under the same experimental conditions.

The complexes $(\eta^5\text{-}C_5H_5)Ir(CO)_2$, $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$, and $(\eta^5\text{-}C_5Me_5)M(PMe_3)(R)(H)$ (M = Rh, Ir) are well-known for generating reactive species capable of intermolecular oxidative addition to single C–H bonds in saturated hydrocarbons.[18-20] We are presently investigating our new compounds with a similar purpose.

**Registry No.** **1a**, 106520-04-1; **1b**, 106500-77-0; **2a**, 106500-79-2; **2b**, 106500-78-1; **3b**, 106520-03-0; $[RhCl(CO)(PPh_3)]_2$, 34676-63-6; *trans*-$IrCO(CO)(PPh_3)_2$, 15318-31-7; $Li(C_5H_4)PPh_2$, 83272-80-4.

**Supplementary Material Available:** Tables of fractional atomic coordinates, hydrogen atomic positional and thermal parameters, final anisotropic thermal parameters, bond lengths and angles, interatomic distances, and least-squares planes (6 pages); a listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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# Uncommon Structural Features of $[Cp_2Zr\text{-}OC(Ph)\text{-}Mo(CO)_5]_2O$, a Zr-O-Zr-Bridged Tetranuclear Bis(carbene)metal Complex Exhibiting a Planar σ-Framework

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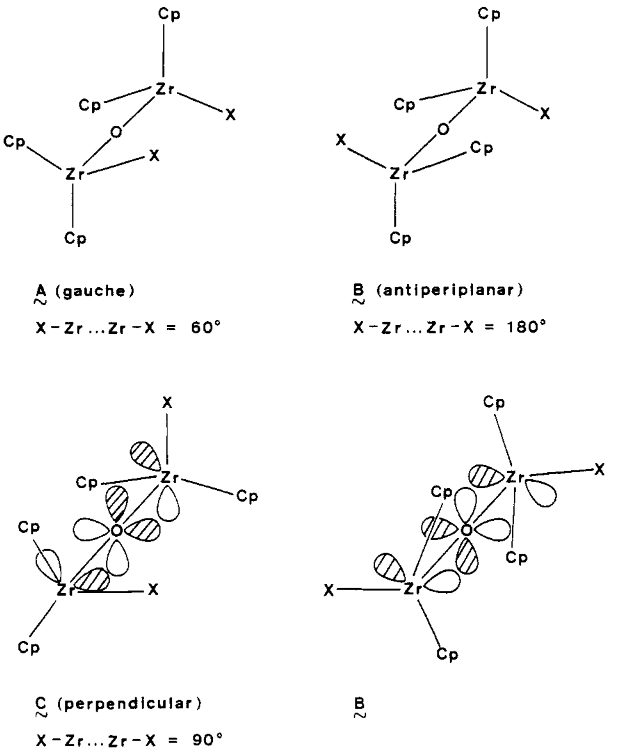
*Summary:* Thermally in situ generated $(\eta^2\text{-}1,2\text{-di-dehydrobenzene})$zirconocene reacts with $M(CO)_6$ (M = W, Mo) to give the benzannelated five-membered metallacyclic zirconoxycarbene complexes **4a,b**. Controlled hydrolysis of **4a** (M = W) with $CuSO_4{\cdot}5H_2O$ yields the tetranuclear Zr–O–Zr-bridged bis(carbene) complex $[(CO)_5W\text{-}C(Ph)O\text{-}Cp_2Zr\text{-}O\text{-}ZrCp_2\text{-}OC(Ph)\text{-}W(CO)_5]$ (**5a**). The molecular structure of the molybdenum analogue **5b** was determined by X-ray diffraction. **5b** crystallizes in the monoclinic space group *C2/c* with cell parameters $a$ = 28.666 (5) Å, $b$ = 11.257 (2) Å $c$ = 16.884 (2) Å, and $\beta$ = 125.84 (1)°. **5b** is characterized by a completely planar σ-framework (Zr–O–Zr* = 180°). The most remarkable structural feature of **5b** is the trans arrangement of the voluminous $(CO)_5Mo$–carbene units at the Zr–O–Zr bridge. This favored antiperiplanar conformation is unique among the family of early-transition-metal $Cp_2M(X)\text{-}O\text{-}M(X)Cp_2$ compounds.

**Chart I. Schematic Representation of Possible Local Conformational $(Cp_2ZrX)_2O$ Minima[a]**



[a] Orbitals drawn for B and C only serve to denote the planes of preferred electronic interaction.

