ature (^{1}H NMR δ 18.35), low solubility in cyclohexane and reaction with benzene have so far precluded solution molecular weight measurements. Unlike formally analogous $[Cp'_2Th(\mu\text{-}H)H]_2$ (**13**),[10,15] the Th–H portion of the infrared spectrum of **12** ((Nujol mull, cm^{-1}) 1275 (mw), 1155 (w), 654 (m), 645 (m); **12**-*d*,[17] 904 (m), ν_{M-H}/ν_{M-D} = 1.41) *does not* exhibit detectable terminal Th–H stretching transitions, suggesting more extensive hydrogen bridging and an increased formal thorium coordination number. Preliminary reactivity comparisons between **12** and **13** have been sought in homogeneous olefin hydrogenation, for which **13** is moderately active.[10] Although mechanistic details have not as yet been fully elucidated, it is noteworthy that at room temperature (1 atm H_2 pressure), **12** is 13 times more active than **13** for 1-hexene hydrogenation (initial N_t = 6.5 h^{-1}) and 21 times more active (initial N_t = 2.5 h^{-1})[18] for hydrogenating sterically more demanding *trans*-2-hexene.

The degree to which the present ligand linkage approach can modify Cp'_2M chemistry in 5f as well as other systems is under continuing investigation.

Acknowledgment. We thank the National Science Foundation (CHE8009060 and CHE8306255) for generous support of this research.

Supplementary Material Available: Spectroscopic and analytical data, a table of fractional atomic coordinates (Table I), and a table of anisotropic thermal parameters (Table II) for non-hydrogen atoms of $(CH_3)_2Si[(CH_3)_4C_5]_2Th[CH_2Si(CH_3)_3]_2$ (8) (5 pages). Ordering information is given on any current masthead page.

(17) By carrying out eq 3 with D_2. Th–D modes other than at 904 cm^{-1} are obscured by $Me_2SiCp''_2$ vibrational transitions.

(18) In this case, catalyst lifetime is only ca. 8 h. The cause is under investigation.

Catalytic Halogen Exchange Mediated by the Dinuclear Gold(I) Complex $[Au(CH_2)_2PPh_2]_2$

John P. Fackler, Jr.,* and H. H. Murray

Department of Chemistry, Texas A&M University College Station, Texas 77843

John D. Basil

Department of Chemistry, Case Western Reserve University Cleveland, Ohio 44106

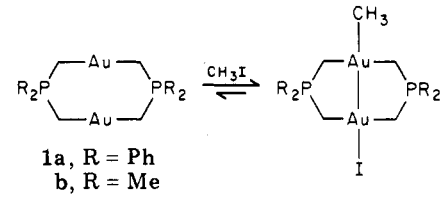
Received January 10, 1984

Summary: In addition to establishing the reversible nature of the oxidative addition of RX (R = CH_3, CD_3; X = Br, I) to $[Au(CH_2)_2PPh_2]_2$, we have observed that $[Au(CH_2)_2PPh_2]_2$ catalyzes halogen exchange between CH_3Br and CD_3I as well as between $[Au(CH_2)_2PPh_2]_2Br_2$ and CH_3I in $CDCl_3$. The results of attempted halogen exchange with a variety of alkyl halides suggests that a S_N2 process is likely via the formation of $[[Au(CH_2)_2PPh_2]_2CH_3]^+I^-$; thus the dinuclear gold(I) complex effects exchange by ionization of CH_3I.

While pursuing studies of the two-center two-electron oxidative addition of alkyl halides to the dinuclear gold(I) ylide complex[1] $[Au(CH_2)_2PPh_2]_2$, **1a**, we observed a catalytic halogen-exchange reaction mediated by **1a**. Many homogeneous catalytic reactions require sequential oxidative addition–reductive elimination cycles[2] in order to effect a given chemical transformation. However, oxidative addition–reductive elimination reactions have not been well studied for complexes containing more than one metal center.[2] Since we have observed[3] that $[Au(CH_2)_2PPh_2]_2(CH_3)I$, **2a**, is in equilibrium with CH_3I and **1a**, this system is particularly well suited for an investigation that addresses the role of the second metal center in the oxidative addition–reductive elimination cycle.

