving acetic acid upon hydrolysis. The occurrence of the reaction of I–III with the CO_2-like molecules is less affected by the substituent R at the metal, while the nature of the CO_2-like molecule has the major influence.

Complex I was found to react with diphenylketene, forming complexes IV and V by the route we propose in eq 1. The insertion of the first $Ph_2C{=}C{=}O$ (DPK) molecule is significantly faster; thus, with use of a 1:1 Zr/DPK molar ratio, complex IV can be isolated in good yield. A longer reaction time along with an excess of Ph_2C_2O allowed us to observe the insertion of a further molecule of DPK into the second Zr–Me bond, and complex V was isolated as a crystalline solid. Complexes IV and V have been structurally characterized by an X-ray analysis (vide infra). The insertion of a second DPK molecule into the Zr–Me bond of complex V can be ascribed to the plausible precoordination of DPK, as depicted in (ii), because of the presence of a vacant coordination site at the metal. Although significantly slower,



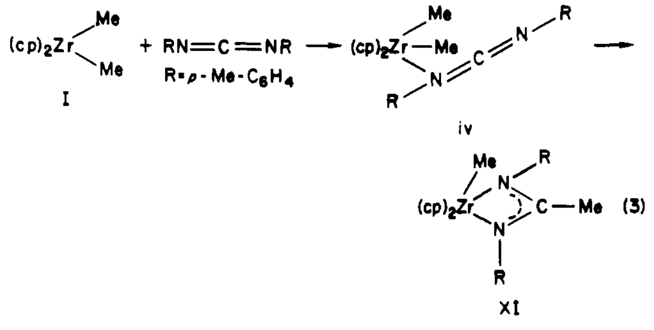
reaction 1 occurred with complexes II and III. Complexes $\{(cp)_2Zr(PhCH_2)[O{-}C(PhCH_2){=}CPh_2]\}$ (VI) and $\{(cp)_2Zr[O{-}C(Ph){=}CPh_2]_2\}$ (VII) were isolated and identified.

The need of a vacant site on the metal for precoordination of the heterocumulene molecule preceding insertion is illustrated by the results from the reaction of I with aryl isocyanates (eq 2).



Reaction 2 is significantly slower than reaction 1, and it occurred only with complexes I and III, while it was not observed with complex II. Complex III reacted with $C_6H_{11}NCO$ to give $\{(cp)_2Zr(Ph)[O{-}C(Ph)NC_6H_{11}]\}$ (X). In spite of a large excess of aryl isocyanate used, a single isocyanate was inserted into the Zr–C bond. The bonding mode of the resulting amido ligand was proven by the X-ray analysis on complex VIII (vide infra). In spite of the chelating bonding mode, the C=N stretching frequency is relatively high at 1660 (VIII) and 1655 cm^{-1} (IX).

p-tolylcarbodiimide was found to react with complexes I and III only by refluxing the toluene solution for days (see Experimental Section), while complex II did not react to any significant extent even with a longer reaction time. A large excess of p-tolylcarbodiimide did not affect the nature of the final compound, a single insertion only being observed. The structure of XI has been proposed not just by analogy with complexes VIII and IX. Insertion of only one carbodiimide molecule into the Zr–Me bonds was observed, as a consequence of the absence of a vacant coordination site in complex XI. Moreover, a C=N stretching frequency lower than 1550 cm^{-1} is in agreement with the symmetric bidentate bonding mode of the amidino ligand.[21b] Before we discuss the common characteristics and differences of reactions 1–3, a common account on the structures of complexes IV, V, and VIII is given below.



