mixture containing PrI (1000 U), PRuK (800 U), AcK (800 U) (each immobilized separately in PAN gel[7]), $MgCl_2$ (30 mmol), DTT (10 mmol), and ATP (1 mmol); solid AcP (0.25 mmol) was added in 10 equal portions over 40 h. Isolation of Ba_2RuDP followed the procedure outlined above: 94 g of solid was obtained, containing 116 mmol of RuDP (72% purity, 58% yield based on R-5-P). The recovered enzymatic activities were PrI, 94%; PRuK, 92%; AcK, 92%.

Both of these preparations of RuDP use commercial PRuK and yield product of moderate purity. To obtain purer RuDP, either this product may be purified or the conditions of synthesis altered to give RuDP of higher initial purity. In order to accomplish the latter, it is necessary to use more PRuK to shorten the reaction time and minimize hydrolysis of RuDP in solution. Commerical PRuK (Sigma, 250 U/313 mg) was passed through a column of Bio-Gel P-150 (2 × 80 cm) in 50 mM Tris-3 mM DTT, concentrated by ultrafiltration, and immobilized, giving gel having activity of 6 U mL^{-1}. Conversion of R-5-P (100 mmol) to RuDP by using 800 U of PRuK in 2 L of solution was complete in 20 h and gave Ba_2RuDP in 92% purity and 80% yield (80 mmol) based on R-5-P.

A purification of lower purity RuDP was accomplished by treating a suspension of 45 g of Ba_2RuDP (72% purity) with 300 g of Dowex 50 (H^+ form, 200-400 mesh) in 800 mL of H_2O to remove Ba^{2+}. The resulting solution was passed through Dowex 1 (800 g, 200-400 mesh, chloride form), supported in a 2-L glass filter, and washed with 5 L of 40 mM aqueous HCl, to remove Ru-5-P and other impurities. RuDP was then desorbed by washing the resin with 2 L of 0.15 M HCl-0.1 M NaCl and precipitated as described previously. The product (32 g) was 94% Ba_2RuDP.

Both ribose 5-phosphate and ribulose 1,5-bisphosphate were prepared by using two different routes. Which route is superior depends on circumstances. The acid-catalyzed hydrolysis of AMP is the shorter route to R-5-P. Since it requires no enzymes, it is preferable when only a modest quantity of R-5-P (a few hundred grams) is required. This procedure has the further advantage that it generates a product uncontaminated by Ru-5-P.[14] The route from glucose to R-5-P is more complex, but it has two advantages: first, it can be used to regenerate NAD(P)H from NAD(P); second, it is potentially much less expensive as a route to large quantities of R-5-P than that starting with AMP. Thus, this procedure is more applicable to large-scale processes and integrated schemes for biotransformations in which the reduced nicotinamide cofactors can be utilized for other purposes. Similar considerations apply to RuDP. We have available in our laboratory large quantities of 6-PG as a byproduct of nicotinamide coenzyme regeneration using G-6-P.[6] The effort required to convert this material to RuDP is comparable to that required when starting with R-5-P.

In summary, for a synthetic effort whose sole purpose is the synthesis of RuDP, the procedure starting from AMP is simpler. When 6-PG is available for other reasons, or when the oxidation of 6-PG to Ru-5-P can be usefully coupled to another reduction via NAD(P)H, the route starting with G-6-P or 6-PG is superior.

Acknowledgment. We thank Professor J. B. Jones (University of Toronto) for pointing out to us the potential utility of G-6-PDH from *Leuconostoc mesenteroides* and our colleages David Walt, Victor Rios-Mercadillo, and Jerry Lewis for developing syntheses of R-5-P. We also thank Professor W. Orme-Johnson for advice concerning RuDP and associated enzymes.

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[14] An equilibrium mixture of Ru-5-P and R-5-P contains 77% R-5-P at pH 7.6; Dobrogrosz, W. J.; Demoss, R. D. *Biochim. Biophys. Acta* **1963**, *77*, 629-638.

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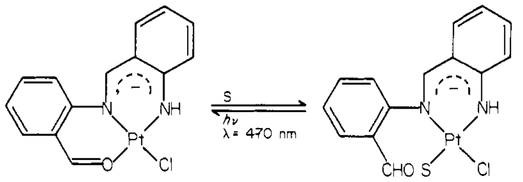
A Photochromic Swinging Gate: Platinum(II) Chelate with a Labile Aldehyde

Sir:

Chelating ligands are noted for imparting stability and special kinetic effects in their transition-metal complexes. Ligand dissociation, for example, becomes a multistep process whereby a coordinated fragment can detach yet remain in the vicinity of the metal ion, influencing ligand and metal ion reactivity. Recently, in the investigation of a platinum(II) complex with a tridentate O,N,N ligand, a novel photochemically controlled "swinging gate" dissociation effect was revealed. The process occurs in certain coordinating solvents such as acetonitrile and dimethyl sulfoxide and involves alternating solvent-terminal carbonyl occupation of a coordination site:



1 2

S = Me_2SO and CH_3CN

The complex **1** was isolated druing mechanistic studies of the template condensation of *o*-aminobenzaldehyde with platinum(II). The dimeric condensate was structurally characterized by using X-ray crystallographic techniques and was found to contain the rarely occurring deprotonated *o*-aminobenzylidene group.[1] In a variety of solvents **1** undergoes a color change over a period of hours from deep purple to light orange. The reaction can be followed spectroscopically by the disappearance of an absorption at 560 nm (ϵ 10 000) and appearance of a new band at 470 nm (ϵ 4000), indicative of **2**. Physical evidence indicates that the process involves solvent replacement of the coordinated aldehyde and in some cases also the chloride. In dimethyl sulfoxide and acetonitrile solvolysis occurs in the dark. Exposure to light results in the reappearance of the purple color indicative of **1**. The distinct isosbestic points in the time spectra of the light-initiated reaction (Figure 1) suggest that only two species, **1** and **2**, are involved, although the presence of a short-lived intermediate cannot be entirely discounted. Wavelength-dependence studies show **2** → **1** when irradiated in the visible between 420 and 500 nm and also with ultraviolet light of 250 and 350 nm. The electronic transitions in these regions are probably charge transfer in nature. Irradiation of **1** at the 560-nm absorption does not promote the formation of **2**, however. Quantum-yield studies at 440 nm in acetonitrile indicate $\phi = 0.15$ mol/einstein.[2] The product **2** is unstable upon solvent evaporation for both acetonitrile and dimethyl sulfoxide solutions, whereupon conversion to **1** occurs over a period of hours. Major evidence for solvolysis, therefore, and structure of **2** in these solvents derives from the infrared spectra. The band at 1621 cm^{-1}, assigned to the coordinated carbonyl in **1**, is shifted to 1690 cm^{-1} in a freshly evaporated solution of **2**.[2] The latter absorption agrees well with that found for other metal complexes with pendant carbonyls.[3] Acetonitrile solutions indicate nonelectrolyte behavior for both **1** and **2**, suggesting retention of the chloride.[4] Almost complete reversibility is exhibited by acetonitrile solutions through

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[1] Timken, M. D.; Sheldon, R. I.; Rohly, W. G.; Mertes, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 4716-4720.

[2] Quantum yield measurements were performed by using a Bausch and Lomb mercury light source HP-100 in conjunction with a Bausch and Lomb monochromator grating, 1350 grooves/mm, No. 33-86-02. Solutions of 10^{-4} M concentration in 50-mL Pyrex cells with a 10-cm pathlength were irradiated at 440 nm. Ferrioxalate was used as an actinometer (Parker, C. A. *Proc. R. Soc. London, Ser. A*, **1953**, *220*, 104-116). Concentrations were monitored spectrophotometrically on a Perkin-Elmer Model 555 UV-visible spectrophotometer. Infrared spectra were recorded from 4000 to 400 cm^{-1} on a Perkin-Elmer Model 421 grating spectrophotometer as KBr pellets.

[3] Ferraudi, G. L.; Endicott, J. F. *Inorg. Chem.* **1977**, *16*, 2762-2766.

[4] Solution conductivities for 10^{-3} M solutions were calculated by using an Industrial Instruments, Inc., Model RC-216B2, conductivity bridge.

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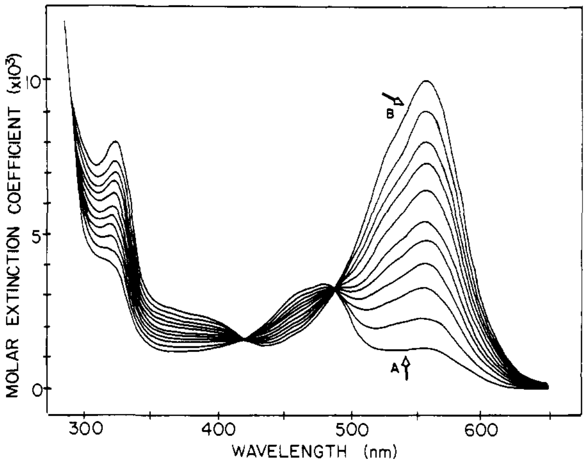

Figure 1. Visible absorption spectrum in acetonitrile as a function of irradiation time for the photochromic reaction **2** → **1**. Curve A is the initial curve, the solvolyzed complex **2**. Curve B is the final curve, corresponding to complex **1**.