**Table I. A Comparison of Selected Structural Data of $(Cp_2MX)_2O$ Compounds Including 5b**

| M | X | X-M···M-X[a] | M-O-M | M-O[b] | ref |
|---|---|---|---|---|---|
| Zr | O-C(Ph)Mo-$(CO)_5$ | 180 | 180 | 1.958 (1) | this work |
| Zr | S-Ph | 61.7 | 165.8 | 1.968 (3)<br>1.964 (3) | 1 |
| Zr | Cl | 74.3 | 168.9 | 1.94 (1)<br>1.95 (1) | 2 |
| Zr | $CH_3$ | 90 | 174.1 | 1.948 (1) | 3 |
| Ti | $-CF_3C{=}CH\text{-}CF_3$ | 54.1<br>53.7 | 170 | 1.857 (6) | 4 |
| $Ti^{+c}$ | $[H_2O]$ | 74.1 | 175.8 | 1.829 (2) | 5 |
| Ti | -PhC=CHPh | 68 | 168.8 | 1.85 (1)<br>1.86 (1) | 6 |
| $Nb^{+d}$ | Cl | 72.5 | 169.3 | 1.88 (1) | 7 |

[a] Dihedral angle θ. [b] Bond distance in Å and bond angles in deg. [c] $ClO_4^-$ salt. [d] $BF_4^-$ salt.

Connection of two pseudotetrahedral bent metallocene units $Cp_2MX$ through a bridging oxygen atom leads to binuclear μ-oxo-metallocene complexes $(Cp_2MX)\text{-}O\text{-}(Cp_2MX)$ usually exhibiting a near to linear M–O–M linkage.[1-7] The stereochemical situation of such an arrangement could principally be similar to that of ordinary

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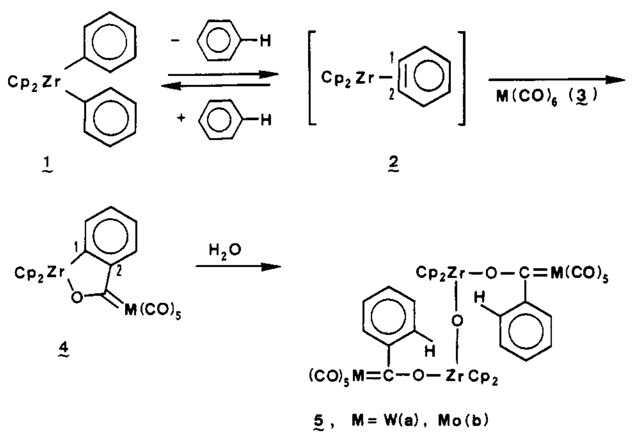
**Scheme I**



alkanes. One might therefore have expected to find a strong preference for two conformers representing local minima on the $(Cp_2MX)_2O$ hypersurface. Both should be close to the idealized geometry A or B, both exhibiting a staggered arrangement of ligands at M along the M–O–M vector. A and B are different from each other only with regard to their relative positioning of the functional groups X [gauche, i.e., $\theta$ (X–M···M–X) = 60°, for A; antiperiplanar ($\theta$ = 180°) for B].

For $d^0$ configurated metal centers, e.g. M = Zr, this sterically favorable situation can be disturbed by an additional electronic effect. $\pi$-Interaction between the bridging oxygen lone pairs with the single available metallocene acceptor orbital stabilizes a linear heteroallene-type structure[3,8,9] with $\theta$ (X–Zr···Zr–X) = 90°, in an idealized representation shown as the "perpendicular" form C in Chart I.

To our knowledge, up to now all $\mu$-oxo–group 4 metallocene compounds characterized by X-ray diffraction show values of $\theta$ (see Table I) that place them somewhere between the structural extremes A and C. We have prepared examples of compounds clearly deviating from this behavior believed as being typical for stable $\mu$-oxo–group 4 metallocene complexes.