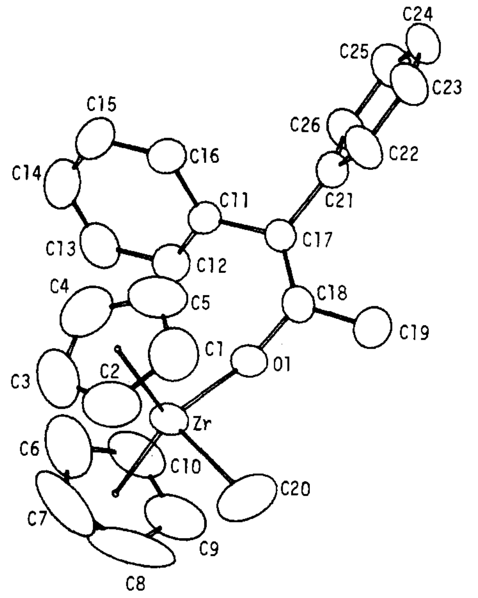


Figure 1. ORTEP drawing for complex IV (30% probability ellipsoids).

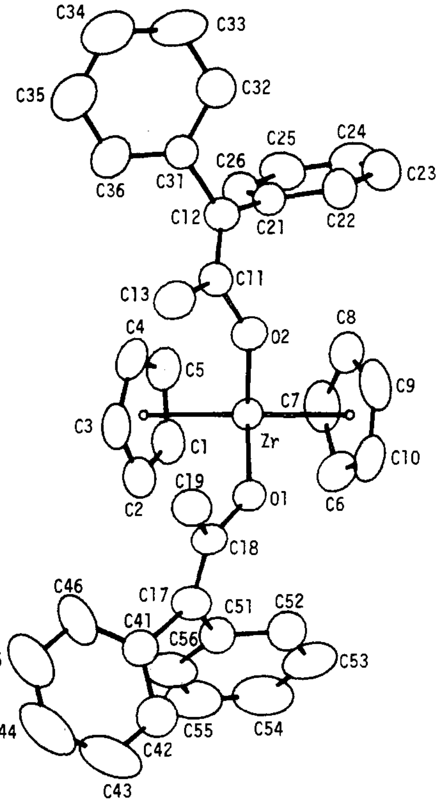


Figure 2. ORTEP drawing for complex V (molecule A) (30% probability ellipsoids).

Description of the Structures. Figures 1–4 show ORTEP views of the molecular structures of complexes IV, V, and VIII. There are two crystallographically independent molecules in the asymmetric unit of complex V. The most relevant bond distances and angles are listed in Tables V and VI. The geometries of the $(cp)_2Zr$ unit in the three complexes are very similar with the cp–Zr

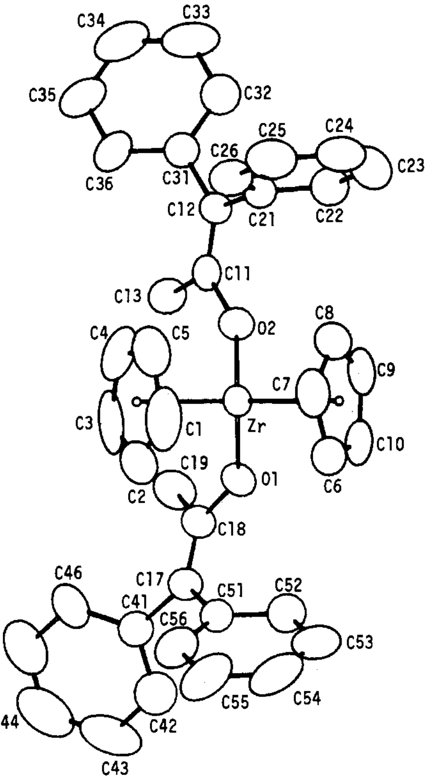


Figure 3. ORTEP drawing for complex V (molecule B) (30% probability ellipsoids).

