Work is in progress to explore the extension of this type of reactions to other carbonylmetal anions.

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Supplementary Material Available: Complete tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for the structures of **2b** and **5** (20 pages); tables of observed and calculated structure factor amplitudes (45 pages). Ordering information is given on any current masthead page.

Photoinduced Net [2 + 2 + 2] Cycloreversion of Platinum(II) Glycolate Complexes: A New Approach to the Generation of Reduced, Coordinatively Unsaturated Metal Species and the Activation of Carbohydrate Carbon-Carbon Single Bonds

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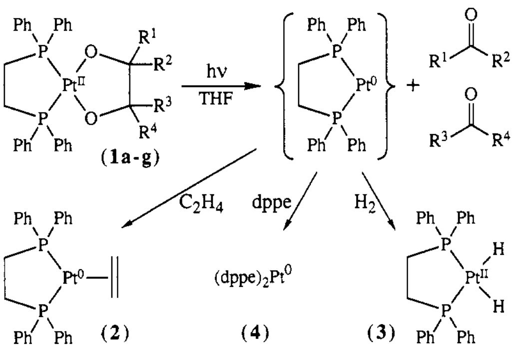
Summary: Photolysis of thermally stable (1,2-bis(diphenylphosphino)ethane)platinum(II) glycolate complexes causes a facile net [2 + 2 + 2] cycloreversion of the 2,5-dioxaplatinacyclopentane moiety to give two organic carbonyl compounds and a reactive (dppe)Pt^0 intermediate, as shown by trapping with dppe, ethylene, or hydrogen. Photolysis under hydrogen in the presence of $(PPh_3)_4RuH_2$ leads to hydrocracking of the glycol carbon-carbon single bond.

Several recent findings have described the photoinduced retrocyclization of heterometallacycles to give reactive organometallic species.[1-4] We predict that this will prove to be a very general and valuable reactivity pattern. In support of this, we report here a new example, the first demonstration of metal glycolate [2 + 2 + 2] cycloreversion,[5] and show how this reaction can be applied not only to the generation of a typical coordinatively unsaturated, low-valent metal fragment (Scheme I) but also to the activation of carbon-carbon single bonds (Scheme II). In addition, the work represents one of the first systematic studies of the chemistry of organometallic glycolate complexes,[7-12] models for potential intermediates in metal-catalyzed reactions of carbohydrates.[13,14]

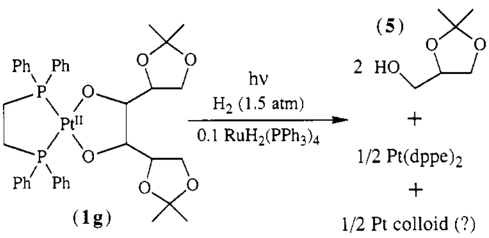
Scheme I



Glycols Employed

a: ethylene glycol
b: propylene glycol
c: 1,2-hexanediol
d: 1,2-dodecanediol
e: pinacol
f: 1,1'-bicyclohexyldiol
g: 1,2:5,6-diisopropylidene-mannitol

Scheme II



(Bis(phosphine))platinum(II) glycolate complexes derived from ethylene glycol[9] and glycerol[10] have previously been prepared by alcohol exchange with $(LL)Pt(OMe)_2$ (LL = 1,2-bis(diphenylphosphino)ethane (dppe) and 1,2-bis(methylphenylphosphino)benzene, respectively). The

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(1) Coordinatively unsaturated, 14-electron Pt(0) intermediates from oxalates: Paonessa, R. S.; Prignano, A. L.; Trogler, W. C. *Organometallics* **1985**, *4*, 647-657.

(2) Iridium alkylidenes from 2-oxametallacyclobutanes: Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3079-3080.

(3) Rhodium oxo complexes from carbonates: Henary, M.; Kaska, W. C.; Zink, J. I. *Inorg. Chem.* **1989**, *28*, 2995-2997.

(4) Photolysis of $(C_5Me_5)Ir(L)(CO_3)$ in the presence of $C^{18}O_2$ leads to ^{18}O incorporation into the coordinated carbonate ligand, presumably via an iridium oxo species (Bergman, R., personal communication of unpublished results).

(5) The oxidative cleavage of alkenes to carbonyls by high-valent metal oxides has been proposed to proceed via [2 + 2 + 2] cycloreversions of possible uncharacterized metal glycolate intermediates.[6] There have also been at least two reports of [4 + 2] retrocyclization of metal glycolate complexes to give metal dioxo complexes and the corresponding alkene.[7,8]

(6) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; pp 144, 181-183, 358.

(7) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574-1583.

