# Stepwise Reduction of Carbon Dioxide to Formaldehyde and Methanol: Reactions of $\mathrm{CO}_{2}$ and $\mathrm{CO}_{2}$-like Molecules with Hydridochlorobis(cyclopentadienyl)zirconium(IV) 

Sandro Gambarotta, ${ }^{\dagger \ddagger}$ Sauro Strologo, ${ }^{\dagger}$ Carlo Floriani, ${ }^{*+\ddagger}$ Angiola Chiesi-Villa, ${ }^{8}$ and Carlo Guastini ${ }^{8}$<br>Contribution from the Istituto di Chimica Generale, Universitá di Pisa, 56100 Pisa, Italy, and the Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Universitá di Parma, 43100 Parma, Italy. Received March 11, 1985


#### Abstract

Stoichiometric reduction of carbon dioxide to formaldehyde and methanol was achieved by using $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{H})(\mathrm{Cl})\right]_{n}$ as the reducing agent. Two steps have been recognized in such a reduction, the first one leading to the formation of formaldehyde and $\left[\mathrm{CP}_{2} \mathrm{Zr}(\mathrm{Cl})\right]_{2} \mathrm{O}$, and the second involving the reduction of formaldehyde to the methoxy ligand in $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{OMe})(\mathrm{Cl})\right]$ by $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{Cl})(\mathrm{H})\right]$. The oxophilicity of metal and the high stability of the $\mu$-oxo complex seem to be the driving force of the reaction. This hypothesis and all the steps involved in the reduction of $\mathrm{CO}_{2}$ by the $\mathrm{Zr}-\mathrm{H}$ functionality have been elucidated by reducing $\mathrm{CO}_{2}$-like molecules with a variable content of oxygen, i.e., $\mathrm{R}-\mathrm{N}=\mathrm{C}=\mathrm{O}$ and $\mathrm{R}^{\prime}-\mathrm{N}=\mathrm{C}=\mathrm{N}-\mathrm{R}^{\prime}$. Carbodiimides insert into the $\mathrm{Zr}-\mathrm{H}$ bond, forming an amidino ligand which might not be futher reduced by the $\mathrm{Zr}-\mathrm{H}$ bond. Isocyanate inserted into the $\mathrm{Zr}-\mathrm{H}$ bond, forming formamido ligands which were further reduced by the $\mathrm{Zr}-\mathrm{H}$ unit to methylamido group by the intermediacy of the $\left[\mathrm{CH}_{2}=\mathrm{NR}\right]$ imine. The presence of an oxygen on the formamido ligand would explain its reducibility to the imine by the simultaneous formation of the very stable $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{Cl})\right]_{2} \mathrm{O}$. The structure of the formamidino complex formed from the insertion of $\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{~N}=\mathrm{C}=\mathrm{NC}_{6} \mathrm{H}_{4}$ into the $\mathrm{Zr}-\mathrm{H}$ bond was determined by an X -ray analysis. Crystallographic details of $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{Cl})\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{~N}-\mathrm{CH}-\mathrm{NC}_{6} \mathrm{H}_{4}\right)\right]$ are as follows: space group $P 2_{1} / n$ (monoclinic); $a=17.930$ ( 5 ) $\AA ; b=13.808$ (4) $\AA ; c=19.295(5) \AA ; \beta=107.70^{\circ} ; V=4551$ (2) $\AA^{3} ; Z=8$; final $R$ factor was 0.040 for 4915 observed reflections.


Two main goals have been envisaged in metal-promoted transformations of carbon dioxide: ${ }^{1-4}$ its reduction to $\mathrm{C}_{1}$ molecules, i.e., $\mathrm{CH}_{2} \mathrm{O}$ and $\mathrm{CH}_{3} \mathrm{OH}$, or its transformation into organic molecules via $\mathrm{C}-\mathrm{C}$ bond formation either with itself or by the incorporation into an organic substrate. The two objectives require different strategies: the first one a detailed investigation on the reaction of $\mathrm{CO}_{2}$ with the $\mathrm{M}-\mathrm{H}$ organometallic functionality; the second one with M-C bonds and the fixation of $\mathrm{CO}_{2}$ by transi-tion-metal complexes leading to $\mathrm{M}-\mathrm{C}$ bonds.