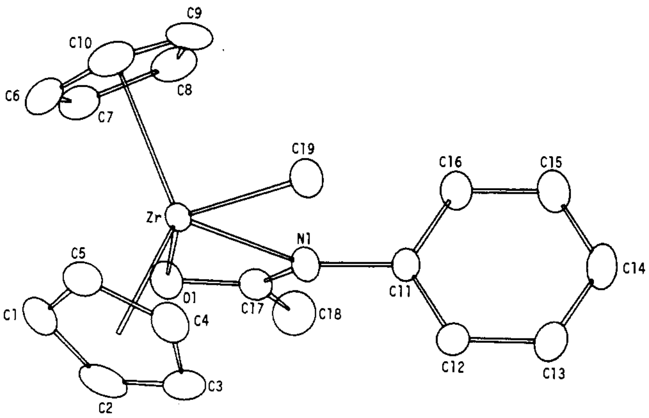


Figure 4. ORTEP drawing for complex VIII (30% probability ellipsoids).

distances ranging from 2.206 (8) to 2.243 (7) Å and with the angles cp1–Zr–cp2 varying from 128.5 (2) to 129.5 (2)°.[21a] The bent $(cp)_2Zr$ makes an equatorial cavity, where the atoms of the skeleton of the organic ligands and the alkyl carbon are located. The dihedral angles between the Zr, cp1, cp2 plane and the "equatorial" best planes Zr, O1, C20 in complex IV, Zr, O1, O2 in complex V, and Zr, O1, N1, C19 in complex VIII are 89.8 (6)° in complex IV, 89.1 (6) and 89.7 (6)° (molecules A and B, respectively) in complex V, and 89.6 (6)° in complex VIII. The features of the $(cp)_2Zr$ fragment are almost independent of the other ligands on the metal.

Zirconium–oxygen bonds in complexes IV (1.975 (3) Å) and V (1.966 (7) Å) are very close to those found in other complexes where this bond has some double-bond character.[22a] Bond distances and angles within the vinyl-oxo ligand are as expected, with

Table V. Selected Bond Distances (Å) and Angles (deg)[a]

		V	
	IV	A	B
Zr–O1	1.975 (3)	2.004 (6)	1.989 (7)
Zr–cp1	2.218 (6)	2.219 (7)	2.222 (8)
Zr–cp2	2.206 (8)	2.226 (8)	2.237 (5)
Zr–X	2.289 (8)	1.999 (6)	1.993 (7)
O1–Zr–cp1	109.5 (2)	106.4 (3)	106.4 (3)
O1–Zr–cp2	109.4 (2)	104.6 (2)	104.8 (3)
O1–Zr–X	95.8 (2)	101.3 (2)	101.4 (3)
X–Zr–cp1	103.8 (3)	106.1 (2)	106.7 (3)
X–Zr–cp2	103.4 (3)	106.8 (3)	106.1 (3)
cp1–Zr–cp2	129.2 (2)	128.5 (2)	128.5 (2)
O1–C18	1.341 (7)	1.35 (1)	1.35 (1)
C17–C18	1.337 (8)	1.34 (1)	1.33 (1)
C18–C19	1.493 (8)	1.52 (1)	1.53 (1)
O2–C11		1.35 (1)	1.35 (1)
C11–C12		1.35 (1)	1.35 (1)
C11–C13		1.52 (1)	1.51 (1)
Zr–O1–C18	150.8 (3)	144.2 (5)	143.5 (6)
O1–C18–C17	122.1 (5)	122.5 (7)	122.3 (8)
C17–C18–C19	125.9 (5)	125.7 (8)	125.5 (9)
O1–C18–C19	112.1 (5)	111.8 (7)	112.1 (8)
Zr–O2–C11		148.6 (5)	153.8 (5)
O2–C11–C12		121.1 (7)	120.2 (7)
C12–C11–C13		126.0 (7)	126.5 (8)
O2–C11–C13		112.9 (7)	113.2 (8)

Complex IV

C17–C11	1.497 (5)	C17–C21	1.488 (7)
C18–C17–C11	121.7 (5)	C11–C17–C21	115.1 (4)
C18–C17–C21	123.1 (4)		

Complex V

	A	B
C17–C41	1.51 (1)	1.52 (1)
C17–C51	1.51 (1)	1.51 (1)
C12–C21	1.51 (1)	1.51 (1)
C12–C31	1.51 (1)	1.50 (1)
C18–C17–C41	120.9 (7)	121.6 (8)
C18–C17–C51	123.2 (8)	123.3 (8)
C41–C17–C51	115.9 (7)	115.2 (7)
C11–C12–C21	121.3 (7)	121.1 (8)
C11–C12–C31	124.9 (7)	122.7 (8)
C21–C12–C31	113.9 (6)	116.2 (7)

[a] X = C20 for complex IV; X = O2 for complex V.

