

resulting suspension was gently heated, and then some undissolved solid was filtered out. Et₂O (30 mL) was added to the final solution, which was cooled to -30 °C for 12 h during which [cp₂ZrCl]₂O crystallized.⁹ The mother liquor was evaporated to dryness and the residue sublimed (0.03 mmHg, 98 °C) to give [cp₂ZrCl(O)Me]¹⁰ 0.37 g, 87% as crystalline solid. A THF (50 mL) suspension of [cp₂Zr(H)(Cl)] (1.9 g) was reacted with formaldehyde obtained by heating solid paraformaldehyde. The solid dissolved in 10 min, giving a solution which was evaporated to dryness. The residue sublimed gave [cp₂ZrCl(O)Me]¹⁰ (70%).

Reaction of [cp₂Zr(H)(Cl)] with RNCO [R = C₆H₁₁, *p*-MeC₆H₄, or Ph]. A THF (50 mL) suspension of [cp₂Zr(H)(Cl)] (3.98 g, 13.2 mmol) was reacted with C₆H₁₁NCO (2.0 mL, 15.6 mmol). The solid dissolved almost completely within a few minutes, and then the solvent was evaporated to dryness. The residue was dissolved in a toluene-hexane (15/70 mL) mixture and refluxed for a few minutes. Sodium chloride was filtered out and the resulting solution was allowed to stand for 1 day. Complex IV (R = C₆H₁₁), [cp₂ZrCl(O)-CH=NC₆H₁₁], crystallized (ca 81.0%). Anal. Calcd for C₁₇H₂₂ClNOZr: C, 53.28; H, 5.79; N, 3.66; Cl, 9.26. Found: C, 53.06; H, 5.86; N, 3.26; Cl, 8.51. ¹H NMR (CHCl₃) δ 0.30 (s, 1 H, C₆H₁₁), 1.60 (m, 10 H, C₆H₁₁), 6.10 (s, 10 H, cp), 8.80 (s, 1 H, CH); IR (C-N) (Nujol) ν 1675 cm⁻¹. Reactions with *p*-MeC₆H₄NCO and PhNCO have been carried out under the same conditions. Complex IV (R = *p*-MeC₆H₄), cp₂ZrCl(O)-*p*-MeC₆H₄N=CH-O, was obtained (ca. 51%), as a crystalline solid. Anal. Calcd for C₁₈H₁₈ClNOZr: C, 55.29; H, 4.64; N, 3.58; Cl, 9.07. Found: C, 54.19; H, 4.79; N, 3.30; Cl, 8.89. ¹H NMR (CHCl₃) δ 2.31 (s, 3 H, Me), 6.25 (s, 10 H, cp), 7.18 (m, 4 H, Ph), 8.21 (s, 1 H, CH); IR (C-N) (Nujol) ν 1665 cm⁻¹.

Complex IV (R = Ph), [cp₂ZrCl(O)(PhN=CH-O)], was obtained (49%) as a crystalline solid. Anal. Calcd for C₁₇H₁₆ClNOZr: C, 54.17; H, 4.28; N, 3.71; Cl, 9.40. Found: C, 53.85; H, 4.19; N, 3.45; Cl, 9.45. ¹H NMR (CHCl₃) δ 6.33 (s, 10 H, cp), 7.23 (m, 5 H, Ph), 8.27 (s, 1 H, CH); IR (C-N) (Nujol) ν 1675 cm⁻¹.