The present report is dealing with the factors affecting the transformation of $\mathrm{CO}_{2}$ to $\mathrm{CH}_{2} \mathrm{O}^{5}$ and $\mathrm{CH}_{3} \mathrm{OH}$ using as a model compound Schwartz's reagent, $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{H})(\mathrm{Cl})\right]_{n}\left[\mathrm{cp}=\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right]$. ${ }^{6}$ Examples of reaction of $\mathrm{CO}_{2}$ with $\mathrm{M}-\mathrm{H}$ bonds are very numerous in the literature. This reaction is producing exclusively metalloformates (reaction 1) by the so-called insertion of $\mathrm{CO}_{2}$ into a $\mathrm{M}-\mathrm{H}$ bond. ${ }^{2.3 .7 .8}$ An unanswered question remains, however: how

to reduce the metalloformato species by a $\mathrm{M}-\mathrm{H}$ functionality (eq 2). We did not find any report concerning reaction 2 and,

$$
\begin{equation*}
\mathrm{L}_{n} \mathrm{M}-\mathrm{O}-\mathrm{C}(=\mathrm{O})-\mathrm{H}+\mathrm{L}_{n} \mathrm{M}^{*}-\mathrm{H} \xrightarrow{?} \tag{2}
\end{equation*}
$$

implicitely, the steps following reaction 1 involved in the reduction of $\mathrm{CO}_{2}$. The stepwise reduction of carbon dioxide has been elucidated in the case of an oxophilic metal by studying the reaction of $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{H})(\mathrm{Cl})\right]$ with $\mathrm{CO}_{2}$ and $\mathrm{CO}_{2}$-like molecules having a different content in oxygen atoms in their structure, i.e., $\mathrm{RN}=$ $\mathrm{C}=\mathrm{O}$ and $\mathrm{RN}=\mathrm{C}=\mathrm{NR}$.

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## Experimental Section

All the operations were carried out under an atmosphere of purified nitrogen. Solvents were purified as described in the literature. IR spectra were recorded with a Perkin-Elmer 283 spectrophotometer. ${ }^{1} \mathrm{H}$ NMR spectra were taken with a E-360 ( 60 MHz ) Varian apparatus. The reported synthesis for $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{H})(\mathrm{Cl})\right]_{n}$ gives the zirconium complex containing $\mathrm{NaCl}{ }^{6}$ Isocyanates and carbodiimides are commercially available products purified by standard methods.

Reduction of Carbon Dioxide to Formaldehyde. $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{H}) \mathrm{Cl}\right](0.64$ $\mathrm{g}, 2.10 \mathrm{mmol}$ on the basis of the hydrogen content) was suspended in THF ( 20 mL ) and reacted with carbon dioxide. The zirconium complex dissolved leaving NaCl as an insoluble solid. The colorless solution was evaporated to dryness to give a white crystalline solid ( 0.58 g ) $\left[\mathrm{cp}_{2} \mathrm{ZrCl}_{2} \mathrm{O} .^{9}\right.$ The mother liquor was distilled carefully in vacuo and reacted with dimedone $(0.40 \mathrm{~g})$ and a few drops of water. The solution was heated for 5 min at $40-50^{\circ} \mathrm{C}$, until crystallization yields a white solid ( $\mathrm{mp} 190^{\circ} \mathrm{C}$ ). The solid was found identical with the dimedone derivative of formaldehyde.

Reduction of Carbon Dioxide to Methanol. A THF suspension of $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{H})(\mathrm{Cl})\right](0.95 \mathrm{~g}, 2.97 \mathrm{mmol})$ was exposed to a $\mathrm{CO}_{2}$ atmosphere. The zirconium complex dissolved leaving a small a mount of NaCl , which was filtered out. The colorless solution was concentrated in vacuo to 20 mL , and then $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{H})(\mathrm{Cl})\right](0.50 \mathrm{~g}, 1.64 \mathrm{mmol})$ was added. The

[^1]resulting suspension was gently heated, and then some undissolved solid was filtered out. $\mathrm{Et}_{2} \mathrm{O}(30 \mathrm{~mL})$ was added to the final solution, which was cooled to $-30{ }^{\circ} \mathrm{C}$ for 12 h during which $\left[\mathrm{cp}_{2} \mathrm{ZrCl}\right]_{2} \mathrm{O}$ crystallized. ${ }^{9}$ The mother liquor was evaporated to dryness and the residue sublimed $\left(0.03 \mathrm{mmHg}, 9{ }^{\circ} \mathrm{C}\right)$ to give $\left.\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{Cl})(\mathrm{OMe})\right]^{10} 0.37 \mathrm{~g}, 87 \%\right)$ as crystalline solid. A THF ( 50 mL ) suspension of $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{H})(\mathrm{Cl})\right](1.9 \mathrm{~g})$ 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 $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{Cl})(\mathrm{OMe})\right]^{10}$ (70\%).

