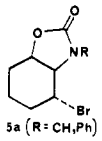
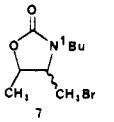
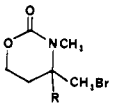
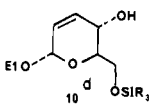
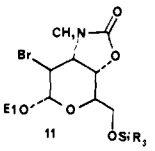
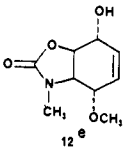
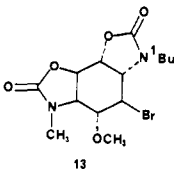
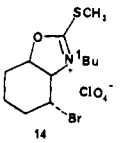
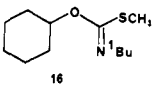
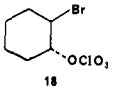
Table I. Synthesis of Bromocarbamates[a]

entry	substrate	isothiocyanate	product	% yield[b]
1	1	$PhCH_2NCS$	 5a (R = CH_2Ph)	83
2	1	tBuNCS	5b (R = tBu)	86
3	 6[c]	tBuNCS	 7 (c:t = 14:1)	68
4	 8a (R = H)	MeNCS	 9a (R = H)	69
5	8b (R = CH_3)	MeNCS	9b (R = CH_3)	83
6	 10[d]	MeNCS	 11	82
7	 12[e]	tBuNCS	 13	75
8	1[f]	tBuNCS	 14	52
9	 15[g]	tBuNCS	 16	99
10	 17[h]		 18	94

[a] Reaction conditions are as described in the text unless otherwise specified. [b] The products were isolated by column chromatography on silica using petroleum ether–ethyl ether mixtures as eluant. Yields refer to the overall conversion of substrate to product. [c] Addition of the bromonium reagent *to* a solution of the thiocarbamidate from 6 gave 7 in 49% yield (1.9:1 cis/trans). [d] This substrate was prepared in 87% yield by selective monosilylation (Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190) of ethyl 2,3-dideoxy-α-D-erythrohex-2-enopyranoside. Ferrier, R. J.; Prasad, N. *J. Chem. Soc. C* **1969**, 570. [e] Compound **12** was prepared in 9 steps from 1,3-cyclohexadiene. Knapp, S.; Sebastian, M. J.; Ramanathan, H. *J. Org. Chem.*, in press. [f] In this experiment the bromocyclization reaction was quenched with aqueous sodium *bicarbonate*. [g] In this experiment the thiocarbamidate (**16**) from 15 was recovered unchanged after treatment with the bromonium reagent under the usual conditions. [h] In this experiment 17 was subjected to the bromocyclization conditions directly.

of these reactions to aminocyclitol total synthesis.

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Supplementary Material Available: Spectroscopic data (IR, ^1H NMR) and melting points for new compounds (3 pages). Ordering information is given on any current masthead page.

Rupture and Realignment of the Bridging Phosphine Framework in the Reactions of Polynuclear Rhodium Complexes of 2,6-Bis(diphenylphosphino)pyridine

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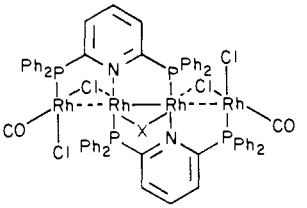
In recent years, a substantial body of information about the reactivity of binuclear, phosphine-bridged, metal complexes has developed.[1] Extensive studies of complexes of bis(diphenylphosphino)methane (dpm) have revealed a variety of reactions that interconvert the geometric forms known as face-to-face, side-to-side, A-frame and double A-frame dimers.[2] The catalytic activities of some species of this type are also believed to involve interconversions of these geometric forms.[3] A notable feature in these transformations is the apparent stability of the *trans*-$M_2(dpm)_2$ unit. A related body of data concerning transformations about a stable *trans*-$Rh_3(dpmp)_2$ core (dpmp is bis[(diphenylphosphino)methyl]phenylphosphine) is also emerging.[4] In contrast to this behavior, we present here an example of skeletal rupture and realignment in the reactions of the recently discovered, tetranuclear complex $Rh_4[\mu\text{-}(Ph_2P)_2py]_2(\mu\text{-}CO)(CO)_2(\mu\text{-}Cl)_2Cl_2$ **1**.[5]