Reaction of Complex IV (R = C₆H₁₁) with [cp₂Zr(H)(Cl)]. A THF solution (50 mL) of complex IV, [cp₂ZrCl(O)-CH=NC₆H₁₁] (1.70 g, 4.45 mmol), was reacted with [cp₂Zr(H)(Cl)] (2.71 g, 8.98 mmol). The suspension was stirred for 2 h until the solid dissolved to form a red-orange solution. The solution was evaporated to dryness, yielding a residue, which was extracted by using boiling *n*-hexane (50 mL). The undissolved solid was filtered out and washed with *n*-hexane (10 mL) and then dissolved in toluene from which the NaCl was filtered out. The toluene solution gave on cooling 1.10 g of [cp₂ZrCl]₂O.⁹ The *n*-hexane solution was concentrated to 30 mL and cooled to -5 °C. Complex V, cp₂ZrCl[(N(Me)Cy)], crystallized as yellow needles which were very sensitive to moisture (0.9 g). Anal. Calcd for C₁₇H₂₄ClN₂Zr: C, 55.33; H, 6.55; N, 3.79; Cl, 9.61. Found: C, 55.73; H, 6.77; N, 3.62; Cl, 9.16. ¹H NMR (CHCl₃) δ 0.33 (s, 1 H, C₆H₁₁), 1.56 (m, 10 H, C₆H₁₁), 2.83 (s, 3 H, Me), 6.05 (s, 10 H, cp).

Reaction of [cp₂Zr(H)(Cl)] with R-N=C=N-R [R = C₆H₁₁ or *p*-MeC₆H₄]. A THF (50 mL) suspension of [cp₂Zr(H)(Cl)] (2.26 g, 7.46 mmol) was reacted with *p*-tolylcarbodiimide (1.70 g, 7.65 mmol) at room temperature. The solid, but NaCl, dissolved in a few minutes. The solution was evaporated to dryness and the residue dissolved in a hot mixture of toluene (30 mL) and *n*-hexane (20 mL), from which NaCl was filtered out. The solution on standing gave crystals of complex VI, [cp₂ZrCl(O)-*p*-MeC₆H₄N=C=N-C₆H₄-*p*-Me] (ca. 40.5%). Anal. Calcd for C₂₅H₂₅N₂ClZr: C, 62.54; H, 5.25; N, 5.83; Cl, 7.38. Found: C, 63.05; H, 5.52; N, 5.15; Cl, 7.91. ¹H NMR (CHCl₃) δ 2.30 (s, 3 H, Me), 2.35 (s, 3 H, Me), 6.20 (s, 10 H, cp), 7.17 (m, 8 H, Ph), 8.20 (s, 1 H, CH); IR (C-N) (Nujol) ν 1545 cm⁻¹. The reaction of C₆H₁₁NC=NC₆H₁₁ with [cp₂Zr(H)(Cl)] was carried out following the same procedure. Complex VI, [cp₂ZrCl(O)(C₆H₁₁N=C=N-C₆H₁₁)], was isolated as crystalline solid (49.5%). Anal. Calcd for C₂₂H₃₃N₂ClZr: C, 59.25; H, 7.11; N, 6.03; Cl, 7.64. Found: C, 59.29; H, 7.17; N, 5.79; Cl, 7.35. ¹H NMR (CHCl₃) δ 0.3 (2 H, C₆H₁₁), 0.8-2.2 (m, 20 H, C₆H₁₁), 6.00 (s, 10 H, cp), 7.80 (s, 1 H, CH); IR (C-N) (Nujol) ν 1550 cm⁻¹.

No reaction was observed on addition of an excess of [cp₂Zr(H)(Cl)] to complex VI.

X-ray Crystallography for Complex VI (R = C₆H₁₁). The crystal selected for study was sealed in a glass capillary under nitrogen. The reduced cell was obtained by using TRACER.¹¹ Crystal data and details of the parameters associated with data collection and refinement are given in Table I. Intensity data were collected at room temperature by using the "three point" technique. The structure amplitudes were ob-