(8) Herrmann, W. A.; Marz, D.; Herdtweck, E.; Schäfer, A.; Wagner, W.; Kneuper, H.-J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 462-464.

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(11) Chisholm, M. H.; Folting, K.; Klang, J. A. *Organometallics* **1990**, *9*, 607-613.

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(13) Andrews, M. A.; Klaeren, S. A. *J. Am. Chem. Soc.* **1989**, *111*, 4131-4133.

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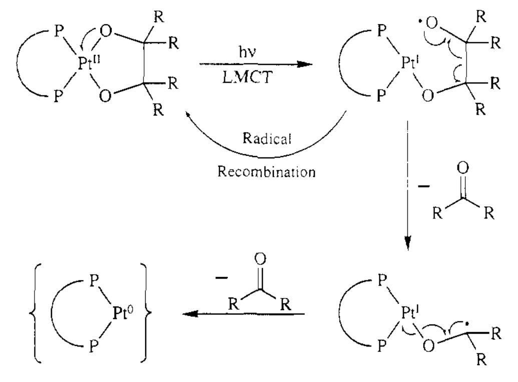
Scheme III



dppe bis(methoxide) complex decomposes at room temperature,[9] however, and proved to be an unsuitable precursor for the generalized synthesis of glycolate complexes, especially those derived from tertiary glycols. In contrast, the bis(siloxide) analogue (dppe)Pt(OSiMe$_3$)$_2$,[15,16] prepared from (dppe)PtCl$_2$ and 2 equiv of potassium trimethylsilanolate at 0 °C, is stable at 100 °C in toluene for over 48 h.[17] Alcohol exchange with a variety of vicinal diols, usually carried out in situ, gives glycolate complexes **1a–g** in 50–80% overall yield.[18] The isolated products are thermally robust[19–21] and are relatively stable toward both air and water. Strong acids (HCl) cleave off the glycol, while weak acids induce slow equilibrium displacement (ArOH)[22] and/or hydrogen bonding (ROH).[23,24]

Photolysis of glycolate complexes **1** at 313 nm[25] leads to clean redox cycloreversion (Scheme I) and the formation of a reactive (dppe)Pt^0 fragment, together with aldehydes and/or ketones corresponding to glycolate cleavage.[26] Evidence for the (dppe)Pt^0 intermediate is provided by trapping experiments utilizing ethylene, hydrogen, or dppe, which give (dppe)Pt(C$_2$H$_4$) (**2**),[27,28] (dppe)PtH$_2$ (**3**; vide infra), and (dppe)$_2$Pt (**4**),[29] respectively. The product quantum yield Φ for 313 ± 8 nm irradiation of the 1,1′-bicyclohexyldiolate complex **1f** to give 2 equiv of cyclohexanone is 0.22 ± 0.02 (25 °C under 1.5 atm of ethylene).[30] We believe that the generation of reduced, coordinatively unsaturated metal species by this technique should not be limited to the conveniently illustrated L$_2$Pt^0 example reported here. For example, Bergman and Glueck have recently found that photolysis of (Me$_5$C$_5$)Rh(pinacolate) yields 2 equiv of acetone and a 14-electron (Me$_5$C$_5$)Rh^I intermediate.[31]

While we do not yet have any solid evidence concerning the mechanism of the observed cycloreversion,[32] there are a few reasonable possibilities. One is a concerted cycloreversion. Such a [2 + 2 + 2] chelotropic elimination[33] would be thermally forbidden, since a symmetry correlation diagram shows that the filled d_{z^2} orbital in the starting glycolate correlates with a ketone π^* orbital in the product.[34] Photoexcitation leading to a ligand field excited state would eliminate the symmetry restriction against a concerted reaction. Another possible mechanism, which we currently feel is less likely on the basis of preliminary UV spectral analyses and the high quantum yield observed, is the odd-electron pathway illustrated in Scheme III. Excitation leading to a LMCT state should effect net transfer of a glycol oxygen nonbonding electron to the platinum $d_{x^2-y^2}$ based Pt–ligand σ^* orbital, resulting in dissociative ring opening to give a glycolate radical. Homolysis of the glycol C–C bond to give 1 equiv of aldehyde or ketone would then be expected.[6] Subsequent expulsion of a second equivalent of aldehyde or ketone from the platinum-bound, carbon-centered alkoxide radical (with or without prior collapse to a η^2-aldehyde or η^2-ketone complex)[35] would then yield the L$_2$Pt^0 fragment. A related radical pathway might be accessible through incipient photochemical oxidation of the platinum by excitation to a MLCT state.[36]

These glycolate cycloreversions are formally analogous to those observed for oxalate complexes, in particular bis(phosphine)Pt(C$_2$O$_4$), which undergoes a formal [2 + 2 + 2] chelotropic elimination to give 2 equiv of carbon

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(15) ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.98–7.90 (m, 8 H), 7.04–6.99 (m, 12 H), 1.56 (m, 4 H), 0.37 (s, 18 H). ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$, 85% H$_3$PO$_4$ external reference, 302 K): δ 27.1 (s with ^{195}Pt satellites, $^1J_{\text{Pt-P}}$ = 3595 Hz). This complex has recently been crystallographically characterized (Bergman, R., personal communication of unpublished results).