The metallacyclic zirconoxycarbene complex **4a** (M = W) was prepared by reacting ($\eta^2$-1,2-didehydrobenzene)zirconocene (**2**)[10] (thermally in situ generated from diphenylzirconocene (**1**) at 80 °C) with $W(CO)_6$.[11] **4a** turned out to be extremely moisture sensitive. Exposition of this carbene complex to water rapidly results in opening of the five-membered metallacycle via cleavage of the Zr–C(1) bond. Upon controlled hydrolysis with a stoichiometric amount of $CuSO_4\cdot5H_2O$ at ambient temperature in methylene chloride (4 equiv of crystal water are used from the reagent under these conditions), two units of **4a** reacted with one molecule of water under C–H and Zr–O bond formation. The resulting Zr–O–Zr bridged tetranuclear bis(tungsten zirconoxycarbene) complex **5a** was obtained in 36% isolated yield.[12]

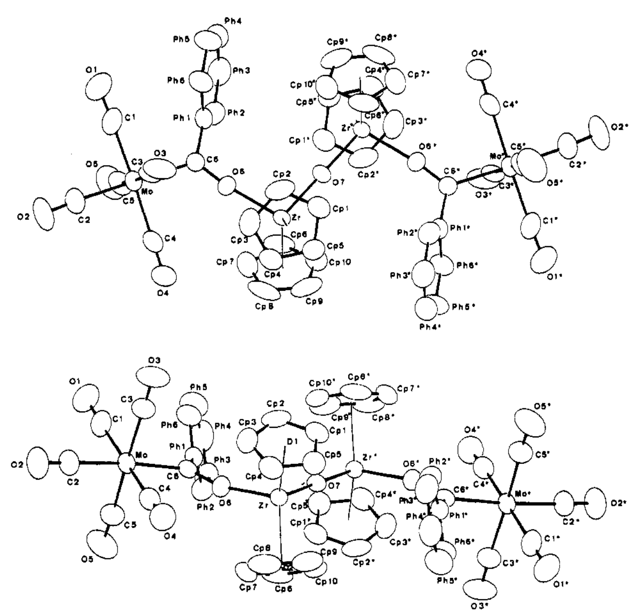


**Figure 1.** Two views of the molecular geometry of **5b** as determined by X-ray diffraction. Thermal ellipsoids are at the 30% probability level.

The corresponding benzannelated metallacyclic zirconoxycarbene complex **4b** of molybdenum hexacarbonyl turned out to be even more sensitive to hydrolysis. It apparently reacted so readily with traces of moisture present in the reaction medium that under the usual conditions applied for its preparation from $Cp_2ZrPh_2$ (**1**) according to Scheme I, the obtained binuclear carbene complex **4b** was always contaminated with substantial amounts of the tetranuclear $H_2O$ addition product **5b**. From the crude reaction mixture, pure **5b** was isolated in moderate yield (29%) after recrystallization from benzene.[12]

The tetranuclear molybdenum zirconoxycarbene complex **5b** was characterized by X-ray diffraction.[13] Two different views of the molecular geometry are shown in Figure 1. The molecule is partitioned in two Fischer-type molybdenum zirconoxyphenylcarbene substructural moieties[14] by a center of inversion, O(7) [Mo–C(6) = 2.195 (6) Å, C(6)–Ph(1) = 1.502 (9) Å, C(6)–O(6) = 1.284 (7) Å; Mo–C(6)–O(6) = 125.6 (4)°, Ph(1)–C(6)–O(6) = 111.3 (5)°, Mo–C(6)–Ph(1) = 122.7 (4)°; the angle between the Ph(1)–(6) and Mo–C(6)–O(6) planes is 62°], which are con-

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(12) For **5a**: mp 192 °C; IR ($\nu$(CO) in $C_6D_6$) 2061 s, 1974 m, 1933 vs, 1912 sh $cm^{-1}$; $^1H$ NMR ($CD_2Cl_2$) $\delta$ 7.55 (m, 6 H, Ph), 7.25 (m, 4 H, Ph), 6.20 (s, 20 H, Cp); $^{13}C$ NMR ($CD_2Cl_2$) $\delta$ 335.7 ($^1J_{WC}$ = 99 Hz, carbene C), 205.5 ($^1J_{WC}$ = 120 Hz, trans CO), 199.6 ($^1J_{WC}$ = 128 Hz, cis CO), 161.2 ($^2J_{WC}$ = 11 Hz, Ph, quarternary C), 130.1 ($^1J_{CH}$ = 162 Hz, *p*-Ph), 128.7 ($^1J_{CH}$ = 160 Hz, *m*-Ph), 122.4 ($^1J_{CH}$ = 159 Hz, *o*-Ph), 114.4 ($^1J_{CH}$ = 173 Hz, Cp). Anal. Calcd for $C_{44}H_{30}O_{13}Zr_2W_2$: C, 40.13; H, 2.30. Found: C, 40.49; H, 2.28. For **5b**: IR ($\nu$(CO) in $C_6D_6$): 2061 s, 1980 s, 1938 vs, 1920 sh $cm^{-1}$; $^1H$ NMR ($CD_2Cl_2$) $\delta$ 7.50 (m, 6 H, Ph), 7.20 (m, 4 H, Ph), 6.19 (s, 20 H, Cp); $^{13}C$ NMR ($CD_2Cl_2$) $\delta$ 354.2 (carbene C), 215.5 (trans CO), 207.6 (cis CO), 159.5 (Ph, quarternary C), 130.0 ($^1J_{CH}$ = 161 Hz, *p*-Ph), 128.7 ($^1J_{CH}$ = 160 Hz, *m*-Ph), 122.2 ($^1J_{CH}$ = 157 Hz, *o*-Ph), 114.3 ($^1J_{CH}$ = 173 Hz, Cp).