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

form	C ₂₂ H ₃₃ ClN ₂ Zr
mol wt	464.2
cell dims at 295 K ^a	
<i>a</i> , Å	17.930 (5)
<i>b</i> , Å	13.808 (4)
<i>c</i> , Å	19.295 (5)
α, deg	90
β, deg	107.70
γ, deg	90
V, Å ³	4551 (2)
Z	8
D _{calcd} , g cm ⁻³	1.355
radiation	graphite monochromated Mo Kα (λ = 0.7107 Å)
space group	P2 ₁ /n
max cryst dimens, mm	0.37 × 0.32 × 0.84
μ, cm ⁻¹	6.02
diffractometer	Philips PW 1100
diffraction geomet	equatorial
scan type	ω/2θ
scan speed	0.100°/s
scan width, deg	1.10
2θ range, deg	6-48
reflcns measd	± <i>h</i> , ± <i>k</i> , <i>l</i>
measd tot data	9157
agreement between equiv reflns	0.027
unique tot data	7108
unique obsv data (NO)	4915
criterion for obsv	I > 3σ(I)
no. of param varied (NV)	487
R	0.040
NO/NV	10.1

^a Unit cell parameters were obtained by least-squares refinement of the setting angles of 20 carefully centered reflections chosen from diverse regions of reciprocal space. ^b A nonstandard setting of C_{2h}⁵ (no. 14). Coordinates of equivalent positions are *x*, *y*, *z*, \bar{x} , \bar{y} , \bar{z} , $1/2 - x, 1/2 + y, 1/2 - z$; $1/2 + x, 1/2 - y, 1/2 + z$.

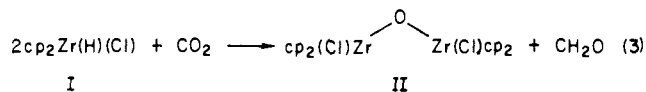
tained after the usual Lorentz and polarization reduction.¹² The absorption effects on the crystal were studied by ψ scans and considered to be negligible. No absorption correction was then applied.

The structure was solved by the heavy-atom method and refined by "blocked" full-matrix least squares first isotropically and then anisotropically. The function minimized was Σw|ΔF|². Unit weights were used since these gave acceptable agreement analyses. During the refinement, the cyclopentadienyl rings were considered as regular pentagons (C-C = 1.420 Å). All the hydrogen atoms were located from difference Fourier maps and introduced in calculations as fixed contributors prior to the final refinement (B_{iso} = 7.8 Å²). The final difference map showed no unusual features with no peak above the general background which was of about 0.3 e Å⁻³. No correction for extinction was deemed necessary.

Scattering factors were taken from ref 13a for Zr, from ref 14 for Cl, N, and C, and from ref 15 for H. Anomalous scattering corrections were included in all structure factor calculations.^{13b} Final atomic coordinates are listed in Tables II and SI, and thermal parameters are given in Table SII.¹⁶

Results and Discussion

Complex I suspended in THF reacted in a few minutes with a large excess of carbon dioxide according to reaction 3. Form-



(12) Data reduction, structure solution, and refinement were carried out on a Cyber 7600 computer of the Centro di Calcolo dell'Italia Nord-Orientale, using the SHELX-76 system of crystallographic computer programs, Sheldrick, G., University of Cambridge, Cambridge, England, 1976. Calculations were performed with the financial support of the University of Parma.

(13) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, (a) p 99, (b) p 149.

(14) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* 1968, A24, 321-324.

(15) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* 1965, 42, 3175-3187.

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

(10) Gray, D. R.; Brubaker, C. H. *Inorg. Chem.* 1971, 10, 2143-2146.

(11) Lawton, S. L.; Jacobson, R. A. TRACER cell reduction program, Ames Laboratory, Iowa State University of Science and Technology, 1965.

