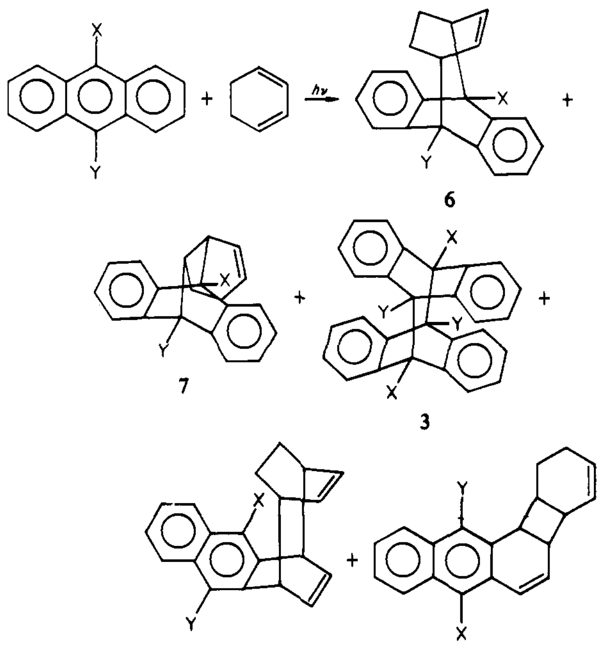

6 7 3 8 9 (3)

similar dependence of the proportions of adducts formed upon arene concentration. The results of representative cases are summarized in Table I.

As noted, photoexcited arene may react competitively either with another molecule of arene in its ground state to form an excimer or with a molecule of 1,3-diene to form an exciplex. The amount of excited arene which will decay via each pathway will depend on the relative concentrations of the two reactive species, the arene and 1,3-diene in their ground state, as well as on the relative extent of the equilibria for excimer and for exciplex formation. The meso positions are the most reactive positions in excited arenes since the MO coefficients of HOMO and LUMO are greatest in magnitude at these positions, i.e., the meso positions have the highest free valences.[13] The excited arene should react in a concerted manner at the meso positions to afford $4\pi_s + 4\pi_s$ adducts with 1,3-dienes, following the rule of conservation of orbital symmetry. However, the rate of this reaction is competitive against other decay processes of excited arene, such as intersystem crossing and radiative decay. In the cases we have studied, there appears to be a general trend in that $4\pi_s + 4\pi_s$ photocycloaddition at the meso positions is favored at lower initial arene concentration when the excited arene mainly decays via the arene–diene exciplex and the monomeric singlet excited arene. At higher initial arene concentration, excimer formation becomes more favorable. Since the excitation energy is delocalized between both components of excimer, each component will be less reactive at the meso positions toward the diene than will the monomeric excited arene. Thus, the formation of $4\pi_s + 4\pi_s$ adducts with 1,3-dienes in the expected manner is suppressed, and competitive processes such as nonconcerted $4\pi_s + 2\pi_s$ cycloaddition, addition at an alternative site, and arene photodimerization become the preferred modes of decay. Different products or different proportions of products are then formed in the reaction.

Liu and co-workers also have reported that 1,3-dienes promote the photodimerization of anthracenes and suggested that excimers are the intermediates in this reaction.[14] Since excimers of anthracenes have been characterized to have finite lifetimes,[3] the excimers may interact with 1,3-dienes to give enhanced yields of photodimers as an additional pathway of excimer decay when 1,3-dienes are present at sufficiently high concentrations in the reaction media. The enhanced quantum yield of anthracene consumption at high initial anthracene concentration in the presence of CHD may be justified by this pathway. Lewis and co-workers recently reported that the photocycloaddition of stilbene to dimethyl fumarate is concentration dependent, and the excimer of stilbene has been suggested as a intermediate at high stilbene concentration.[15] Therefore, excimers of arenes may play a more general role than previously anticipated in photocycloadditions of arenes to unsaturated systems.

Acknowledgment. We thank the National Science Foundation and the National Institute of General Medical Sciences for the support of this work, Dr. Bongsub Kim for carrying out the preliminary studies on the reaction of 9,10-difluoroanthracene, Professor L. M. Stock for a sample of 9,10-difluoroanthracene, and the Institute of Photographic Chemistry of the Academia Sinica (Beijing) for research fellowships to two of us (H.S. and T.W.) in the United States.