The dimers **1a** and **1b** were prepared according to established methods.[2b,3,4] The syntheses of **2a** and **2b** were carried out as described by Fackler[1] and Schmidbaur.[2b] Complexes **2c** and **2d** were obtained by the addition of excess CH_3Br (Matheson) and CD_3I (Aldrich) to **1a** in benzene, respectively. After 18 h of reaction at room temperature, the solvent was removed in vacuo, leaving a yellow powder,[5] **2c**, mp (uncorrected) 174 °C (loss of CH_3Br by reductive elimination), and the residue **1a**, mp 228–229 °C dec (lit.[3] mp 230–231 °C). The FT ^{2}H NMR spectra were obtained by using a Varian XL-200 spectrometer operating at 30.71 MHz. The $CHCl_3$ solvent used was distilled from P_4O_{10} before use. Chemical shifts were relative to internal $CDCl_3$ (δ 7.24). The ^{1}H NMR spectra were obtained by using a Varian EM 390 spectrometer (90 MHz), and chemical shifts are relative to internal Me_4Si (δ 0).

Our attention was drawn to the halide-exchange reaction when we observed[3a] the previously unreported[6] and possibly the first example[3b] of an intermolecular reversible two-center oxidative addition–reductive elimination equilibrium (eq 1). The reversibility of the reaction has been established by temperature-dependent NMR measurements.



(1)

1a, R = Ph
b, R = Me

2a, R = Ph
b, R = Me

(1) Fackler, J. P., Jr.; Basil, J. D. *Organometallics* **1982**, *1*, 871. Structural characterization of **2c**, $[Au(CH_2)_2PPh]_2(CH_3)Br$, undertaken in our laboratory indicates the Au–Au bond to be 2.680 (3) Å. The Au–Au bond in **2b** is 2.663 (9) Å.

(2) (a) Lewis, N. S.; Mann, K. R.; Gordon II, J. G.; Gray, H. B., *J. Am. Chem. Soc.* **1976**, *98*, 7461. (b) Schmidbaur, H., Franke, R. *Inorg. Chim. Acta* **1975**, *13*, 85. (c) Coleman, A. W.; Eadie, D. T.; Stobart, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 922. (d) Chisholm, M. H.; Kirkpatrick, C. C.; Huffman, J. C. *Inorg. Chem.* **1981**, *20*, 871. (e) For a discussion of oxidative addition of alkyl halides to mononuclear gold(I) complexes see: Kochi, J. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978. As well as: Kuch, P. L.; Tobias, R. S. *J. Organomet. Chem.* **1976**, *122*, 429.

(3) (a) Basil, J. D., Ph.D. Thesis, Case Western Reserve University, 1982. (b) R. J. Puddephatt has observed the reversible oxidative addition of MeI to the dinuclear Pt complex $[Pt(CH_3)_2(C_2H_5)_2P\text{-}CH_2\text{-}P(C_2H_5)_2]_2$, "but it occurs at only one metal center" giving a Pt(IV)/Pt(II) dimer (private communication).

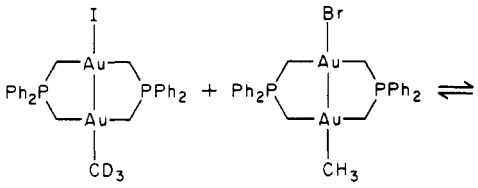
(4) Schmidbaur, H. "Inorganic Synthesis"; Douglas, B. E., Ed., Wiley-Interscience: New York, 1978; Vol. XVIII, p 138.

(5) ^{1}H NMR of **3** (90 MHz, $CDCl_3$ solvent, relative Me_4Si internal) in equilibrium with **1a** and CH_3Br: **3**, C_6H_5, δ 7.59 (m) and 7.29 (m), Au–CH_2–P, δ 1.77 (d, J_{PH} = 10.8 Hz) and 1.42 (d, J_{PH} = 10.5 Hz), $AuCH_3$, δ 1.10 (t, J = <0.6 Hz); **1a**, C_6H_5, δ 7.55 (m) and 7.25 (m), δ 1.35 (d, J_{PH} = 12.9 Hz), CH_3Br, δ 2.63 (s).

(6) In Schmidbaur's original report of the oxidative addition of CH_3I to $[Au(CH_2)_2P(CH_3)_2]_2$ there is no mention that the ^{1}H NMR spectrum of this gold(II) dinuclear methyl iodide adduct shows it to be in equilibrium with the gold(I) dinuclear ylide and CH_3I. See ref 2b and: Schmidbaur, H. *Acc. Chem. Res.* **1975**, *8*, 62.