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

atom	molecule A			molecule B		
	X/A	Y/B	Z/C	X/A	Y/B	Z/C
Zr	6199 (0)	2446 (0)	2112 (0)	2569 (0)	4491 (0)	3469 (0)
Cl	4685 (1)	2364 (1)	1684 (1)	2825 (1)	3577 (2)	4668 (1)
N1	6020 (2)	2390 (3)	905 (2)	3522 (2)	3457 (3)	3377 (3)
N2	7233 (2)	2459 (3)	1642 (2)	2963 (2)	4399 (3)	2438 (2)
C1	5906 (2)	651 (3)	2211 (2)	3586 (5)	5564 (4)	4332 (5)
C2	5878 (2)	1079 (3)	2871 (2)	2856 (5)	5820 (4)	4426 (5)
C3	6643 (2)	1401 (3)	3258 (2)	2388 (5)	6252 (4)	3770 (5)
C4	7145 (2)	1172 (3)	2836 (2)	2829 (5)	6263 (4)	3270 (5)
C5	6689 (2)	708 (3)	2189 (2)	3570 (5)	5837 (4)	3618 (5)
C6	6578 (3)	4221 (3)	2077 (3)	1502 (3)	3475 (4)	2592 (4)
C7	5790 (3)	4227 (3)	2088 (3)	1424 (3)	3330 (4)	3296 (4)
C8	5777 (3)	3858 (3)	2771 (3)	1191 (3)	4222 (4)	3532 (4)
C9	6558 (3)	3624 (3)	3182 (3)	1124 (3)	4918 (4)	2975 (4)
C10	7053 (3)	3848 (3)	2753 (3)	1316 (3)	4456 (4)	2394 (4)
C11	5452 (3)	2379 (4)	167 (3)	4131 (3)	2736 (4)	3723 (4)
C12	4961 (4)	1461 (5)	38 (3)	4758 (4)	3124 (4)	4336 (4)
C13	4338 (4)	1463 (6)	-720 (4)	5379 (4)	2383 (5)	4682 (4)
C14	3843 (4)	2369 (7)	-811 (4)	5055 (5)	1440 (6)	4830 (5)
C15	4333 (4)	3266 (6)	-721 (4)	4437 (4)	1067 (4)	4225 (4)
C16	4954 (3)	3283 (4)	30 (3)	3786 (4)	1816 (4)	3864 (4)
C17	6778 (3)	2423 (4)	968 (3)	3480 (3)	3724 (4)	2704 (3)
C18	8093 (3)	2495 (4)	1832 (3)	2837 (3)	4785 (4)	1700 (3)
C19	8380 (3)	3310 (4)	1450 (4)	2567 (4)	3990 (5)	1109 (4)
C20	9280 (4)	3339 (5)	1683 (4)	2450 (6)	4429 (7)	356 (4)
C21	9609 (3)	2379 (5)	1544 (4)	3144 (6)	4945 (7)	272 (4)
C22	9343 (3)	1578 (5)	1933 (4)	3406 (5)	5696 (7)	856 (5)
C23	8447 (3)	1527 (4)	1713 (3)	3557 (4)	5306 (5)	1625 (4)

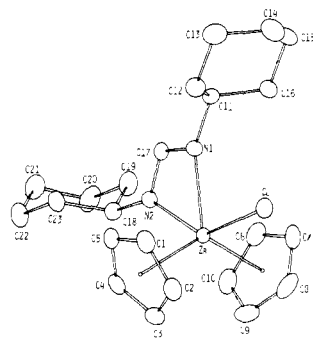
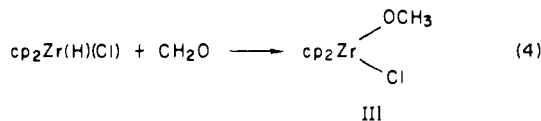
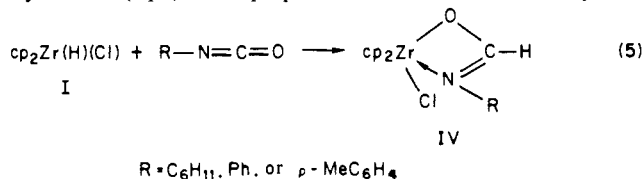


Figure 1. ORTEP drawing of complex VI (molecule A) (30% probability ellipsoids).