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[12] The discrepancy concerns the relative ratios of **6b** and **7b** reported from two different laboratories.[2,9] The reactions were carried out at different initial anthracene concentrations, and the results were analyzed by different types of NMR spectrometers, 60 MHz[9] vs. 270 MHz.[2] When the reaction was repeated in our laboratory at higher initial anthracene concentration and the results were analyzed with a 270-MHz NMR spectrometer, the higher yield of **7b** reported[9] may be attributed to the method of analysis as well as to the formation of **8b** and **9b** and their secondary reactions.

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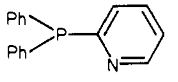
2-(Diphenylphosphino)pyridine as a Bridging Ligand. Synthesis and Structure of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ and $RhPd(Ph_2Ppy)_2(CO)Cl_3$

Sir:

There has been considerable current interest in the reactions between two metal complexes and in the reactivity of binuclear metal complexes.[1-5] The ligand 2-(diphenylphosphino)pyridine,[6,7] Ph_2Ppy (**1**), is a convenient building block for constructing binuclear complexes. Because of its similarity to triphenylphosphine, it should be capable of substitution for triphenylphosphine in any of the numerous complexes of this popular ligand while the presence of the pyridine nitrogen should allow the ligand to bind a second metal ion. Consequently, a metal complex containing



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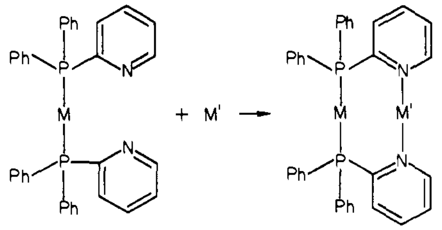

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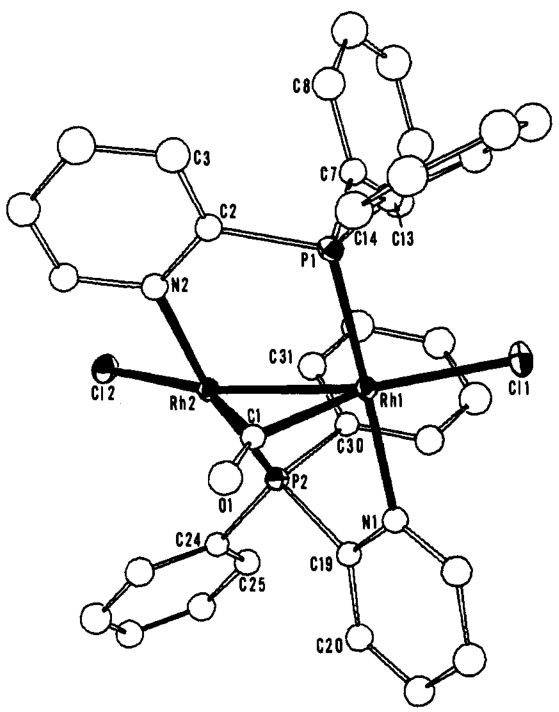
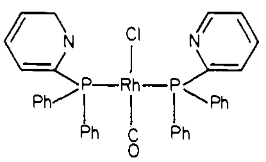


Figure 1. A perspective drawing of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$. Some bond lengths are the following: Rh-Rh, 2.612 (1); Rh(1)-Cl(1), 2.355 (1); Rh(2)-Cl(2), 2.355 (1); Rh(1)-P(1), 2.206 (1); Rh(2)-P(2), 2.215 (1); Rh(1)-N(1), 2.116 (5); Rh(2)-N(2), 2.114 (5) Å. The Rh-C-Rh angle is 84.3° (0.2)°.

a trans pair of Ph_2Ppy ligands should be capable of chelating a second metal by reaction 1. Herein we report some preliminary observations with Ph_2Ppy as a bridging ligand in cases where metal-metal bond formation is facilitated.

