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Photochemical Reactivity of Diplatinum μ-Alkenylidene Complexes: Evidence of Atom-Transfer Chemistry

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The diplatinum μ-phenylethenylidene complex, $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_4]BF_4$, reacts under photolysis with lithium halide or KSCN salts, iodine, and alkyl or aryl halides to give mono- or dihalide (or SCN) complexes of the types $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_3X]$ or $[Pt_2(\mu\text{-}C{=}CHPh)(PEt_3)_3X_2]$. This complex and selected derivatives also induce the photolytic oxidation of 2-propanol to acetone and hydrogen. These atom-transfer reactions are similar to those exhibited by the well-studied complex, $[Pt_2(P_2O_5H_2)_4]^{4-}$.

Introduction

We recently reported the results of a comprehensive, though preliminary, study of the reactivity, structure, bonding, and photophysics of the diplatinum μ-phenylethenylidene complex, $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_4]BF_4$ (**1**) and its derivatives.[1] Complex **1** reacts thermally with halide or pseudohalide salts to form neutral compounds of the type $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_3X]$ (Pt_2X) by displacement of a PEt_3 ligand. These complexes react with a protic acid and a second equivalent of halide of pseudohalide salt to give the neutral Pt_2X_2 compounds $[Pt_2(\mu\text{-}C{=}CHPh)(PEt_3)_3X_2]$, by loss of phenylacetylene. However, complex **1** also reacts under photolysis with MeI to form Pt_2I and Pt_2I_2 and with 2-propanol to produce acetone and hydrogen through atom-transfer reactions. This type or reactivity is similar to that known for the well-studied compound $[Pt_2(P_2O_5H_2)_4]^{4-}$ ($[Pt_2(POP)_4]^{4-}$) as reported by Roundhill and Gray.[2] Although complex **1** and $[Pt_2(POP)_4]^{4-}$ are structurally dissimilar, these compounds exhibit some similarity in photochemical reactivity. In addition, several of the Pt_2X or Pt_2X_2 derivatives of **1** are luminescent molecules, as is $[Pt_2(POP)_4]^{4-}$.

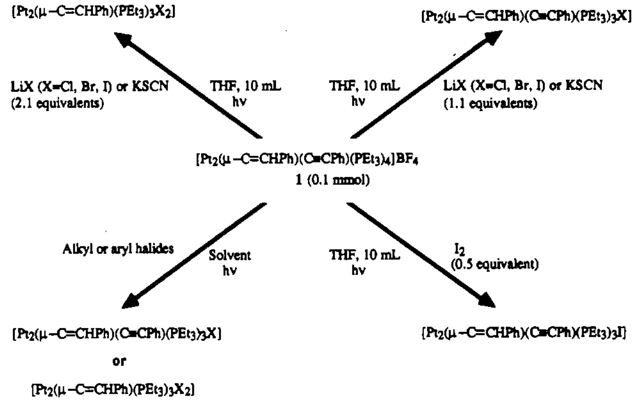
Because of the high, current interest in photochemically initiated atom-transfer reactivity, we now report the results of the photochemical reactions of **1** with halide or pseudohalide salts, iodine, and alkyl or aryl halides. Several of these reactions provide an alternate route for the preparation of such Pt_2X or Pt_2X_2 compounds. We also report the results of an additional study of the catalytic oxidation of 2-propanol to acetone and hydrogen by complex **1** or selected derivatives upon irradiation.

Experimental Section

All reactions were performed under dry, prepurified nitrogen. Solvent purification procedures, spectroscopic methods, and characterization data for the Pt_2X or Pt_2X_2 products and the preparation of complex **1** have been reported previously.[1] Photochemical reactions were conducted on a synthetic scale (usually 1 mmol of complex **1**) and were effected by using a either a 100-W Hanovia medium-pressure mercury lamp or a Rayonet preparative photochemical reactor (Model RPR-208) and a RPR 3500-Å lamp and a Pyrex glass vessel fitted with a cold finger to maintain a reaction temperature of 16 °C. The Pt_2X or Pt_2X_2 products were purified by chromatography and were isolated as reported earlier.[1]