aldehyde formed can be trapped either to form the dimedone derivative or by adding an excess of I, reducing CH_2O to methoxy group in complex III (reaction 4). Separation of complexes II

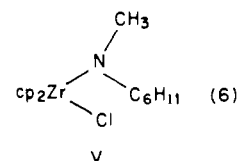
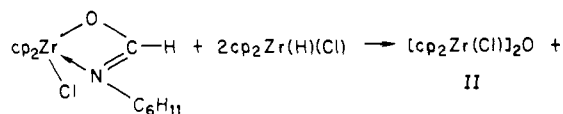


and III was carried out as reported in the Experimental Section. The reaction of I with CO_2 did not lead to an observable or detectable metalloformate complex, as normally occurs for all the other hydrido complexes so far investigated.^{2,3,7,8} I was reacted with isocyanates, RNCO [$\text{R} = \text{C}_6\text{H}_{11}$, Ph, or $p\text{-MeC}_6\text{H}_4$] with the purpose to understand the steps preceding the reduction of CO_2 to formaldehyde and methanol. Reaction 5 was carried out in THF with a slight excess of RNCO over complex I (see Experimental Section). From the resulting solution, compound IV crystallized (eq 5). The proposed formula is based on analytical,

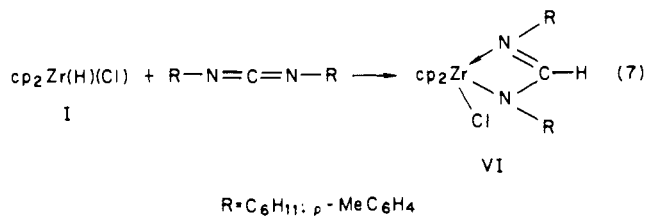


IR, and NMR data. The bidentate bonding mode of the form-

amido ligand is based on the CN stretching value (1675 cm^{-1}) and by analogy with the solid-state structure determined for complex VI ($\text{R} = \text{C}_6\text{H}_{11}$) (vide infra) and for complexes $\text{cp}_2\text{Zr}(\text{R})[\text{O}-\text{C}(\text{R})-\text{NR}']$ [$\text{R} = \text{Me}$, PhCH_2 , or Ph; $\text{R}' = \text{Ph}$, 1-naphthyl, or C_6H_{11}], for which an X-ray analysis was reported.¹⁷ The formamido ligand underwent reduction with an excess of complex I. Two moles of I was consumed per mole of complex IV ($\text{R} = \text{C}_6\text{H}_{11}$), to form an orange THF solution from which, by the procedure reported in the Experimental Section, complexes II and V were separated and identified (eq 6). Complex V was obtained



as yellow crystalline solid, very sensitive to moisture. We must point out that the oxygen is removed from both substrates, CO_2 and RNCO , in the form of oxo ligand found in complex II and that the oxophilicity of zirconium seems to be the driving force of those steps subsequent to reaction 1. In order to prove this hypothesis, I was reacted with carbodiimides: $\text{R}-\text{N}=\text{C}=\text{N}-\text{R}$ [$\text{R} = \text{C}_6\text{H}_{11}$ or $p\text{-MeC}_6\text{H}_4$]. The reaction occurred as reported in eq 7, independently of the carbodiimide/I molar ratio, and gave complexes VI which were isolated as crystalline solids (eq 7). The



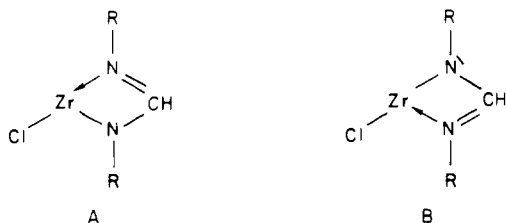
(17) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.*, in press.