1, X = CO

2, X = SO_2

Treatment of green **1** with carbon monoxide (1 atm) in chloroform produces a red orange solution from which crystals of $[Rh_2[\mu\text{-}(Ph_2P)_2py]_2(CO)_2(CH_3OH)Cl][PF_6]$ **2** are obtained in 65% yield by the gradual addition of ammonium hexafluoro-

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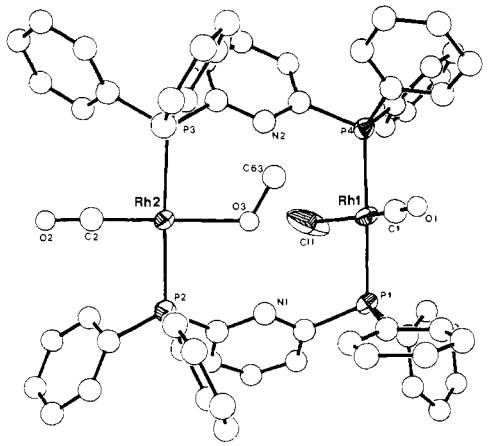
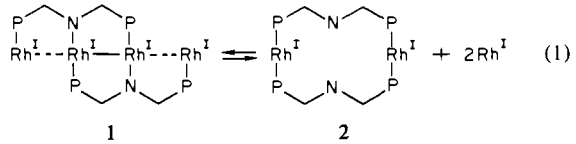


Figure 1. A perspective view of $[Rh_2[\mu\text{-}(Ph_2P)_2py]_2(CO)(CH_3OH)Cl]^+$. Some selected interatomic distances (Å) and angles (deg): Rh(1)–P(1), 2.313 (4); Rh(1)–P(4), 2.314 (4); Rh(1)–Cl(1), 2.321 (6); Rh(1)–C(1), 1.78 (1); Rh(2)–P(2), 2.333 (4); Rh(2)–P(3), 2.329 (4); Rh(2)–C(2), 1.809 (16); Rh(2)–O(3), 2.144 (6); N(1)···O(3), 2.679 (18); Rh(1)···Rh(2), 5.425 (2); Cl(1)–Rh(1)–C(1), 160.6 (2); P(1)–Rh(1)–P(4), 176.8 (1); C(2)–Rh(2)–O(3), 173.3 (9); P(2)–Rh(2)–P(3), 177.8 (2).

phosphate in methanol. The infrared spectrum of **2** shows the presence of two terminal carbonyl groups (ν(CO): 2075, 1991 cm^{-1}) and the methanol (ν(H): 3052 cm^{-1}). The $^{31}P\{^1H\}$ NMR spectrum indicates that two equally populated, rhodium-bound phosphorus environments are present (δ 31.3, ^1J(Rh,P) = 128.2 Hz; δ_2 20.4, ^1J(Rh,P) = 128.9). The crystal structure of the compound has been determined by X-ray diffraction at 140 K.[6] Figure 1 shows a view of the cation. The two rhodium atoms, the four phosphorus atoms, and the two nitrogen atoms form a nearly planar framework. Each of the two nonequivalent rhodium atoms is four coordinate and planar with trans phosphorus atoms. To complete its coordination, Rh(1) has trans carbonyl and chloride ligands, which are inclined at an angle of 67° with respect to the $Rh_2P_4N_2$ framework. Rh(2) has trans carbonyl and methanol ligands, which lie on a line that is directed 17° away from the $Rh_2P_4N_2$ plane. The orientation of ligands on Rh(2) is largely determined by the constraints imposed by hydrogen bonding N(1)···HO(3). The methanol ligand and one carbonyl group, C(1)–O(1), lie within a wall-like structure of four phenyl rings (those closest to the viewer in Figure 1). Within this cavity both the methyl group, which pivots about the N(1)···HO(3) hydrogen bond, and the carbonyl group show evidence of high thermal motion or disorder.