Results and Discussion

Scheme I. Photochemical Reactions of Complex 1



Photochemical Reactivity of Complex 1 with Halide or Pseudohalide Salts, Iodine, and Alkyl or Aryl Halides. The results of this study are summarized in Scheme I. Compound **1** reacts with LiCl, LiBr, LiI, or KSCN in a 1.0:1.1 stoichiometry under photolysis in THF solution at 16 °C to give the corresponding Pt_2X complexes in the respective yields of 98, 80, 87, or 79%. The total reaction time for the formation of Pt_2Cl and Pt_2Br is 15 min, while the Pt_2I and Pt_2SCN compounds are formed in 30 min. In control reactions, these Pt_2X complexes are formed thermally at room temperature in yields of 54–75% with reaction times varying from 2 to 4 h. Reaction of **1** with a 50% excess of NaI in THF solution at reflux gives an essentially quantitative yield of Pt_2I within 30 min.

Compound **1** reacts with the same LiX or KSCN reagents in a 1.0:2.1 or 2.2 stoichiometry under photolysis in THF solution at 16 °C to give the corresponding Pt_2X_2 complexes in the respective yields of 44, 31, 33, or 23%. Total reaction times for these reactions vary from 30 to 40 min. Although the yields of the Pt_2X_2 complexes are low, this photolytic synthesis is the only one-step method known for the direct conversion of **1** to Pt_2X_2 compounds. Both the phenylacetylide ligand and a PEt_3 ligand of **1** are lost in the process. Phenylacetylene is observed by TLC upon chromatographic separation of the reaction products. The phenylacetylide salt obtained as a coproduct is presumably protonated during the chromatographic procedure. A major byproduct of these reactions is the corresponding PtL_2X_2 mononuclear compounds. An analogous thermal reaction does not occur.

Thermal reaction of **1** and I_2 in THF solution at room temperature gives a mixture of compounds that are difficult to separate. The major product appears to be the mononuclear PtL_2I_2 species. Photochemical reaction of **1** with I_2 in a 2:1 stoichiometry in THF solution using a Hanovia lamp fitted with a blue filter gives the Pt_2I complex in 90% yield. In this reaction, I_2 acts as a source of iodide. By comparison, $[Pt_2(POP)_4]^{4-}$ reacts thermally with halogens by oxidative addition to give the $[Pt_2(POP)_4X_2]^{4-}$ derivatives.[3]

Interesting atom-transfer reactivity occurs in the photochemical reaction of **1** with organohalides. Complex **1** does not react thermally at room temperature with any of the organohalides studied. Photolysis of **1** and MeI in a 1.0:4.6 stoichiometry in acetone solution for 8 h gives Pt_2I in 46% yield. Repeating this reaction with a large excess of MeI gives Pt_2I and Pt_2I_2 in 26% and 10% yield, respectively. When this latter reaction is photolyzed

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for 4 h, Pt_2I and Pt_2I_2 are formed in 35% and 25% yield, respectively. In other reactions, Pt_2I is formed in 20% yield from 2-iodopropane, Pt_2Cl is formed in 26% or 15% yield from reactions with excess CCl_4 or $CHCl_3$ (neat), respectively, and Pt_2Br is obtained in 12% yield from CBr_4. These reaction solutions were photolyzed for 16–17 h. Complex **1** does not react with CH_2I_2 even after 24 h of irradiation. By comparison, $[Pt_2(POP)_4]^{4-}$ reacts thermally with several alkyl iodides to give the corresponding $[Pt_2(POP)_4(R)(I)]^{4-}$ complexes.[3] Also, mononuclear dialkyl complexes of Pt(II) of the type $[PtL_2R_2]$ undergo an alkyl/chloride exchange reaction when photolyzed in chlorinated solvents.[4]

Control reactions indicate that **1** does not react thermally with either PhBr or PhI even under reflux. However, **1** reacts photochemically with PhI (1.5 equiv or in excess) over 26–27 h to give Pt_2I (in 27% or 18% yield). Photolysis of **1** with an excess of PhBr gives Pt_2Br and Pt_2Br_2 in 16% and 5% yield, respectively, over the same time period. Similarly, aryl bromides and iodides react with $[Pt_2(POP)_4]^{4-}$ only upon irradiation to give either $[Pt_2(POP)_4(X)(aryl)]^{4-}$ or $[Pt_2(POP)_4X_2]^{4-}$ species.[5]