15 cycles followed by increasingly limited reversibility until the 20th cycle, whereupon no color change occurs during irradiation. Convincing structural evidence for **2** was obtained from the pyridine reaction which yields a crystalline product. Solvolysis in pyridine also appears to be occurring, as evidenced by the free carbonyl band at 1690 cm^{-1} in the infrared. Unlike the dimethyl sulfoxide and acetonitrile cases the process is irreversible. Elemental analysis is in agreement with two pyridines per platinum which, along with solution conductivity data, suggests both aldehyde and chloride displacement.[5] In an effort to trap the free carbonyl by a strongly coordinating ligand, **1** was treated with a 1:1 molar ratio of triphenylphosphine in acetonitrile in the dark. The resulting red crystalline product analyzes for one triphenylphosphine per platinum,[6] and its infrared spectrum indicates the presence of the free carbonyl. A structural determination using X-ray crystallographic methods is currently under way.[6]

The photochromic process encountered in this reaction is related to that observed for chromium,[7,8] cobalt,[9] and rhodium[10] complexes with ethylenediamine. $[Cr(en)_3]^{3+}$, for example, undergoes light-initiated solvolysis in acidic media, resulting in detachment and protonation of an amine end. The complex then proceeds via a thermal route to the diaquo product.[7,8] In similar rhodium(III) complexes monodentate ethylenediamine with either protonated or nonprotonated detached amine is observed depending on the pH.[10] In the ethylenediamine complexes the ethylenediamine, once protonated, does not close to form the bidentate ligand.

Also unlike the ethylenediamine complexes, the pendant ligand in **2** becomes attached in the presence of light, while the solvent molecule is the photolabile species. Such a process appears to be the reverse of previously studied systems in which the chelating ligand is photolabile and is either completely lost or becomes reattached via a subsequent thermal process. It is possible that the lability of the aldehyde to solvolysis in **1** is promoted by the trans imine, reminiscent of the conjugate base mechanism in the solvolysis of octahedral amine complexes. A contributing factor to lability may also involve the strength of Pt–O vs. Pt–NH bonds. The X-ray data for **1** do show a significant difference in the Pt–O and Pt–NH bond lengths (2.01 (1) and 1.93 (2) Å, respectively) which could be a reflection of relative bond strengths.[1] The mechanistic pathway, as is common in square-planar substitutions, most probably involves a five-coordinate intermediate in the thermal solvolysis and possibly in the photosubstitution. The term "swinging gate" aptly describes the reaction in view of the on-again–off-again nature of the aldehyde. Similar processes could play major roles in template mechanisms whereby condensations may occur only on the uncoordinated or "open gate" ends of chelated ligands. Further investigations of this and related systems are currently in progress.

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(5) Anal. Calcd for $PtClON_2C_{24}H_{21}\cdot H_2O$: C, 45.75; H, 3.68; N, 8.89; Found: C, 45.54; H, 3.92; N, 8.90. $\Lambda_m(CH_3OH) = 107\ \Omega^{-1}\ cm^2\ mol^{-1}$. A 1:1 electrolyte in CH_3OH ranges from 80 to 115 $\Omega^{-1}\ cm^2\ mol^{-1}$ (Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122).

(6) Anal. Calcd for $PtClPON_2C_{32}H_{26}$: C, 53.67; H, 3.66; N, 3.91; Found: C, 53.98; H, 4.28; N, 3.91. The complex crystallizes in the space group *C*2/*c* with unit cell $a = 35.75$ (9), $b = 10.04$ (2), $c = 19.71$ (6) Å, $\beta = 118.5(2)°$, $\rho_{calcd} = 1.70$ g cm^{-1} (flotation $CHCl_3$–CH_2I_2), and $\rho_{obsd} = 1.67$ g cm^{-1} for $Z = 8$.

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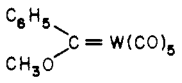
Induction of Olefin Metathesis by Acetylenes

Sir:

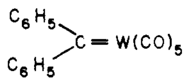
If the reason that metal carbenes polymerize acetylenes[1] is that the transformations involve the steps in Scheme I,[1,2] then combining metal carbenes and acetylenes should generate other, possibly more reactive metal carbenes that might initiate transformations their precursors could not. We recently discovered that acetylenes can induce olefin metatheses,[3,4] and we are reporting here how the process can be made to work generally and remarkably stereospecifically. We have discovered that acetylenes not only induce the reactions but quench them as well, and in an accompanying paper we analyze why.[5]

Table I shows that if 200 equiv of three cycloalkenes are combined with 1 equiv of (phenylmethoxycarbene)pentacarbonyltungsten (**1**),[6] no polyalkenamers[1a,7] form, but if phenylacetylene is present, the reactions (eq 1) do indeed take place, even if slowly. However, preliminary attempts to effect the analogous transformation with the seemingly related molecule *cis*-2-pentene were ineffective, even when larger amounts of acetylene and large amounts of metal carbenes were used as



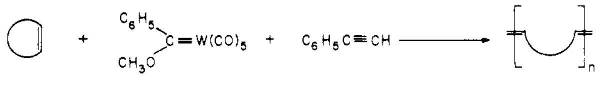
$(C_6H_5)(CH_3O)C{=}W(CO)_5$

1



$(C_6H_5)_2C{=}W(CO)_5$

2



(1)

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(1) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.

(2) Masuda, T.; Sasaki, N.; Higashimura, T. *Macromolecules* **1975**, *8*, 717.

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(4) Some of the results were discussed at the 3rd NSF Workshop on Organometallic Chemistry, Pingree Park, CO, July 16, 1979, and at the 3rd International Symposium on Olefin Metathesis, Lyons, France, Sept 12, 1979. See Katz, T. J.; Lee, S. J.; Shippey, M. A. *J. Mol. Catal.* **1980**, *8*, 219.

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