0276-7333/84/2303-0821$01.50/0

Facile halogen exchange occurs (^{2}H NMR spectroscopy) when $[Au(CH_2)_2PPh_2]_2(CH_3)Br$ and $[Au(CH_2)_2PPh_2]_2(CD_3)I$ are combined in $CHCl_3$ at 22 °C (eq 2).



2d 2c

$$CD_3Br + CH_3I + \text{1a, 2a, and other products} \quad (2)$$

Since CD_3Br is observed within 3 min of mixing **2c** and **2d** in $CHCl_3$ at 22 °C, halogen scrambling must occur or otherwise *only* CD_3I would be observed in the ^{2}H NMR spectrum.[7] A much slower process involving halogen exchange with the solvent also is observed by the eventual detection of CD_3Cl.[8] Equation 1 describes only the overall reaction between **1a** and one type of alkyl halide. Clearly, for scrambling to occur at least one other step involving a second alkyl halide must be involved. This step may be the addition of a second alkyl halide molecule to **2c** or **2d** or promotion by **2c** or **2d** of nucleophilic halide attack on free alkyl halide.[9]

In order to distinguish between these two possible pathways, halogen exchange was attempted between **2a** and the four alkyl halides 1-bromoadamantane, neopentyl bromide, ethyl bromide, and benzyl bromide. Halogen exchange was observed (^{1}H NMR spectroscopy, by the appearance of CH_3Br) only in the latter two cases. Furthermore, no rearrangement of the neopentyl bromide to 2-bromo-2-methylbutane was observed.

A S_N2 mechanism is postulated for the halogen-exchange process. This is based on the results of halogen-exchange attempts between **2a** and ethyl bromide and neopentyl bromide. Since ethyl bromide[10] does not give a stable dinuclear gold(II) adduct when reacted with **1a** *yet* undergoes halogen exchange with **2a**, we suggest that the intermediate *responsible for halogen exchange* is likely $[[Au(CH_2)_2PPh]_2(CH_3)]^+I^-$. The role of the dinuclear gold(I) complex appears to be the promotion of ionization of CH_3I allowing for S_N2 halogen exchange (eq 3). The lack of reactivity of neopentyl bromide with **1a** suggests steric constraints are important.

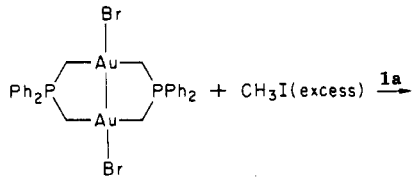
$$[[Au(CH_2)_2PPh_2]_2CH_3]^+I^- + CH_3CH_2Br \rightarrow CH_3CH_2I + [[Au(CH_2)_2PPh_2]_2CH_3]^+Br^- \quad (3)$$

To test for catalytic halogen exchange, a measured ratio of CD_3I to **1a** (100:1) was combined with excess CH_3Br in $CHCl_3$ at 25 and 50 °C. Following the appearance of CD_3Br and the disappearance of CD_3I with time, we were able to establish that more than one molecule of CD_3I per molecule of **1a** is converted to CD_3Br in the presence of excess CH_3Br (eq 4). Furthermore, the rate of this process is increased with increased temperature.

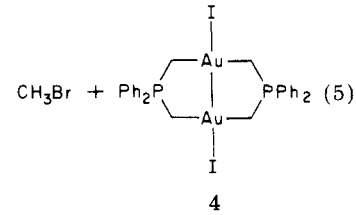
$$CH_3Br \text{ (excess)} + CD_3I \xrightarrow{\textbf{1a}} CD_3Br + CH_3I \quad (4)$$

As the dinuclear gold(I) complex **1a** promotes catalytic halogen exchange between CH_3Br and CD_3I and involves complexes **2c** and **2d**, the stabilities of these dinuclear gold(II) alkyl halides were investigated under the reaction conditions. We have found that **2c** and **2d** can produce $[Au(CH_2)_2PPh_2]_2Br_2$, **3**, and $[Au(CH_2)_2PPh_2]_2I_2$, **4**, respectively, with light or upon heating in $CDCl_3$. Complexes **3** and **4** were tested for catalytic activity toward halogen exchange.

When $[Au(CH_2)_2PPh_2]_2Br_2$, **3**, was added to $CDCl_3$ in the presence of CH_3I, no halogen exchange was observed after 20 h of mixing. However, when **3** and CH_3I were combined in $CDCl_3$ *with* the dinuclear gold(I) complex **1a**, halogen exchange *was* observed within minutes of mixing (eq 5).