(13) Crystal data: $C_{44}H_{30}O_{13}Zr_2Mo_2$, $M_r$ 1141.04; monoclinic; space group $C2/c$ (No. 15); $a$ = 28.666 (5) Å, $b$ = 11.257 (2) Å, $c$ = 16.884 (2) Å, $\beta$ = 125.84 (1)°; $V$ = 4417 Å$^3$; $Z$ = 4; $D_{calcd}$ = 1.72 g/cm$^3$. Data were measured on an Enraf-Nonius CAD 4 diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71069 Å). $R$ = 0.037 ($R_w$ = 0.041) for 277 refined parameters and 4519 independent reflections, of which 2773 were considered observed ($I \geq 2\sigma(I)$).

(14) See for comparison: Schubert, U. In *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim/Bergstr., West Germany, 1983; p 74.

nected by a perfectly linear bridging $-Cp_2Zr-O-ZrCp_2-$ unit [O(6)–Zr = 2.061 (4) Å, Zr–O(7) = 1.958 (1) Å, O(6)–Zr–O(7) = 99.4 (1)°]. The truly remarkable structural feature of **5b** in the crystal is that all four metal atoms are arranged in one plane. Central atoms of the carbene fragments [C(6), O(6), Ph(1)] deviate only slightly from the plane of the $\sigma$-framework that even extends to the trans-oriented Mo-bonded carbonyl ligands [C(2), O(2)]. It should be noted that according to the crystallographic center of inversion, the two Fischer carbene structural subunits are arranged trans to each other at the bridging ($\mu$-oxo)bis(zirconocene) moiety.

A comparison with selected structural data as typically found for $\mu$-oxo–metallocene complexes (see Table I) substantiates the unique geometric situation found here. Obviously, the observed molecular structure of **5** represents an example of the hitherto not experimentally realized antiperiplanar conformational situation B as depicted in Chart I.

Searching for an explanation for this remarkable phenomenon, it is tempting to hold sterical features of the large $(CO)_5M-C(Ph)O-$"substituents" responsible for the observed effect. However, it should be noted that for this special bonding situation $\pi$-conjugation between oxygen lone pairs and acceptor orbitals at zirconium ranging from O(6) all the way through O(6)* is possible *in the plane* of the $\sigma$-framework and might help to create this favored molecular geometry.

**Acknowledgment.** Financial aid from the Deutsche Forschungsgemeinschaft, the Fritz Thyssen Stiftung, and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Dr. R. Mynott for the $^{13}C$ NMR spectra.

**Supplementary Material Available:** Tables of atomic coordinates and thermal parameters and a table of selected interatomic distances and angles for **5b** (6 pages); a listing of observed and calculated structure factors for **5b** (14 pages). Ordering information is given on any current masthead page.

# Novel Phosphorus Ylide Transfer Reactions from Gold(I) to Gold(I) or from Gold(I) to Gold(III) Centers

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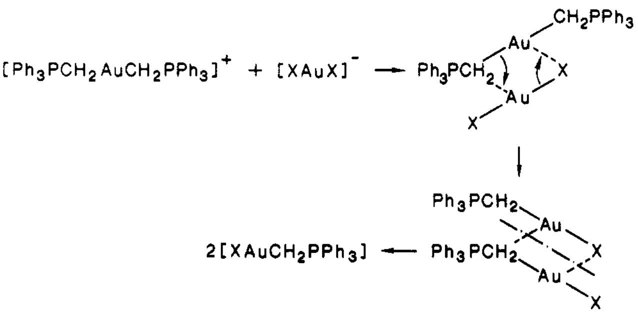
*Summary:* One phosphorus ylide in an $[Au(ylide)_2]ClO_4$ complex can be transferred to another gold(I) center in aurate(I) $[AuX_2]^-$ (X = Cl, Br, $C_6F_5$, $C_6Cl_5$) complexes or to a gold(III) center in $[AuR_3(OEt_2)]$ or $[Au_2(\mu\text{-}Cl)_2R_4]$ (R = $C_6F_5$) to afford neutral derivatives of the types [AuX(ylide)], $[AuR_3(ylide)]$, or *cis*-$[AuR_2Cl(ylide)]$.