Addition of $Rh_2(\mu\text{-}Cl)_2(CO)_4$ to Ph_2Ppy in dichloromethane solution followed by precipitation with ether yields yellow crystalline $Rh(CO)Cl(Ph_2Ppy)_2$ (**2**) [IR ν(C≡O) 1969 cm^{-1}, ν(Rh-Cl) 304 cm^{-1}; $^{31}P\{^1H\}$ NMR (in chloroform solution) δ 30.13 from external 85% H_3PO_4, $^1J_{Rh-P}$ = 127.8 Hz]. While otherwise similar to the well-studied $Rh(CO)Cl(PPh_3)_2$, **2** does have the additional ability of bonding to a second metal ion.



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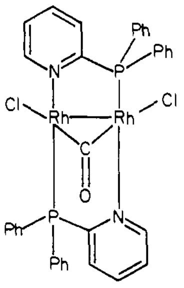
Treatment of $Rh(CO)Cl(Ph_2Ppy)_2$ with $^1/_2$ mol of $Rh_2(\mu\text{-}Cl)_2(CO)_4$ in benzene solution produces red-brown crystals of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ (**3**). The infrared spectrum indicates the presence of a bridging carbonyl [ν(CO) 1797 cm^{-1}] and terminal chloride ligands [ν(Rh-Cl) 320, 305 cm^{-1}]. The $^{31}P\{^1H\}$ NMR spectrum of **3** has been analyzed as an AXX′A′ spin system with δ 44.18 ($^1J_{Rh-P}$ = 144.0 Hz, $^2J_{Rh-P}$ = −7.39 Hz, J_{P-P} = 16.0 Hz, J_{Rh-Rh} = 12.0 Hz). The detailed geometry has been established by X-ray crystallography.[8] The structural results are shown in Figure 1. The complex has approximate C_2 symmetry with the twofold axis passing along the carbonyl C-O bond. The geometry is that of a distorted molecular A frame with the $Rh_2(\mu\text{-}CO)Cl_2$ portion lying in a plane. While the trans PRhN units are nearly linear, the two PRhN units are skewed so that they are neither parallel to one another nor perpendicular to the $Rh_2(\mu\text{-}CO)Cl_2$ plane. Each rhodium center in the complex possesses 16 valence electrons, and there is a direct Rh-Rh bond. Thus, **3** is a rare example of an electron-deficient species possessing a bridging carbonyl. Because of its low symmetry, the complex is chiral. In general, A-frame complexes constructed from unsymmetrical bidentate bridging ligands will be chiral so long as these bidentate ligands adopt a head-to-tail orientation.



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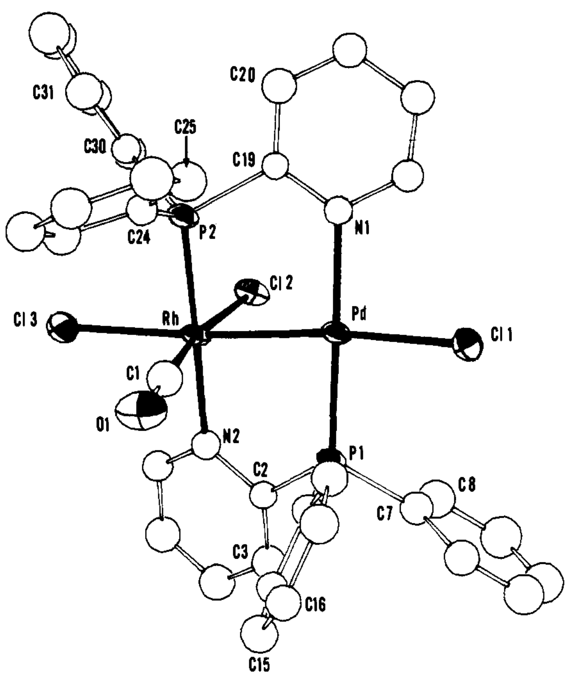
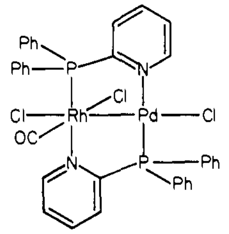


Figure 2. A perspective drawing of $RhPd(Ph_2Ppy)_2(CO)Cl_3$. Some bond lengths are the following: Rh-Pd, 2.594 (1); Rh-Cl(2), 2.399 (3); Rh-Cl(3), 2.499 (4); Pd-Cl(1), 2.393 (4); Rh-P(2), 2.243 (3); Pd-P(1), 2.220 (4); Rh-N(2), 2.16 (1); Pd-N(1), 2.13 (1); Rh-C(1), 1.82 (1) Å.