In the conversion of **1** to **2**, the phosphine ligands have undergone realignment and two rhodium atoms have been eliminated as shown schematically in eq 1. The rhodium atoms that are



1 **2** (1)

removed are converted into well-known species, $Rh(CO)_2Cl_2^-$ and $Rh_2(\mu\text{-}Cl)_2(CO)_4$, which have been detected by infrared spectroscopy. The overall stoichiometry of the reaction is given by eq 2. This reaction is reversible. Treatment of **2** with $Rh_2(\mu\text{-}Cl)_2(CO)_4$ and $[n\text{-}Bu_4N]Cl$ in chloroform solution reforms **1**, which has been reisolated in 64% yield.

$$Rh_4[\mu\text{-}(Ph_2P)_2py]_2(\mu\text{-}CO)(CO)_2Cl_4 + CH_3OH + 3CO \rightleftarrows [Rh_2[\mu\text{-}(Ph_2P)_2py]_2(CO)_2(CH_3OH)Cl]^+ + Rh(CO)_2Cl_2^- + {}^1/_2Rh_2(\mu\text{-}Cl)_2(CO)_4 \quad (2)$$

Not all reactions of **1** result in such drastic rearrangement. Addition of sulfur dioxide to **1** yields green $Rh_4[\mu\text{-}(Ph_2P)_2py]_2(\mu\text{-}SO_2)(CO)_2Cl_4$ (**3**) (IR ν(CO) 2079, 2003, $\nu(SO_2)$ 1210, 1062; $^{31}P\{^1H\}$ NMR δ 35.7, ^1J(Rh,P) = 131 Hz; δ_2 30.7, ^1J(Rh,P) = 138), and **3** may be reconverted to **1** by the careful addition of a limited amount of carbon monoxide. The conversion of **1** to **3** appears to simply involve substitution of the bridging carbonyl by a bridging sulfur dioxide.[7]

The occurrence of the reversible realignment shown in eq 1 establishes a new aspect of the coordination chemistry of this type of polynuclear complex. In dealing with phosphine bridged complexes, it is certainly presumptive to expect that the phosphine/metal framework will remain inviolate during chemical reactions.

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Registry No. 1, 87555-67-7; **2**·CH_2Cl_2, 87555-70-2; **3**, 87566-97-0.

Supplementary Material Available: A list of atomic fractional coordinates and thermal parameters for $[Rh_2[\mu\text{-}(Ph_2P)_2py]_2(CO)_2(CH_3OH)Cl][PF_6]\cdot CH_2Cl_2$ and a stereoscopic drawing of the cation (3 pages). Ordering information is given on any current masthead page.

(6) Orange crystals (dec 250 °C) of $[Rh_2[\mu\text{-}(Ph_2P)_2py]_2(CO)_2(CH_3OH)Cl][PF_6]\cdot CH_2Cl_2$ were grown by diffusion of ethyl ether into a dichloromethane solution of the complex. At 140 K, a = 10.181 (5) Å, b = 37.708 (24) Å, c = 16.193 (11) Å, β = 105.14 (5)°. The space group is $P2_1/c$ (No. 14) with Z = 4. Of 8473 observed unique reflections, $4008 > 6\sigma(F)$ were used in the refinements. The ω scan speed was 60° min^{-1}, using Mo (λ = 0.71069 Å) radiation. The structure was solved by Patterson methods, refinements were by least squares to R = 0.062. All atoms were included in the refinements, except the hydrogen atoms of methanol.

(7) A similar reaction sequence interconverts $Rh_2(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ and $Rh_2(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}SO_2)Cl_2$: Farr, J. P.; Olmstead, M. M.; Hunt, C. H.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 1182–1187.

Biosynthesis of Estrogens: The Steric Mode of the Initial C-19 Hydroxylation of Androgens by Human Placental Aromatase

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In this communication we report the results of our studies on the steric mode of the initial ("first") C-19 hydroxylation[1] in the biosynthetic conversion of androgens to estrogens by human placental enzymes.[2-5]

Previously we have proven that the steric mode of enzymatic hydroxylation at a primary carbon atom can be determined with the use of a substrate having a chiral methyl (labeled with ^3H, ^2H, ^1H) provided that the oxygenation involves a kinetic (normal) hydrogen isotope effect[6-9] ($k_H > k_D > k_T$) (D = ^2H; T = ^3H).

Our approach to the investigation of the elaboration of estrogens was as follows. For the sake of argument we will assume that the "first" *C-19* hydroxylation[1] of, eg., (19*R*)-[19-^3H,19-^2H,19-^1H]-3β-hydroxyandrost-5-en-17-one (**1**) proceeds in a retention mode and with a kinetic isotope effect $k_H > k_D > k_T$. Thus the main product of the reaction will be the (19*S*)-alcohol **2**, which will be accompanied by a minor amount of (19*R*)-alcohol **3**. Since

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