Reaction of $\left[\mathrm{CP}_{2} \mathrm{Zr}(\mathrm{H})(\mathrm{Cl})\right]$ with $\mathrm{RNCO}\left[\mathrm{R}=\mathbf{C}_{6} \mathbf{H}_{11}, \boldsymbol{p}-\mathrm{MeC}_{6} \mathbf{H}_{4}\right.$, or Ph). A THF ( 50 mL ) suspension of $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{H})(\mathrm{Cl})\right](3.98 \mathrm{~g}, 13.2 \mathrm{mmol})$ was reacted with $\mathrm{C}_{6} \mathrm{H}_{11} \mathrm{NCO}(2.0 \mathrm{~mL}, 15.6 \mathrm{mmol})$. 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 $\left(\mathrm{R}=\mathrm{C}_{6} \mathrm{H}_{11}\right),\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{Cl})\left(\mathrm{O}-\mathrm{CH}=\mathrm{NC}_{6} \mathrm{H}_{11}\right)\right]$, crystallized (ca $81.0 \%$ ). Anal. Caled for $\mathrm{C}_{17} \mathrm{H}_{22} \mathrm{CINOZr}: \mathrm{C}, 53.28 ; \mathrm{H}, 5.79 ; \mathrm{N}$, 3.66; Cl, 9.26. Found: C, $53.06 ; \mathrm{H}, 5.86 ; \mathrm{N}, 3.26 ; \mathrm{Cl}, 8.51 .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CHCl}_{3}\right) \delta 0.30\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{11}\right), 1.60\left(\mathrm{~m}, 10 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{11}\right), 6.10(\mathrm{~s}, 10 \mathrm{H}$, $\mathrm{cp}), 8.80(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}) ;$ IR (C-N) (Nujol) $\nu 1675 \mathrm{~cm}^{-1}$. Reactions with $p-\mathrm{Me}_{6} \mathrm{H}_{4} \mathrm{NCO}$ and PhNCO have been carried out under the same conditions. Complex IV ( $\mathrm{R}=p-\mathrm{MeC}_{6} \mathrm{H}_{4}$ ), $\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{Cl})\left(p-\mathrm{MeC}_{6} \mathrm{H}_{4} \mathrm{~N}=\right.$ $\mathrm{CH}-\mathrm{O}$ ), was obtained (ca. $51 \%$ ), as a crystalline solid. Anal. Calcd for $\mathrm{C}_{18} \mathrm{H}_{18} \mathrm{ClNOZr}: \mathrm{C}, 55.29 ; \mathrm{H}, 4.64 ; \mathrm{N}, 3.58 ; \mathrm{Cl}, 9.07$. Found: C , $54.19 ; \mathrm{H}, 4.79 ; \mathrm{N}, 3.30 ; \mathrm{Cl}, 8.89 .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CHCl}_{3}\right) \delta 2.31(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Me})$, $6.25(\mathrm{~s}, 10 \mathrm{H}, \mathrm{cp}), 7.18(\mathrm{~m}, 4 \mathrm{H} . \mathrm{Ph}), 8.21(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH})$; IR (C-N) (Nujol) $v 1665 \mathrm{~cm}^{-1}$.

Complex IV $(\mathrm{R}=\mathrm{Ph}),\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{Cl})(\mathrm{PhN}=\mathrm{CH}-\mathrm{O})\right]$, was obtained (49\%) as a crystalline solid. Anal. Calcd for $\mathrm{C}_{17} \mathrm{H}_{16} \mathrm{ClNOZr}$ : C, 54.17; $\mathrm{H}, 4.28 ; \mathrm{N}, 3.71 ; \mathrm{Cl}, 9.40$. Found: $\mathrm{C}, 53.85 ; \mathrm{H}, 4.19 ; \mathrm{N}, 3.45 ; \mathrm{Cl}, 9.45$. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CHCl}_{3}\right) \delta 6.33(\mathrm{~s}, 10 \mathrm{H}, \mathrm{cp}), 7.23(\mathrm{~m}, 5 \mathrm{H}, \mathrm{Ph}), 8.27(\mathrm{~s}, 1 \mathrm{H}$, CH ); IR (C-N) (Nujol) $\nu 1675 \mathrm{~cm}^{-1}$.