Table VI. Selected Bond Distances (Å) and Angles (deg) for Complex VIII

Zr–O1	2.298 (4)	O1–C17	1.289 (6)
Zr–N1	2.297 (4)	N1–C17	1.296 (6)
Zr–cp1	2.233 (6)	C17–C18	1.501 (8)
Zr–cp2	2.243 (7)	N1–C11	1.435 (6)
Zr–C19	2.322 (6)		
O1–Zr–cp1	99.5 (2)	cp1–Zr–cp2	129.5 (2)
O1–Zr–cp2	99.1 (2)	Zr–O1–C17	94.2 (3)
O1–Zr–N1	56.5 (1)	Zr–N1–C17	94.1 (3)
O1–Zr–C19	132.9 (2)	Zr–N1–C11	142.4 (3)
N1–Zr–cp1	112.3 (2)	C17–N1–C11	122.9 (4)
N1–Zr–cp2	117.1 (2)	O1–C17–N1	114.7 (4)
N1–Zr–C19	76.5 (2)	O1–C17–C18	119.1 (5)
C19–Zr–cp1	100.4 (2)	N1–C17–C18	126.3 (5)
C19–Zr–cp2	100.2 (3)		

C–O distances having "single-bond" character (see Table V) and C–C distances double-bond character (C17–C18 = 1.337 Å in complex IV and 1.34 (1) and 1.33 (1) Å for molecules A and B, respectively, in complex V). The sets of atoms O1, C17, C18, C19 (complexes IV and V and O2, C11, C12, C13 (complex V) are coplanar; the dihedral angles between the two planes in complex V are 34.8 (4) and 25.8 (4)° for molecules A and B, respectively. The zirconium atom is out of the planes of the vinyl–oxo ligand, by a distance varying from 0.84 (1) to 1.146

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(22) (a) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, 101, 1767–1775. (b) Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Floriani, C.; Fachinetti, G.; Chiesi-Villa, A. *Inorg. Chem.* **1980**, *19*, 3182–3817. (c) Hunter, W. E.; Atwood, J. L.; Fachinetti, G.; Floriani, C. *J. Organomet. Chem.* **1981**, *204*, 67–74. (d) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1983**, *22*, 2029–2034.

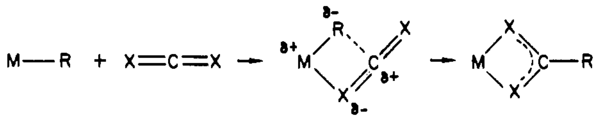
(1)° Å (Table SVII). The two independent A and B molecules of complex V are correlated by a pseudo glide plane and differ significantly only in the twist of some fragments, probably as a consequence of crystal-packing effects. The most significant differences concern the torsion around the Zr–O2 bond (the torsion angle O1–Zr–O2–C11 is 111.1 (9) and 103.7 (10)° in molecules A and B, respectively) and the mutual orientation of the C21...C26 and C31...C36 phenyl rings, the dihedral angles between them being 90.6 (8) and 76.6 (8)° in A and B, respectively.

In complex VIII the N1–C17 distance (1.296 (6) Å) is slightly but significantly longer than the value accepted for a $N_{sp^2}{=}C_{sp^2}$ double bond (1.26 Å) and the O1–C17 distance (1.289 (6) Å) is slightly but significantly shorter than the value observed for $O{-}C_{sp^2}$ single bond (e.g. 1.35 (1) Å (mean value) in complexes IV and V). This suggests some electronic delocalization over the O–C–N unit. The values of N1–C11 and C17–C18 distances (Table VI) correspond well to single bonds. The O1, C17, C18, N1, C11 atoms are coplanar within experimental error, and zirconium is out of this plane by 0.264 (1) Å. The nitrogen atom is slightly pyramidal, deviating by 0.071 (4) Å from the plane through Zr, C17, C11. Zr–Me bond distances are very close to those found in other methyl derivatives[6,21d] (Zr–C20 = 2.289 (8) Å, complex IV; Zr–C19 = 2.322 (6) Å, complex V).

