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 σ -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 (μ -oxo)bis(zirconocene) moiety.

A comparison with selected structural data as typically found for μ -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 π -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 σ -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 ¹³C 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 Yilde Transfer Reactions from Gold(I) to Gold(I) or from Gold(I) to Gold(III) Centers

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Received October 9, 1986

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, C₆F₅, C₆Cl₅) complexes or to a gold(III) center in $[AuR_3(OEt_2)]$ or $[Au_2(\mu-Cl)_2R_4]$ (R = C₆F₅) 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

Scheme I



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.

(A) Ylide-Transfer Reactions between Two Gold(I) Centers. Reaction³ between $[Au(CH_2PPh_3)_2]ClO_4^4$ and several aurate(I) derivatives $Q[AuX_2]$ ($Q = Ph_3P = N =$ PPh₃, X = Cl; Q = N-n-Bu₄, X = Br, C₆F₅, or C₆Cl₆) affords neutral derivatives 1-4 of the type $[Au(X)(CH_2PPh_3)]$, according to eq 1.

$$[\operatorname{Au}(\operatorname{CH}_{2}\operatorname{PPh}_{3})_{2}]\operatorname{ClO}_{4} + \operatorname{Q}[\operatorname{Au}X_{2}] \xrightarrow{\operatorname{CHCl}_{3}} 2[\operatorname{Au}(X)(\operatorname{CH}_{2}\operatorname{PPh}_{3})] + \operatorname{QClO}_{4} (1)$$

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

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 $(n-Bu_4N)[Au(C_6F_5)_3Br]$ 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 $[Au_2(\mu-Cl)_2(C_6F_5)_4]^{6a}$ readily undergo ylide transfer on reaction with $[Au(CH_2PPh_3)_2]ClO_4$ (eq 2 and 3).

$$[\operatorname{Au}(C_6F_5)_3(\operatorname{OEt}_2)] + [\operatorname{Au}(\operatorname{CH}_2\operatorname{PPh}_3)_2]\operatorname{ClO}_4 \rightarrow [\operatorname{Au}(C_6F_5)_3(\operatorname{CH}_2\operatorname{PPh}_3)] + [\operatorname{Au}(\operatorname{CH}_2\operatorname{PPh}_3)(\operatorname{OEt}_2)]\operatorname{ClO}_4 \\ 5$$
(2)

$$\begin{array}{l} {}^{1}/{}_{2}[\operatorname{Au}_{2}(\mu-\operatorname{Cl})_{2}(\operatorname{C}_{6}\operatorname{F}_{5})_{4}] + [\operatorname{Au}(\operatorname{CH}_{2}\operatorname{PPh}_{3})_{2}]\operatorname{ClO}_{4} \rightarrow \\ cis \cdot [\operatorname{Au}(\operatorname{C}_{6}\operatorname{F}_{5})_{2}\operatorname{Cl}(\operatorname{CH}_{2}\operatorname{PPh}_{3})] + [\operatorname{Au}(\operatorname{OClO}_{3})(\operatorname{CH}_{2}\operatorname{PPh}_{3})] \\ & 6 \end{array}$$

$$(3)$$

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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_8) 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). (4) Usón, R.; Laguna, A.; Laguna, M.; Usón, A.; Gimeno, M. C. Inorg.

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Table I

	analyses						¹ H NMR $({}^{2}J_{P-H})^{e}$		v(Au-C).	ν (Au–Cl).
complex	C	н	Au	$\Lambda_{M}{}^{a}$	mol wt ^b	mp, ^d °C	-CH2-	$PPh_{3-n}Me_n$	cm ⁻¹	cm ⁻¹
$\overline{Au(C_6Cl_5)CH_2PPh_3(4)}$	41.47 (41.55)	2.64 (2.37)	27.48 (27.26)	3	713 (723)	170	1.86 (13.0)		561	
$Au(C_6F_5)_2Cl(CH_2PPh_3)$ (6)	43.93 (44.18)	2.26 (2.03)	23.20 (23.37)	1	850 (843)	214 (d)	2.61 (13.3)		577	328
$Au(C_6F_5)_3(CH_2PPh_2Me)$ (7)	42.34 (42.12)	1.80 (1.65)	21.82 (21.58)	0	952 (912)	293	2.21 (13.6)	2.35 (13.3)	578	
$Au(C_6F_5)_3(CH_2PPhMe_2)$ (8)	38.24 (38.13)	1.81 (1.54)	22.53 (23.16)	2	с	219	1.91 (13.3)	1.92 (13.0)	554	
$Au(C_6F_5)_2Cl(CH_2PPh_2Me)$ (9)	40.16 (40.00)	2.26 (1.94)	25.30 (25.23)	3	820 (781)	166 (d)	2.33 (13.05)	2.53 (13.6)	564	320
$Au(C_6F_5)_2Cl(CH_2PPhMe_2) (10)$	35.45 (35.10)	1.61 (1.82)	27.07 (27.40)	1	740 (719)	172 (d)	1.93 (13.0)	2.16 (13.3)	567	314

^a In acetone (5 × 10⁻⁴ M), Ω^{-1} cm² mol⁻¹. ^b Isopiestic methods in CHCl₃. ^c Not sufficiently soluble. ^d Or decomposition point. ^e In CDCl₃, relative to SiMe₄ internal reference. Chemical shifts in ppm and coupling constants in Hz.