Reaction of Complex IV $\left(\mathbf{R}=\mathbf{C}_{6} \mathrm{H}_{11}\right)$ with $\left[\mathbf{c p}_{2} \mathbf{Z r}(\mathrm{H})(\mathrm{Cl})\right]$. A THF solution ( 50 mL ) of complex IV, $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{Cl})\left(\mathrm{O}-\mathrm{CH}=\mathrm{NC}_{6} \mathrm{H}_{11}\right)\right](1.70$ $\mathrm{g}, 4.45 \mathrm{mmol})$, was reacted with $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{H})(\mathrm{Cl})\right](2.71 \mathrm{~g}, 8.98 \mathrm{mmol})$. 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 $(10 \mathrm{~mL})$ and then dissolved in toluene from which the NaCl was filtered out. The toluene solution gave on cooling 1.10 g of $\left[\mathrm{cp}_{2} \mathrm{ZrCl}\right]_{2} \mathrm{O} .{ }^{9}$ The $n$-hexane solution was concentrated to 30 mL and cooled to $-5^{\circ} \mathrm{C}$. Complex V, $\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{Cl})[(\mathrm{N}(\mathrm{Me})(\mathrm{Cy})]$, crystallized as yellow needles which were very sensitive to moisture ( 0.9 g ). Anal. Calcd for $\mathrm{C}_{17} \mathrm{H}_{24} \mathrm{ClNZr}$ : C, 55.33; $\mathrm{H}, 6.55 ; \mathrm{N}, 3.79 ; \mathrm{Cl}, 9.61$. Found: $\mathrm{C}, 55.73 ; \mathrm{H}, 6.77, \mathrm{~N}, 3.62 ; \mathrm{Cl}, 9.16$. ${ }^{1} \mathrm{H}^{2} \mathrm{NMR}\left(\mathrm{CHCl}_{3}\right) \delta 0.33\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{11}\right), 1.56\left(\mathrm{~m}, 10 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{11}\right), 2.83$ ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Me}$ ) , $6.05(\mathrm{~s}, 10 \mathrm{H}, \mathrm{cp})$.

Reaction of $\left[\mathbf{c P}_{2} \mathrm{Zr}(\mathrm{H})(\mathbf{C l})\right]$ with $\mathbf{R}-\mathbf{N}=\mathbf{C}=\mathbf{N}-\mathbf{R}\left[\mathbf{R}=\mathbf{C}_{6} \mathrm{H}_{11}\right.$ or $\left.\boldsymbol{p}-\mathrm{MeC}_{6} \mathrm{H}_{4}\right]$. A THF $(50 \mathrm{~mL})$ suspension of $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{H})(\mathrm{Cl})\right](2.26 \mathrm{~g}, 7.46$ mmol) was reacted with $p$-tolylcarbodiimide ( $1.70 \mathrm{~g}, 7.65 \mathrm{mmol}$ ) 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, $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{Cl})\left(p-\mathrm{MeC}_{6} \mathrm{H}_{4} \mathrm{~N}=\mathrm{CH}=-\mathrm{NC}_{6} \mathrm{H}_{4}-p-\mathrm{Me}\right)\right]$ (ca. 40.5\%). Anal. Caled for $\mathrm{C}_{25} \mathrm{H}_{25} \mathrm{~N}_{2} \mathrm{ClZr}$ : C, 62.54; H, 5.25; $\mathrm{N}, 5.83 ; \mathrm{Cl}, 7.38$. Found: C, 63.05; H, 5.52; N, 5.15; Cl, 7.91. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CHCl}_{3}\right) \delta 2.30(\mathrm{~s}, 3 \mathrm{H}$, Me ), 2.35 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Me}$ ), $6.20(\mathrm{~s}, 10 \mathrm{H}, \mathrm{cp}), 7.17(\mathrm{~m}, 8 \mathrm{H}, \mathrm{Ph}), 8.20(\mathrm{~s}$, $1 \mathrm{H}, \mathrm{CH}$ ); IR (C-N) (Nujol) $\nu 1545 \mathrm{~cm}^{-1}$. The reaction of $\mathrm{C}_{6} \mathrm{H}_{11} \mathrm{NC}$ $\mathrm{NC}_{6} \mathrm{H}_{11}$ with $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{H})(\mathrm{Cl})\right]$ was carried out following the same procedure. Complex VI, $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{Cl})\left(\mathrm{C}_{6} \mathrm{H}_{11} \mathrm{~N}=\mathrm{CH}=\mathrm{NC}_{6} \mathrm{H}_{11}\right)\right]$, was isolated as crystalline solid (49.5\%). Anal. Caled for $\mathrm{C}_{23} \mathrm{H}_{33} \mathrm{~N}_{2} \mathrm{ClZr}$ : C , $59.25 ; \mathrm{H}, 7.11 ; \mathrm{N}, 6.03 ; \mathrm{Cl}, 7.64$. Found: C, $59.29 ; \mathrm{H}, 7.17$; N, 5.79 ; $\mathrm{Cl}, 7.35 .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CHCl}_{3}\right) \delta 0.3\left(2 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{11}\right), 0.8-2.2(\mathrm{~m}, 20 \mathrm{H}$, $\left.\mathrm{C}_{6} \mathrm{H}_{11}\right), 6.00(\mathrm{~s}, 10 \mathrm{H}, \mathrm{cp}), 7.80(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}) ;$ IR (C-N) (Nujol) v 1550 $\mathrm{cm}^{-1}$.