3



4

The process expressed by eq 5 was further investigated by ^{1}H NMR. The ^{1}H NMR spectrum of **3** in $CDCl_3$ is a doublet (δ 1.90 ($^2J_{HP}$ = 9.9 Hz, $W_{1/2}$ = 3.0 Hz)). The ^{1}H NMR spectrum obtained upon the addition of a small amount of **1a** to the $CDCl_3$ solution of **3** shows significant broadening and shifting of the major resonance. The $CHCl_3$ resonance shows no broadening upon the addition of **1a**. The broadening observed in the ^{1}H NMR spectrum indicates that **1a** and **3** are undergoing an exchange process, likely involving Br ligands. Exchange of Br between **1a** and **3** is not surprising considering that **1a** and the dinuclear gold(III) tetrabromide $[Au(CH_2)_2PPh_2]_2Br_4$, **5**, when combined in a 1:1 ratio, gives **3** in quantitative yield.[3] These observations demonstrate that once formed, **3** and **4** in the presence of **1a** and an alkyl halide allow for halogen exchange, likely via $[[Au(CH_2)_2PPh_2]_2X]^+X^-$, analogous to the alkyl halide intermediate proposed above.

The role played by the second metal atom in this oxidative addition–reductive elimination cycle appears to relate to the formation of the Au–Au bond in the Au(II) dinuclear ylide complexes. The constrained proximity of the second gold atom allows for the formation of this bond while requiring little nuclear motion. An enhanced nucleophilicity of the metal atom center undergoing "oxidation" is the result, although completely valid comparisons of relative reactivity are not yet available. The dearth of mixed valent Au(I)–Au(III) species, at least to date, and the plethora of Au(II)–Au(II) bonded species further suggests that the second metal atom influences the reactivity of the dimer. In the gold(II) alkyl halide adducts, ionization of the halide can lead to the observed halogen exchange by an S_N2 process. The structural trans effect[1] observed in the lengthened Au–I bond corroborates this viewpoint.

(7) The chemical shifts of CD_3Br and CD_3I are sufficiently different (δ 2.61 and 2.12, respectively, relative $CDCl_3$ at δ 7.24) to allow their ^{2}H NMR resonances to be resolved easily.

(8) In the original report of the structural characterization of the methyl iodide gold(II) ylide complex,[1] $CHCl_3$ was observed to be generated in the photodecomposition of **1a** in $CDCl_3$.

(9) Halide exchange in organic systems is sometimes called the Finkelstein reaction and is believed to proceed via an S_N2 mechanism. See: March, J. "Advanced Organic Chemistry: Reactions, Mechanisms and Structure"; McGraw-Hill: New York, 1968, Chapter 10, p 342.

(10) Neither ethyl iodide or ethyl bromide react with the dinuclear gold(I) ylide **2a** to give a stable gold(II) alkyl halide adduct.

Acknowledgment. These studies are supported by the National Science Foundation, Grant CHE-83-05046, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. The Robert A. Welch Foundation has supported some chemical purchases.

Registry No. 1a, 81457-56-9; **2a**, 81457-57-0; **2c**, 89462-49-7; **2d**, 89462-48-6; **3**, 89462-50-0; **4**, 81457-58-1; MeI, 74-88-4; MeBr, 74-83-9.

Book Reviews

Topics in Phosphorus Chemistry. Vol. 11. M. Grayson and E. J. Griffith, Eds. Wiley, New York. 1983. $85.00.

The first chapter by J. Feder is a short (13 pages), noncritical review designed to provide sufficient structural and chemical information on ATP for the reader to better understand its biochemistry. The author accomplishes his aim, although in this reviewer's opinion a nonspecialist in this area would benefit from additional reaction schemes and a more interpretative discussion. Additional care in proofreading would have eliminated a few confusing statements, such as (p 4) "...the sites of protonation are not necessarily identical with the location of the positive charge".

The following chapter by Y. Abe is a very readable, current, and well-organized treatment of the physical and chemical properties of alkaline-earth phosphate glasses, which focuses mainly on the extensive research carried out in the author's laboratories. Of particular interest to this reviewer was the discussion of the role of elemental phosphorus in the thermochromism and photochromism of some of these glasses and also the elaboration of the author's tension–induction model for the spontaneous crystallization below the "glass temperature". In addition to industrial chemists interested in the optical and mechanical properties of glasses, biomedical researchers in the field of ceramic materials as bone implants will find this chapter useful.