When cyclooctadienepalladium dichloride is added to $Rh(CO)Cl(Ph_2Ppy)_2$ in dichloromethane solution, a red solution forms from which $RhPd(Ph_2Ppy)_2(CO)Cl_3$ (**4**) may be crystallized by the addition of ether. The infrared spectrum indicates that the carbonyl ligand occupies a terminal site [ν(CO) 2040 cm^{-1}]. The structure has been elucidated by a combination of X-ray crystallography and ^{31}P NMR spectroscopy. Figure 2 shows a drawing of the molecule. One metal is 6-coordinate with two



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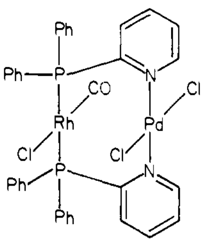
[8] Single crystals of **3** were grown by diffusion of diethyl ether into a dichloromethane solution of **3**. They belong to space group $P\bar{1}$ with a = 9.920 (6), b = 12.509 (6), c = 13.860 (7) Å, α = 93.06 (4), β = 107.57 (4), γ = 100.01 (4)°, Z = 2. R = 3.4% for 3746 reflections with $I > 3\sigma(I)$.

[9] Single crystals of **4** were grown by diffusion of diethyl ether into a dichloromethane solution. The crystals are orthorhombic, space group $Pc2_1b$, with a = 10.353 (5), b = 15.426 (7), c = 21.219 (11) Å, Z = 4. R = 3.8% for 2018 reflections with $I > 3\sigma(I)$.

terminal chloride ligands, a carbonyl ligand and bonds to each of the bridging Ph_2Ppy ligands. The second metal possesses nearly square coordination. The metal–metal separation [2.594 (1) Å] is indicative of the presence of a direct bond between the metals. The $^{31}P\{^1H\}$ NMR spectrum allows the location of the two metals to be specified and indicates that each particular metal occupies a unique site in the molecule. The spectrum consists of two groups of four equally intense lines and has been analyzed in terms of the following parameters: δ_1 21.89; δ_2 16.15 ($^1J_{Rh-P} = 112.7$ Hz, $^3J_{P-P} = 17.4$ Hz, $^2J_{Rh-P} = 2.3$ Hz). The values of $^3J_{P-P}$ and $^2J_{Rh-P}$ are consistent with the parameters observed for other binuclear complexes. The value of $^1J_{Rh-P}$ is sensitive to metal oxidation state/coordination geometry. In the present case, this value, which has decreased from the value found for $Rh(CO)Cl(Ph_2Ppy)_2$, is consistent with placing the rhodium ion at the 6-coordinate site in the molecule.[10]

The formation of **4** involves the oxidative addition of a d^8 Pd(II) complex to an isoelectronic, d^8 Rh(I) complex, a reaction which is otherwise unknown. It must occur because the bridging Ph_2Ppy ligands bring the two metals into close proximity. Face-to-face dimers such as **5**, with a head-to-head orientation of the bridging ligands, or **6**, with a head-to-tail arrangement of the Ph_2Ppy ligands, may be intermediates in the formation of **4**. Several such face-to-face dimers, which involve d^8 metal ions but which lack direct metal–metal bonds, are known.[11,12] Both **3** and **4** deviate from the expected product of reaction 1 in that the ligands are found in the head-to-tail arrangement. This reorientation emphasizes the mobility of phosphine ligands in binuclear species.



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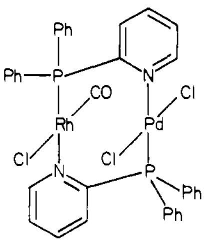

6

We are continuing to explore the ability of Ph_2Ppy to act as a bridging ligand in constructing polynuclear complexes and in promoting the transfer of ligands between metal centers.