Although the chemistry of transition-metal complexes of ylides has received a good deal of attention,[1,2] transfer of an ylide ligand from a metal center to a different one has so far not been reported. Here we describe the first intermolecular ylide transfer reactions from a gold(I) complex of ylide either to another gold(I) center or to a gold(III) center.

**Scheme I**



**(A) Ylide-Transfer Reactions between Two Gold(I) Centers.** Reaction[3] between $[Au(CH_2PPh_3)_2]ClO_4$[4] and several aurate(I) derivatives $Q[AuX_2]$ ($Q = Ph_3P{=}N{=}PPh_3$, X = Cl; Q = N-*n*-$Bu_4$, X = Br, $C_6F_5$, or $C_6Cl_5$) affords neutral derivatives **1**–**4** of the type $[Au(X)(CH_2PPh_3)]$, according to eq 1.

$$[Au(CH_2PPh_3)_2]ClO_4 + Q[AuX_2] \xrightarrow{CHCl_3} 2[Au(X)(CH_2PPh_3)] + QClO_4 \quad (1)$$

X = Cl (**1**); Br (**2**); $C_6F_5$ (**3**); $C_6Cl_5$ (**4**)

Complexes **1**–**3** have previously been reported.[4,5] Complex **4** is an air- and moisture-stable white solid, monomeric (in $CHCl_3$ solution) and nonconducting (in acetone solution).

We think that the above reactions (eq 1) follow a nondissociative path (Scheme I) similar to that proposed for the transfer of $C_6F_5$ groups.[6]

**(B) Ylide Transfer Reactions from a Gold(I) to a Gold(III) Center.** Neither $(n\text{-}Bu_4N)[Au(C_6F_5)_3Br]$ nor $[Au(C_6F_5)_3(tht)]$ (tht = tetrahydrothiophene) reacts with $[Au(CH_2PPh_3)_2]ClO_4$, but gold(III) complexes containing a very weakly coordinating ligand as in $[Au(C_6F_5)_3(OEt_2)]$[7] or binuclear halide-bridged derivatives $[Au_2(\mu\text{-}Cl)_2(C_6F_5)_4]$[6a] readily undergo ylide transfer on reaction with $[Au(CH_2PPh_3)_2]ClO_4$ (eq 2 and 3).

$$[Au(C_6F_5)_3(OEt_2)] + [Au(CH_2PPh_3)_2]ClO_4 \rightarrow \underset{\mathbf{5}}{[Au(C_6F_5)_3(CH_2PPh_3)]} + [Au(CH_2PPh_3)(OEt_2)]ClO_4 \quad (2)$$

$$^{1}/_{2}[Au_2(\mu\text{-}Cl)_2(C_6F_5)_4] + [Au(CH_2PPh_3)_2]ClO_4 \rightarrow \underset{\mathbf{6}}{cis\text{-}[Au(C_6F_5)_2Cl(CH_2PPh_3)]} + [Au(OClO_3)(CH_2PPh_3)] \quad (3)$$

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[3] To a chloroform solution (25 mL) of $[Au(CH_2PPh_3)_2]ClO_4$ (0.3 mmol, 0.255 g) was added 0.3 mmol of $Q[AuX_2]$. The mixtures were stirred (room temperature, 2 h, X = Cl; room temperature, 3 h, X = Br; refluxed 5 h, X = $C_6F_5$; refluxed 8 h, X = $C_6Cl_5$) and then evaporated to dryness. For complexes **1** and **2** the residues were washed with ethanol (3 × 20 mL) and recrystallized from $CH_2Cl_2$/*n*-hexane. Yields: 62% (**1**), 54% (**2**). Complexes **3** and **4** were extracted from the residues with diethyl ether (3 × 20 mL) and, after vacuum evaporation to ~5 mL, crystallized by addition of *n*-hexane (20 mL). Yields: 75% (**3**), 72% (**4**).

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