No reaction was observed on addition of an excess of $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{H})(\mathrm{Cl})\right]$ to complex VI.

X-ray Crystallography for Complex VI ( $R=\mathrm{C}_{6} \mathrm{H}_{11}$ ). 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-
(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 I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

| form | $\mathrm{C}_{23} \mathrm{H}_{33} \mathrm{ClN} \mathrm{N}_{2} \mathrm{Zr}$ |
| :---: | :---: |
| mol wt | 464.2 |
| cell dimens at $295 \mathrm{~K}^{\text {a }}$ |  |
| $a, \AA$ | 17.930 (5) |
| $b, \AA$ | 13.808 (4) |
| $c, \AA$ | 19.295 (5) |
| $\alpha$, deg | 90 |
| $\beta$, deg | 107.70 |
| $\gamma$, deg | 90 |
| $V, \AA^{3}$ | 4551 (2) |
| $Z$ | 8 |
| $D_{\text {calcd }}, \mathrm{g} \mathrm{cm}^{-3}$ | 1.355 |
| radiation | graphite monochromated <br> Mo $K \alpha(\lambda=0.7107 \AA)$ |
| space group | $P 21 / n$ |
| max cryst dimens, mm | $0.37 \times 0.32 \times 0.84$ |
| $\mu, \mathrm{cm}^{-1}$ | 6.02 |
| diffractometer | Philips PW 1100 |
| diffraction geomet | equatorial |
| scan type | $\omega / 2 \theta$ |
| scan speed | $0.100^{\circ} / \mathrm{s}$ |
| scan width, deg | 1.10 |
| $2 \theta$ range, deg | 6-48 |
| reflecns measd | $\pm h, \pm k, l$ |
| measd tot data | 9157 |
| agreement between equiv reflns | 0.027 |
| unique tot data | 7108 |
| unique obsv data (NO) | 4915 |
| criterion for obsvn | $I>3 \sigma(I)$ |
| no. of paramet 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 $C_{2 h}{ }^{5}$ (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 $\psi$ 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 $\sum w|\Delta F|^{2}$. Unit weights were used since these gave acceptable agreement analyses. During the refinement, the cyclopentadienyl rings were considered as regular pentagons ( $C-C=1.420 \AA$ ). All the hydrogen atoms were located from difference Fourier maps and introduced in calculations as fixed contributors prior to the final refinement ( $B_{\text {iso }}=7.8 \AA^{2}$ ). The final difference map showed no unusual features with no peak above the general background which was of about 0.3 e $\AA^{-3}$. No correction for extinction was deemed necessary.

Scattering factors were taken from ref 13 a 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. ${ }^{136}$ 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-

$I$ II
(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.