Table III. Selected Bond Distances (Å) and Angles (deg)

	molec A	molec B		molec A	molec B
Zr-Cl	2.589 (2)	2.551 (2)	N1-C17	1.328 (6)	1.329 (8)
Zr-N1	2.252 (4)	2.275 (5)	N2-C17	1.309 (6)	1.305 (6)
Zr-N2	2.298 (4)	2.310 (5)	N1-C11	1.477 (6)	1.479 (7)
Zr-Cp1	2.248 (4)	2.235 (6)	N2-C18	1.473 (6)	1.472 (7)
Zr-Cp2	2.252 (4)	2.243 (5)			
Cp1-Zr-Cp2	130.4 (2)	127.6 (3)	Zr-N1-C17	94.8 (3)	94.7 (3)
N2-Zr-Cp2	97.7 (2)	97.9 (2)	Zr-N1-C11	146.8 (4)	148.9 (4)
N2-Zr-Cp1	97.4 (2)	100.0 (2)	C11-N1-C17	118.3 (4)	116.3 (5)
N1-Zr-Cp2	113.8 (2)	119.0 (2)	Zr-N2-C17	93.3 (3)	93.8 (3)
N1-Zr-Cp1	114.3 (2)	112.2 (3)	Zr-N2-C18	144.2 (3)	144.7 (3)
N1-Zr-N2	58.1 (2)	57.6 (2)	C17-N2-C18	122.5 (4)	121.5 (5)
Cl-Zr-Cp2	99.0 (1)	98.8 (2)	N1-C17-N2	113.8 (5)	113.9 (5)
Cl-Zr-Cp1	98.8 (1)	100.2 (2)			
Cl-Zr-N2	140.2 (1)	137.4 (1)			
Cl-Zr-N1	82.1 (1)	80.1 (1)			

characterization of complexes VI was carried out by the usual analytical means, including an X-ray analysis on VI [R = C₆H₁₁].

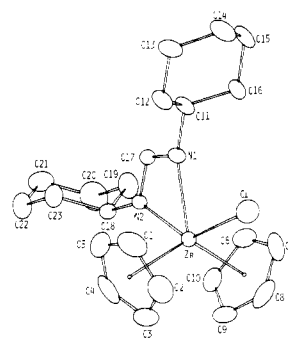
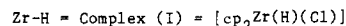
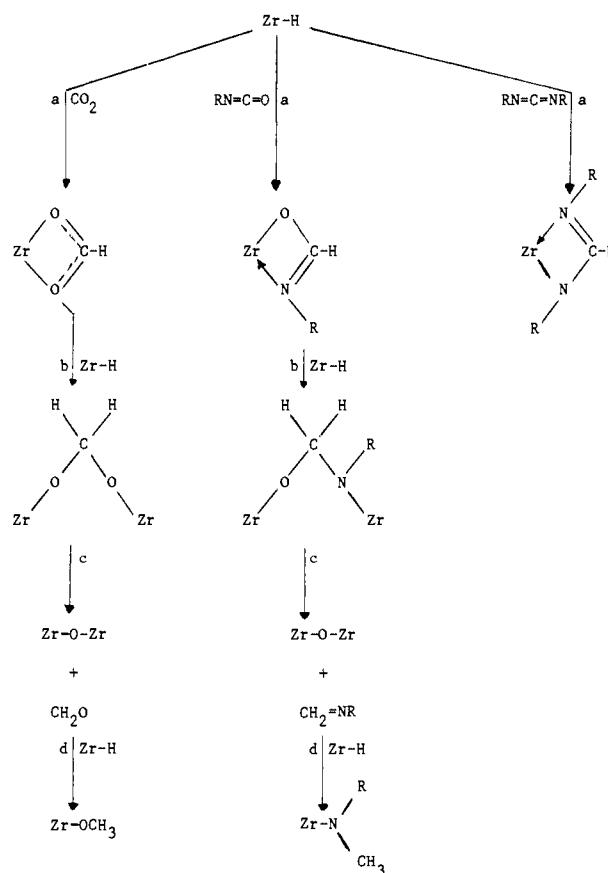
In the asymmetric unit, there are two crystallographically independent molecules [Figures 1 and 2] which are not significantly different. The two cp rings, which are η⁵-bonded to zirconium, make a cavity in the equatorial plane for Cl and the amidino ligand, which is bonded to the metal through both nitrogen atoms. Chlorine is only slightly out [0.021 (2) Å in molecule A and 0.216 (2) Å in molecule B] of the plane defined by Zr, N1, N2, and C17 atoms (Table SV). Zr-Cl bond distances [Table III] fall in the range expected for complexes having a five-coordinate zirconium,^{18,19} but they are significantly different to each other [2.589 (2) Å in molecule A and 2.551 (2) Å]. This difference, however, must be ascribed to packing forces. N-C bond distances are close [C17-N1, 1.328 (6), C17-N2, 1.309 (6) Å in molecule A; C17-N1, 1.329 (8), C17-N2, 1.305 (6) Å in molecule B], and they have a double bond character [Table III]. A slight difference can be observed for the N1 and N2 atoms, N1 having a distorted pyramidal geometry. N1 is out by 0.026 (4) Å [molecule A] and 0.033 (5) Å [molecule B] from the plane defined by Zr, C17, and C18, while N2 is coplanar with Zr, C17, and C18. These values are in favor of the canonical form A vs. B for complex VI: The