On the basis of spectroscopic evidence, the Pt_2X_2 compounds also undergo halide exchange with different halide reactants that is accelerated substantially by photolysis. The expected mixed-halide products apparently undergo a facile exchange to give only the symmetrical Pt_2X_2 and Pt_2Y_2 compounds. A similar photoacceleration of halide exchange in $[Pt_2(POP)_4X_2]^{4-}$ complexes is known.[6]

Photolytic Oxidation of 2-Propanol to Acetone. The most interesting atom-transfer reactivity exhibited by complex **1** is its photochemical catalytic conversion of 2-propanol to acetone and hydrogen. When solutions of **1** and 2-propanol at 16 °C are irradiated, hydrogen gas evolution occurs at a rate sufficient to be monitored through a bubbler system with concomitant formation of acetone (as monitored by ^1H NMR). This reaction is photoinduced, because the reaction ceases upon removal of the photoexcitation. An induction period of 15–30 min is observed. Irradiation of neat solutions of **1** and 2-propanol causes decomposition of the catalyst in less than 30 min. However, the lifetime of the catalyst is prolonged in more dilute solutions. Irradiation of a solution of 8.6 μmol of **1** in 10 mL of CH_2Cl_2 and 1 mL of 2-propanol actively produces acetone and hydrogen over at least 16 h. The total number of catalyst turnovers at intervals of 2, 4, 8, and 16 h are, respectively, 32, 49, 98, and 194 mol of product/mol of catalyst. Production of acetone ceases after 48 h of irradiation.

In related systems, photolysis of a solution of 0.01 mmol of the corresponding Pt_2Cl complex in 10 mL of CH_2Cl_2 and 1 mL of 2-propanol produces acetone and hydrogen over 24 h with a total turnover number of 48. Irradiation of a solution containing a derivative of **1** (where the two phenyl groups are replaced by hydrogen atoms) in 20 mL of CH_2Cl_2 and 5 mL of 2-propanol for 8 h gives product formation with a total turnover number of 56.

Under similar reaction conditions, complex **1** did not produce the expected organic products or hydrogen gas evolution in reactions with either ethanol or 1-propanol. Also, an attempt to catalyze hydrogen transfer from 2-propanol to cyclooctene failed. In this latter reaction, the catalyst decomposes within the first 5 min of irradiation. Control reactions indicate that solutions containing **1** and cyclooctene are stable to irradiation for at least 12 h. Presumably, radical formation occurs when 2-propanol is present, and these species cause degradation of the catalyst in this system.

We speculate that complex **1** reacts photochemically with 2-propanol by a mechanism similar to that elucidated for $[Pt_2(POP)_4]^{4-}$.[2] Such a mechanism would require transfer of the methine hydrogen atom of 2-propanol to the photoexcited diplatinum complex forming a dinuclear hydride compound and $Me_2C(OH)$ radicals. Reaction of this carbon radical with a second diplatinum complex would give a dinuclear hydride and acetone. The diplatinum hydride complexes disproportionate to evolve hydrogen and to re-form the catalyst in its ground state. The complex $[Pt_2(POP)_4]^{4-}$ is a more reactive catalyst in the oxidation of 2-propanol (having a total turnover number exceeding 400 in 3 h reaction) than is **1**, and a Pt_2H intermediate species has been detected in hydrogen transfer reactions of this species. Although a platinum hydride derivative of **1** has not been isolated and characterized, we have obtained spectroscopic evidence of the formation of such a species in its photochemical reaction with 2-propanol. This species exhibits a proton resonance at δ -6.15 (doublet of triplets) with coupling constants of ca. 34 and 169 Hz.

Although detailed mechanistic and photophysical studies of the above reactions have not been completed, these results indicate that complex **1** has distinctly different reactivity under thermal or photochemical activation. This difference can be exploited for the synthetic preparation of selected compounds within this series. Most importantly, complex **1** represents another type of system that exhibits photochemical atom-transfer reactivity.

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