Migratory aptitudes of the alkyl ligands in complexes I–III are rather close in reaction with carbon monoxide,[7a] while they behave differently with CO_2 and CO_2-like molecules. It is quite difficult, in the absence of any quantitative assessment, to define a trend, through methyl is more reactive than phenyl, while benzyl is the least reactive and it reacts only with DPK. The observed difference is higher than that observed in the case of carbon monoxide, and this depends on the completely different characteristics of these two molecules. The polarization, i.e., of the M–R bond may have a much greater influence in the insertion of an electrophilic molecule such as CO_2. The insertion of DPK into both Zr–C bonds, while isocyanates and *p*-tolylcarbodiimide insert into a single Zr–C bond, emphasizes the crucial role the coordination of the CO_2-like molecule to the metal has before the migration of the alkyl group to the carbon of the heterocumulene can occur. Such a kind of precoordination seems to have a double function, that of providing in a close geometrical proximity the group to which the alkyl group can migrate and that of enhancing the polarization of the inserting molecule. A combination of the two factors may be responsible for the occurrence of the insertion of CO_2 and CO_2-like molecules into a metal–carbon bond.

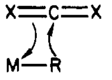
Therefore, the easiest insertion of DPK can be related to the fact that it is the most polarized cumulene structure. Isocyanates insert better than *p*-tolylcarbodiimide, which has a symmetric structure. Coordination of one of the nitrogen atoms of the carbodiimide to the acidic metal can promote, in a preliminary step, a polarization of the X=C=X structure, suitable for the migration of R. Carbodiimides are known to bind a metal through the lone pairs of the nitrogen atoms,[23] while such a bonding mode has never been found for CO_2 even in the presence of very strong Lewis acids. On these basis, we expect CO_2 to be the most difficult to insert into a Zr–C bond.

Following the observation outlined above, insertion of CO_2 and heteroallenes into a M–C σ-bond, in complexes such as I–III, can be promoted as reported in (4). Precoordination of the hetero-cumulene molecule can be viewed as involving the interaction with the M–R polarized structure rather than with the single metallic site, in a sort of bifunctional activation b.[24] Such a picture is very similar to that (a) given in reaction 4. Carbon dioxide has been reported to prefer such a kind of "bifunctional" interaction either when it is involved in simple reactions[25] or when it is interacting with inorganic complexes.[26] The present results emphasize how the utilization of molecules resembling CO_2 can help the understanding of the factors controlling metal-promoted CO_2 transformations.



a

(4)



b

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Registry No. I, 12636-72-5; II, 37206-41-0; III, 51177-89-0; IV, 94294-83-4; V, 94294-84-5; VI, 94294-85-6; VII, 94294-86-7; VIII, 94294-87-8; IX, 94294-88-9; X, 94294-89-0; XI, 94294-90-3; $\{(cp)_2Zr(Ph)[p\text{-}MeC_6H_4N{\cdots}C(Ph){\cdots}NC_6H_4Me\text{-}p]\}$, 94294-91-4; DPK, 525-06-4; $C_6H_{11}NCO$, 3173-53-3; PhNCO, 103-71-9; $p\text{-}MeC_6H_4N{=}C{=}NC_6H_4Me\text{-}p$, 726-42-1; CO_2, 124-38-9; CH_3COOH, 64-19-7; 1-naphthyl isocyanate, 86-84-0.

Supplementary Material Available: Listings of observed and calculated structure factors, unrefined hydrogen coordinates for complexes IV (Table SI) and VIII (Table SII), thermal parameters (Tables SIII–V), nonessential bond distances and angles (Table SVI), and least-squares planes (Table SVII) (62 pages). Ordering information is given on any current masthead page.

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