Acknowledgment. We thank the National Science Foundation and the U.C.D. NMR Facility for support, Matthey Bishop for a loan of precious metal salts, and C. H. Lindsay for experimental assistance. Acquisition of the X-ray diffractometer and NMR spectrometer used in this study was made possible through NSF instrument grants.

Supplementary Material Available: A list of atomic fractional coordinates and temperature factors for $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ and $RhPd(Rh_2Ppy)_2(CO)Cl_3$ (2 pages). Ordering information is given on any current masthead page.

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Book Reviews

Photometric and Fluorometric Methods of Analysis, Metals. By Foster Dee Snell. Wiley-Interscience, New York. 1978. In two parts: xi + 1003 pp; xi + (1005 to) 2167 pp. $160/set.

Many practicing analytical chemists have long been familiar with the much earlier forerunner of this work. The present, totally new, treatment employs two volumes to embrace the content of 8700 relevant references spanning the past 20-year period. The emphasis is on typical colorimetric and spectrophotometric procedures; a very few involve colloidal systems, and there remains little explicit reference to turbidimetric or nephelometric methodology. A fair number of fluorometric methods are included, and some flame photometric procedures. There is virtually no reference to atomic absorption methods.

While the treatment is necessarily abbreviated, most of the methods indicate a suitable dissolution procedure, desirable preliminary separations, the method of color formation, and a suitable wavelength for reading. Prominent interferences may be noted and the sensitivity is often implied, indirectly, by some of the given data or modus operandi. Few fundamentals are given such as full absorption curves, molar absorptivities, or partition coefficients for L–L extractions, etc. There are no critical evaluations of methods or comparisons of their relative merits. Sometimes, but not always, the procedural descriptions are adequately full for application of the method without consulting the original references.

A very helpful feature is the 204-pp Index, in which a given metal may be listed in three different respects. The determination of other components in the metal as matrix will be listed. The determination of the metal in various kinds of samples is listed. Finally, the various reagents or color-forming reactions of the metal are tabulated.

Any criticism of this compilation would probably relate to its relatively indiscriminate approach to complete coverage and the resulting brief, almost cryptic, outlines of some of the procedures. There are 134 pp, each, of Cu and Fe methods, while treatments of 36 elements in Part 2 average 27 pp, each. Concise exposition sometimes leads the author into sentences which are four to five lines in length, or into the use of short verbless phrases. A typical sentence, "Reading is against a sample reverted with sulfuric acid in addition to subtraction of a blank", is clear enough within its context, yet illustrative of some sacrifices on the altar of compactness. The journal name, *Talanta*, is misspelled, *Talenta*, in all citations.

Despite some flaws inherent in such an ambitious coverage, the practicing analyst will find in this work a broad selection of methods, some more useful than others, for photometric measurements of metals.

Charles L. Rulfs, *University of Michigan*

Liquid Chromatographic Analysis of Food and Beverages. Edited by G. Charalambous. Academic Press, New York. 1979. xii + 326 pp. $25.00.

This book on the use of HPLC in food analysis joins Volume 1 on the same topic. The book consists of 14 chapters contributed by 32 authors on a wide range of HPLC methods dealing with the analysis of foods and beverages. Included are HPLC applications to beer, wine, carbohydrate products, cough remedies, and fruit juices. Constituents for which detailed experimental analytical procedures are provided include carbohydrates, gluconic acids, flavor constituents, hop compounds, vitamins, polymers, and flavones. There are two chapters which are particularly useful for those who wish to consider using HPLC for food analysis, but who have had no previous experience. One of these chapters is by Howard and Hodgin and deals with instrument selection for HPLC. These authors have provided extensive coverage of HPLC instrumentation and component systems and they have included very useful information for potential purchasers of HPLC equipment from the standpoint of cost, efficiency, overall performance, and utility. The chapter by Popovich and Southern on the advantages of HPLC for the analysis of foods and beverages provides a very valuable overview of HPLC and includes a wide range of useful applications to food chemistry. An incorrect use of terminology, which appears throughout the book, is the