Zr-N bond distances are slightly different (Zr-N1 [2.252 (4) Å in molecule A, and 2.275 (5) Å in molecule B]; Zr-N2 [2.298 (4) Å in molecule A, and 2.275 (5) Å in molecule B]), and they compare well with those found in related complexes.^{17,18} All the other structural parameters are in the usual ranges.¹⁸ The cyclohexyl rings have a chair conformation.

Attempts of reducing VI by using a large excess of I were unsuccessful. Reduction [see reaction 2] of organometallic functionalities formed from the insertion of CO₂ and CO₂-like molecules into the M-H bond by using a Zr complex occurs only when there is an oxygen atom on the substrate. This result is in agreement with the oxophilicity of the metal being the driving force of these reductions. On the basis of the results outlined above, we can sketch the pathways in Scheme I for the reduction of CO₂ and its analogues by complex I.

This pathway is justified by the isolation and identification of the compounds formed in the steps a, c, and d. The impossibility to reduce carbodiimide behind step a depends on the absence of

**Figure 2.** ORTEP drawing of complex VI (molecule B) (30% probability ellipsoids).**Scheme I**

(18) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1983**, *22*, 2029-2034 and references therein.

(19) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690-1691.

any oxygen atom in the structure. Step b is so easy in the case of CO₂ that [cp₂Zr(O₂CH)Cl] has not been detected. This is not

surprising since the inorganic functionality [ZrO₂CH] can be related to an ester, which is very easily reduced by complex I^{5b,20,21} in a related reaction. Step d is proven by having carried out the reaction between I and formaldehyde leading to [cp₂Zr(Cl)(OMe)], while addition of a C=N multiple bond to the Zr-H bond in complex I was recently reported.²² The oxophilicity of zirconium and the formation of a very stable complex II are the real driving force of the reduction of CO₂ in the reactions outlined above.

The present study suggests that reduction of CO₂ by a M-H

(20) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333-340.

(21) Wailes, P. C.; Weigold, H. J. *Organomet. Chem.* **1970**, *24*, 413-417.

(22) Erker, G.; Fromberg, W.; Atwood, J. L.; Hunter, W. E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 68-69; *J. Organomet. Chem.* **1984**, *280*, 343-354, 355-363.

bond could be an interesting process provided two fundamental research lines are pursued. The first one is a study on the reduction of the metalloformate functionality, while the second one, which is the most crucial problem in the activation of oxygen containing molecules, is how to react the M-O-M, M-O-R, and M=O inorganic functionalities.