Processes 2 and 3 take place slowly: 6-12 h of refluxing in CHCl₃ are required.⁸ Under these conditions the unstable hypothetical byproducts ([Au(CH₂PPh₃)-(OEt₂)]ClO₄ and [Au(OClO₃)(CH₂PPh₃)]) decompose to metallic gold and other unidentified products.

The above gold(III) precursors can also be ylidated by using other gold(I) compounds as ylide sources (eq 4 and 5).

$$[\operatorname{Au}(C_{6}F_{5})_{3}(\operatorname{OEt}_{2})] + [\operatorname{Au}(C_{6}F_{5})(\operatorname{CH}_{2}\operatorname{PR}_{3})] \rightarrow [\operatorname{Au}(C_{6}F_{5})_{3}(\operatorname{CH}_{2}\operatorname{PR}_{3})] + \operatorname{Au}^{0} + \frac{1}{2}C_{12}F_{10} \quad (4)$$
7, 8
$$\operatorname{PR}_{3} = \operatorname{PPh}_{2}\operatorname{Me} \quad (7), \operatorname{PPh}\operatorname{Me}_{2} \quad (8)$$

$${}^{1}/{}_{2}[\operatorname{Au}_{2}(\mu-\operatorname{Cl})_{2}(\operatorname{C}_{6}\operatorname{F}_{5})_{4}] + [\operatorname{Au}(\operatorname{C}_{6}\operatorname{F}_{5})(\operatorname{CH}_{2}\operatorname{PR}_{3})] \rightarrow cis - [\operatorname{Au}(\operatorname{C}_{6}\operatorname{F}_{5})_{2}\operatorname{Cl}(\operatorname{CH}_{2}\operatorname{PR}_{3})] + \operatorname{Au}^{0} + {}^{1}/{}_{2}\operatorname{C}_{12}\operatorname{F}_{10} (5)$$
9, 10

$$PR_3 = PPh_2Me$$
 (9), $PPhMe_2$ (10)

Table I summarizes analytical and other data for complexes 4-10. To the best of our knowledge, such ylide transfer reactions as those described above are novel. Further work using other gold-ylide complexes and other transition metals is in progress in our laboratory. The ¹⁹F NMR spectra of complexes 6 and 9 confirm their cis configuration.⁹

Acknowledgment. We thank CAICYT (Spain) for financial support.

Registry No. 1, 105101-72-2; 2, 106223-54-5; 3, 88008-95-1; 4, 106402-57-7; 5, 88009-00-1; 6, 106418-13-7; 7, 106402-59-9; 8, 106402-60-2; 9, 106402-61-3; 10, 106402-62-4; $[Au(CH_2PPh_3)_2]ClO_4$, 106223-63-6; PPn[AuCl_2], 106402-58-8; N-*n*-Bu₄[AuBr_2], 50481-01-1; N-*n*-Bu₄[Au(C₆F₅)₂], 60748-81-4; N-*n*-Bu₄[Au(C₆Cl_5)₂], 63374-13-0; $[Au(C_6F_5)_3(OEt_2)]$, 106418-12-6; $[Au_2(\mu-Cl)_2(C_6F_5)_4]$, 87105-61-1; $[Au(C_6F_5)(CH_2PPh_2Me)]$, 106236-54-8; $[Au(C_6F_5)-(CH_2PPhMe_2)]$, 106223-65-8.

⁽⁸⁾ Procedure as for complexes 3 and 4.³ Yields: 60% (5), 64% (6), 67% (7), 84% (8), 93% (9), 95% (10).

^{(9) &}lt;sup>19</sup>F NMR spectra: complex 6, δ –163.3, –162.4 (m, F^{3,5}) –160.2, –155.3 [t, F⁴, $J(F^4F^3) = 19.9$ Hz], –123.7, –122.6 (m, F^{2,5}); complex 9, δ –163.4, –162.2 (m, F^{3,5}), –160.1, –158.9 [t, F⁴, $J(F^4F^3) = 19.9$ Hz], –124.1, –122.3 (m, F^{2,6}).