The third chapter is an update by M. W. G. de Bolster on the syntheses, structures, NMR properties, and applications of phosphoryl compounds reported since 1975. The current review is timely in that more papers in this area (>1400) have been published since 1975 than in the period 1854–1975 covered by an earlier review by de Bolster and Groeneveld in Volume 8 of this series. Most of the current review is devoted to a very well-organized 138-page compilation of phosphoryl coordination compounds along with the physical methods with which they were studied. (The publisher's failure to insert page numbers in the outline for this table does not detract seriously from the usefulness of the compilation.) Of special interest is the section wherein is described the usefulness of several phosphoryl coordination compounds in high-power liquid laser amplification and the catalysis of olefin polymerization and the potential application of volatile complexes in the preparation of thin metal films and metal isotope separation.

The fourth chapter by R. L. Hilderbrand, J. Curley-Joseph, H. J. Lubansky, and T. O. Henderson is a compactly written yet thorough and critical review of the distribution, metabolism, and structural properties of naturally occurring alkylphosphonic acids. Such molecules which contain a C–P bond have been isolated from a variety of organisms including human tissue and are found free as well as bound in lipids and proteins. The biological role of such alkylphosphonic acid derivatives, though probably important, is apparently not well-understood. Biomedical researchers interested in the antiviral properties of phosphonate systems (which are also discussed) should find this review stimulating.

The last chapter by H. R. Hudson consists of a broadly based and very informative review of quasi-phosphonium intermediates and compounds. Such species can be formally written as Z_4P^+ wherein one or more Z substituents is not an alkyl, aryl, or hydrogen. The treatment is very nicely systematized and covers in considerable detail the various routes to quasi-phosphonium systems as well as their mechanisms of thermal decomposition, reactions with nucleophiles, and their applications in organic syntheses. The only substantive errors noticed by this reviewer occur in Schemes 14 and 173 wherein the ring oxygens should not have changed positions with neighboring ring methylenes in the product and in Scheme 142 wherein the product should be $(MeO)_3P^+OCH(Me)COMe$.

A wide spectrum of phosphorus chemists as well as researchers in other specialties will find at least certain of these chapters sufficiently useful to justify considering the addition of this volume to their personal libraries, although the price ($85.00) may make it more attractive to request its purchase by their institutional libraries. Considering that camera-ready copy was used, the number of errors does not appear to be unusually large.

John G. Verkade, *Iowa State University*

Houben-Weyl Methoden der Organischen Chemie. 4th Edition. Organobor-Verbindungen I. Volume 13, Part 3a. R. Köster, Editor. 1982. xiv + 910 pages. DM 1040. Organobor-Verbindungen II. Volume 13, Part 3b. R. Köster, editor. 1983. xiv + 893 pages. DM 1080. Georg Thieme Verlag, Stuttgart/New York (in German).

The organoboron chemist is extraordinarily well supported by the review literature. There are books by Brown, Onak, Matteson, and Grimes that cover various aspects of the field; there are the many volumes of the Gmelin boron series and now organoboron compounds are treated within the framework of the well-known Houben-Weyl series. Two such volumes, 1703 pages total, have appeared and one more will join them shortly.

It is the concern of the Houben-Weyl series to bring not lists of compounds and their properties but rather a detailed account of the chemistry (synthesis, reactions, analysis) of the classes of compounds in question. As such, it complements the Gmelin inorganic and Beilstein organic handbooks.

The present volumes are concerned with the preparation of organoboron compounds of all kinds—in the first volume—triorganoboranes of all sorts, organoboron hydrides and halides, and organoboron compounds that contain substituents bonded via oxygen, sulfur, and selenium; in the second volume, organoboron compounds with substituents bonded via nitrogen, phosphorus, and arsenic and via group 4 elements, carboranyl organoboranes, organodiboron(4) compounds, organoboron compounds with σ bonds to transition metals, cationic organoboron(3) compounds, and four-coordinate organoboron compounds.

The organization of this wealth of information about the many preparative routes to these many different types of organoboron compounds into a coherent whole is a monumental accomplishment, and it is a successful one, thanks due to the efforts of Dr. Roland Köster and his collaborators. These volumes will be a great help to any chemist who wants to prepare any kind of organoboron compound.

Some useful features of these books should be pointed out: the excellent, detailed tables of contents; the large number of tables in which much preparative information is summarized (and an index of tables at the end of each volume); the many detailed preparative procedures from the literature; the many equations that greatly help the user who does not read German well to find his way about these books; the excellent bibliographies of reviews and monographs (particularly valuable is the cross-indexing to