Acknowledgment. We thank CNR (Rome) for financial support.

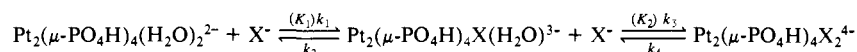
Supplementary Material Available: Listing of observed and calculated structure factors, hydrogen coordinates (Table SI), anisotropic thermal parameters (Table SII), nonessential bond distances and angles (Table SIII), torsion angles in cyclohexyl rings (Table SIV), and equation of least-squares planes (Table SV) (26 pages). Ordering information is given on any current masthead page.

Axial Ligand Anation and Aquation Reactions in Diplatinum(III) Complexes. Comparison of Aquation Rates between PtCl₆²⁻ and Diplatinum(III) Chloro Complexes Having μ-Phosphato or μ-Pyrophosphito Ligands

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Abstract: The diplatinum(III) complex [Pt₂(μ-PO₄H)₄(H₂O)₂]²⁻ reacts with halide ions X⁻ (X = Cl, Br) to give first [Pt₂(μ-PO₄H)₄X(H₂O)]³⁻ and then [Pt₂(μ-PO₄H)₄X₂]⁴⁻. The reaction establishes an equilibrium situation between the three complexes:



Using pseudo-first-order conditions in halide ion at 25 °C, we have used a biphasic analysis to evaluate the rate constants. The values are $k_1 = 0.9$ (2) M⁻¹ s⁻¹, $k_2 = 5$ (1) × 10⁻² s⁻¹, $k_3 = 0.8$ (2) M⁻¹ s⁻¹, $k_4 = 8$ (2) × 10⁻² s⁻¹ (X = Cl) and $k_1 = 0.3$ (1) M⁻¹ s⁻¹, $k_2 = 1.5$ (3) × 10⁻² s⁻¹, $k_3 = 0.4$ (1) M⁻¹ s⁻¹, $k_4 = 1.9$ (3) × 10⁻² s⁻¹ (X = Br). Under comparable conditions of temperature (25 °C), pH (3.0), and ionic strength (0.1 M), we have measured the equilibrium constants as $K_1 = 19$ (2) M⁻¹, $K_2 = 11$ (1) M⁻¹ (X = Cl) and $K_2 = 21$ (2) M⁻¹, $K_2 = 22$ (2) M⁻¹ (X = Br). In all cases, $k_1 > k_2$ and $k_3 > k_4$, and $k_1 \approx k_3$ and $k_2 \approx k_4$. The axially coordinated halide ligands at 6-coordinate platinum are substituted some 4 orders of magnitude faster than axial halides in the μ-pyrophosphito complexes [Pt₂(μ-P₂O₅H₂)₄X₂]⁴⁻ or chloride in PtCl₆²⁻. This axial halide labilization in [Pt₂(μ-PO₄H)₄X₂]⁴⁻ (X = Cl, Br) as compared to PtCl₆²⁻ is believed to be a consequence of a strong intermetallic bond between platinum.

The chemistry of metal-metal bonded complexes continues to be a subject of active interest.¹ A large body of work now exists describing the synthesis of numerous transition-metal complexes having a wide variety of bridging ligands and terminal end groups. Many of these complexes have been structurally characterized, but only a relatively small amount of work has been published correlating differences in substitution patterns and rates with variations in intermetallic bonding between sets of complexes. Such studies are valuable if major changes in reactivity or selectivity are to be identified because they confirm that an intermetallic bond is a variable quantity that can be changed to induce desired differences in reaction chemistry.

Recently three series of diplatinum(III) complexes have been prepared that allow us to test this premise. One set of complexes has a bridging pyridinato-*N,O* ligand,² and a second set has a pyrophosphito-*P,P* group as a bridge.³ A third group, which we classify as a single set, has either a bridging sulfato-*O,O* or hy-

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