Table II. Fractional Atomic Coordinates $\left(\times 10^{4}\right)$

| 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) |
| Cl | 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) |
| C 23 | 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 $\mathrm{CH}_{2} \mathrm{O}$ 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 $\mathrm{CO}_{2}$ 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, $\mathrm{RNCO}\left[\mathrm{R}=\mathrm{C}_{6} \mathrm{H}_{11}, \mathrm{Ph}\right.$, or $\left.p-\mathrm{MeC}_{6} \mathrm{H}_{4}\right]$ with the purpose to understand the steps preceding the reduction of $\mathrm{CO}_{2}$ 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 ( $1675 \mathrm{~cm}^{-1}$ ) and by analogy with the solid-state structure determined for complex VI ( $\mathrm{R}=\mathrm{C}_{6} \mathrm{H}_{11}$ ) (vide infra) and for complexes $\mathrm{cp}_{2} \mathrm{Zr}$ (R) $\left[\mathrm{O}-\mathrm{C}(\mathrm{R})-\mathrm{NR}^{\prime}\right]\left[\mathrm{R}=\mathrm{Me}, \mathrm{PhCH}_{2}\right.$, or $\mathrm{Ph} ; \mathrm{R}^{\prime}=\mathrm{Ph}, 1$-naphthyl, or $\left.\mathrm{C}_{6} \mathrm{H}_{11}\right]$, 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 ( $\mathrm{R}=$ $\mathrm{C}_{6} \mathrm{H}_{11}$ ), to form a 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


V
as yellow crystalline solid, very sensitive to moisture. We must point out that the oxygen is removed from both substrates, $\mathrm{CO}_{2}$ 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: $\mathrm{R}-\mathrm{N}=\mathrm{C}=\mathrm{N}-\mathrm{R}$ $\left[\mathrm{R}=\mathrm{C}_{6} \mathrm{H}_{11}\right.$ or $\left.p-\mathrm{MeC}_{6} \mathrm{H}_{4}\right]$. 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

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Table III. Selected Bond Distances ( $\AA$ ) and Angles (deg)

|  | molec A | molec B |  | molec A | molec B |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Zr}-\mathrm{Cl}$ | 2.589 (2) | 2.551 (2) | N1-C17 | 1.328 (6) | 1.329 (8) |
| $\mathrm{Zr}-\mathrm{Nl}$ | 2.252 (4) | 2.275 (5) | N2-C17 | 1.309 (6) | 1.305 (6) |
| $\mathrm{Zr}-\mathrm{N} 2$ | 2.298 (4) | 2.310 (5) | N1-C11 | 1.477 (6) | 1.479 (7) |
| $\mathrm{Zr}-\mathrm{Cpl}$ | 2.248 (4) | 2.235 (6) | N2-C18 | 1.473 (6) | 1.472 (7) |
| $\mathrm{Zr}-\mathrm{Cp} 2$ | 2.252 (4) | 2.243 (5) |  |  |  |
| $\mathrm{Cpl}-\mathrm{Zr}-\mathrm{Cp} 2$ | 130.4 (2) | 127.6 (3) | $\mathrm{Zr}-\mathrm{N} 1-\mathrm{Cl} 7$ | 94.8 (3) | 94.7 (3) |
| $\mathrm{N} 2-\mathrm{Zr}-\mathrm{Cp} 2$ | 97.7 (2) | 97.9 (2) | $\mathrm{Zr}-\mathrm{N} 1-\mathrm{Cl} 1$ | 146.8 (4) | 148.9 (4) |
| $\mathrm{N} 2-\mathrm{Zr}-\mathrm{Cpl}$ | 97.4 (2) | 100.0 (2) | Cll-N1-Cl7 | 118.3 (4) | 116.3 (5) |
| $\mathrm{N} 1-\mathrm{Zr}-\mathrm{Cp} 2$ | 113.8 (2) | 119.0 (2) | $\mathrm{Zr}-\mathrm{N} 2-\mathrm{Cl} 7$ | 93.3 (3) | 93.8 (3) |
| $\mathrm{N} 1-\mathrm{Zr}-\mathrm{Cpl}$ | 114.3 (2) | 112.2 (3) | $\mathrm{Zr}-\mathrm{N} 2-\mathrm{Cl} 18$ | 144.2 (3) | 144.7 (3) |
| $\mathrm{N} 1-\mathrm{Zr}-\mathrm{N} 2$ | 58.1 (2) | 57.6 (2) | C17-N2-C18 | 122.5 (4) | 121.5 (5) |
| $\mathrm{Cl}-\mathrm{Zr}-\mathrm{Cp} 2$ | 99.0 (1) | 98.8 (2) | N1-C17-N2 | 113.8 (5) | 113.9 (5) |
| $\mathrm{Cl}-\mathrm{Zr}-\mathrm{Cpl}$ | 98.8 (1) | 100.2 (2) |  |  |  |
| $\mathrm{Cl}-\mathrm{Zr}-\mathrm{N} 2$ | 140.2 (1) | 137.4 (1) |  |  |  |
| $\mathrm{Cl}-\mathrm{Zr}-\mathrm{N} 1$ | 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 $\left[\mathrm{R}=\mathrm{C}_{6} \mathrm{H}_{11}\right]$.

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 $\eta^{5}$-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) $\AA$ in molecule $A$ and 0.216 (2) $\AA$ in molecule B] of the plane defined by $\mathrm{Zr}, \mathrm{N} 1, \mathrm{~N} 2$, and C 17 atoms (Table SV). $\mathrm{Zr}-\mathrm{Cl}$ 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) $\AA$ in molecule A and 2.551 (2) $\AA$ ]. This difference, however, must be ascribed to packing forces. $\mathrm{N}-\mathrm{C}$ bond distances are close $[\mathrm{C} 17-\mathrm{N} 1,1.328$ (6), C17-N2, 1.309 (6) $\AA$ in molecule $\mathrm{A} ; \mathrm{C} 17-\mathrm{N} 1,1.329$ (8), C17-N2, 1.305 (6) $\AA$ 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) $\AA$ [molecule A] and 0.033 (5) $\AA$ [molecule B] from the plane defined by $\mathrm{Zr}, \mathrm{C} 17$, and C 18 , while N 2 is coplanar with $\mathrm{Zr}, \mathrm{C} 17$, and C 18 . These values are in favor of the canonical form A vs. B for complex Vi: The


A


B
$\mathrm{Zr}-\mathrm{N}$ bond distances are slightly different ( $\mathrm{Zr}-\mathrm{N} 1[2.252$ (4) $\AA$ in molecule A, and 2.275 (5) $\AA$ in molecule B]; $\mathrm{Zr}-\mathrm{N} 2$ [ 2.298 (4) $\AA$ in molecule A, and $2.275(5) \AA$ 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 $\mathrm{CO}_{2}$ and $\mathrm{CO}_{2}$-like molecules into the $\mathrm{M}-\mathrm{H}$ 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 $\mathrm{CO}_{2}$ and its analogues by complex I.

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

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Figure 2. ORTEP drawing of complex VI (molecule B) ( $30 \%$ probability ellipsoids).

any oxygen atom in the structure. Step $b$ is so easy in the case of $\mathrm{CO}_{2}$ that $\left[\mathrm{cp}_{2} \mathrm{Zr}\left(\mathrm{O}_{2} \mathrm{CH}\right) \mathrm{Cl}\right]$ has not been detected. This is not
surprising since the inorganic functionality $\left[\mathrm{ZrO}_{2} \mathrm{CH}\right]$ can be related to an ester, which is very easily reduced by complex ${ }^{5 b .20,21}$ in a related reaction. Step $d$ is proven by having carried out the reaction between I and formaldehyde leading to $\left[\mathrm{cp}_{2} \mathrm{Zr}(\mathrm{Cl})\right.$ ( OMe )], while addition of a $\mathrm{C}=\mathrm{N}$ multiple bond to the $\mathrm{Zr}-\mathrm{H}$ 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 $\mathrm{CO}_{2}$ in the reactions outlined above.

The present study suggests that reduction of $\mathrm{CO}_{2}$ by a $\mathrm{M}-\mathrm{H}$
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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 $\mathrm{M}-\mathrm{O}-\mathrm{M}, \mathrm{M}-\mathrm{O}-\mathrm{R}$, and $\mathrm{M}=\mathrm{O}$ inorganic functionalities.

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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 $\mathrm{PtCl}_{6}{ }^{2-}$ and Diplatinum(III) Chloro Complexes Having $\mu$-Phosphato or $\mu$-Pyrophosphito Ligands 

Ramadan El-Mehdawi, Samuel A. Bryan, and D. Max Roundhill*<br>Contribution from the Department of Chemistry, Tulane University, New Orleans, Louisiana 70118. Received March 25, 1985


#### Abstract

The diplatinum(III) complex $\left[\mathrm{Pt}_{2}\left(\mu-\mathrm{PO}_{4} \mathrm{H}\right)_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2-}$ reacts with halide ions $\mathrm{X}^{-}(\mathrm{X}=\mathrm{Cl}, \mathrm{Br})$ to give first $\left[\mathrm{Pt}_{2}\left(\mu-\mathrm{PO}_{4} \mathrm{H}\right)_{4} \mathrm{X}\left(\mathrm{H}_{2} \mathrm{O}\right]^{3-}\right.$ and then $\left[\mathrm{Pt}_{2}\left(\mu-\mathrm{PO}_{4} \mathrm{H}\right)_{4} \mathrm{X}_{2}\right]^{4-}$. The reaction establishes an equilibrium situation between the three complexes: $$
\mathrm{Pt}_{2}\left(\mu-\mathrm{PO}_{4} \mathrm{H}\right)_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}^{2-}+\mathrm{X}^{-} \stackrel{\left(K_{1}\right) k_{1}}{k_{2}} \mathrm{Pt}_{2}\left(\mu-\mathrm{PO}_{4} \mathrm{H}\right)_{4} \mathrm{X}\left(\mathrm{H}_{2} \mathrm{O}\right)^{3-}+\mathrm{X}^{-} \stackrel{\left(K_{2}\right) k_{3}}{k_{4}} \mathrm{Pt}_{2}\left(\mu-\mathrm{PO}_{4} \mathrm{H}\right)_{4} \mathrm{X}_{2}^{4-}
$$

Using pseudo-first-order conditions in halide ion at $25^{\circ} \mathrm{C}$, we have used a biphasic analysis to evaluate the rate constants. The values are $k_{1}=0.9(2) \mathrm{M}^{-1} \mathrm{~s}^{-1}, k_{2}=5(1) \times 10^{-2} \mathrm{~s}^{-1}, k_{3}=0.8(2) \mathrm{M}^{-1} \mathrm{~s}^{-1}, k_{4}=8(2) \times 10^{-2} \mathrm{~s}^{-1}(\mathrm{X}=\mathrm{Cl})$ and $k_{1}=$ $0.3(1) \mathrm{M}^{-1} \mathrm{~s}^{-1}, k_{2}=1.5(3) \times 10^{-2} \mathrm{~s}^{-1}, k_{3}=0.4(1) \mathrm{M}^{-1} \mathrm{~s}^{-1}, k_{4}=1.9(3) \times 10^{-2} \mathrm{~s}^{-1}(\mathrm{X}=\mathrm{Br})$. Under comparable conditions of temperature ( $25^{\circ} \mathrm{C}$ ), $\mathrm{pH}(3.0)$, and ionic strength ( 0.1 M ), we have measured the equilibrium constants as $K_{1}=19$ (2) $\mathrm{M}^{-1}, K_{2}=11(1) \mathrm{M}^{-1}(\mathrm{X}=\mathrm{Cl})$ and $K_{2}=21(2) \mathrm{M}^{-1}, K_{2}=22(2) \mathrm{M}^{-1}(\mathrm{X}=\mathrm{Br})$. 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 $\mu$-pyrophosphito complexes $\left[\mathrm{Pt}_{2}\left(\mu-\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4} \mathrm{X}_{2}\right]^{4-}$ or chloride in $\mathrm{PtCl}_{6}{ }^{2-}$. This axial halide labilization in $\left[\mathrm{Pt}_{2}\left(\mu-\mathrm{PO}_{4} \mathrm{H}\right)_{4} \mathrm{X}_{2}\right]^{4-}(\mathrm{X}=\mathrm{Cl}, \mathrm{Br})$ as compared to $\mathrm{PtCl}_{6}{ }^{2-}$ is believed to be a consequence of a strong intermetallic bond between platinums.


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.
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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-

[^3]
[^0]:    ${ }^{\dagger}$ Universitå di Pisa.
    ${ }^{\ddagger}$ Present address: Chemistry Department, Columbia University, New York, NY 10027.
    ${ }^{\text {§ }}$ Universitả di Parma.

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