(16) Further experimental details and compound characterization are available as supplementary material.

(17) The bis(siloxide) is quite unstable in the presence of excess potassium siloxide or phosphines, however. Details of these reactions will be published elsewhere.

(18) Compounds **1a–d** are prepared in tetrahydrofuran (THF) and compounds **1e–g** in toluene. Representative ^{31}P{^{1}H} NMR data for glycolate complexes are as follows. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): **1b**, δ 30.4 (d with ^{195}Pt satellites, $J_{\text{P-P}}$ = 9 Hz, $^1J_{\text{Pt-P}}$ = 3224 Hz), 30.1 (d with ^{195}Pt satellites, $J_{\text{P-P}}$ = 9 Hz, $^1J_{\text{Pt-P}}$ = 3258 Hz); **1f**, δ 26.8 (s with ^{195}Pt satellites, $^1J_{\text{Pt-P}}$ = 3187 Hz); **1g**, δ 30.4 (s with ^{195}Pt satellites, $^1J_{\text{Pt-P}}$ = 3269 Hz).

(19) Heating of diisopropylidenemannitolate complex **1g** at 145 °C for 3 days in 1-methyl-2-pyrrolidinone under argon gave no detectable decomposition, as evidenced by ^{31}P NMR and GC analysis. At 200 °C, slow decomposition occurred (ca. 75% in 6 h) to give substantial amounts of 1,2:5,6-diisopropylidenemannitol by an unknown process.

(20) Cf. the report by Bryndza et al.[9] that (dppe)Pt(1,2-ethanediolate) does not decompose after 3 days in toluene at 120 °C.

(21) The chelating phosphine is not necessary for thermal stability, as we have also prepared bis(triphenylphosphine)(1,2-ethanediolato)platinum and heated it to 80 °C in 1-methyl-2-pyrrolidinone without significant decomposition.

(22) Treatment of a dichloromethane solution of pinacolate complex **1e** (57 mM) with 2.2 equiv of *p*-cresol led over a period of days to an equilibrium mixture of **1e**·2(cresol) (80%) and (dppe)Pt(*p*-OC$_6$H$_4$OMe)$_2$ (20%).

(23) Addition of aliquots of 1,2-hexanediol to glycolate complex **1c** caused the colorless solution to turn light yellow and led to incremental changes in chemical shifts and Pt–P coupling constants in the ^{31}P NMR spectrum.

(24) Cf. ref 10 and the hydrogen bonding of phenols to late-metal phenoxide complexes: Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 6563–6565. Di Bugno, C.; Pasquali, M.; Leoni, P.; Sabatino, P.; Braga, D. *Inorg. Chem.* **1989**, *28*, 1390–1394.

(25) The UV–vis spectrum of **1a** in THF consists of a number of overlapping strong absorption features, the lowest energy band occurring at ca. 240 nm ($\epsilon \approx$ 20 000 L mol^{-1} cm^{-1}), having a distinct shoulder at $\lambda_{\text{max}} \approx$ 295 nm ($\epsilon \approx$ 2000 L mol^{-1} cm^{-1}). This shoulder is red-shifted ca. 10 nm on conversion to the fully substituted glycolate **1f**. A detailed analysis of the UV–vis spectra of these complexes is currently in progress.

(26) Photolysis at 313 nm of dilute solutions of **1f** (i.e., ca. 10 mM or less) in THF under Ar gives cyclohexanone in up to 94% yield. In the absence of trapping ligands, the reaction yields a mixture of unidentified platinum products.

(27) Head, R. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1637–1639.

(28) Head, R. A. *Inorg. Synth.* **1986**, *24*, 213–216.

(29) Clark, H. C.; Kapoor, P. N.; McMahon, I. J. *J. Organomet. Chem.* **1984**, *265*, 107–115.

(30) Quantum yield determinations were carried out with use of a 100-W Hg-Xe lamp, IR filter, and monochromator (all from Photon Technology International), a glass filter, and a thermostated sample cell holder. The incident photon flux was 3.2 × 10^{-9} einstein s^{-1} (calibrated thermopile, Eppley Labs).

(31) Bergman, R., personal communication of unpublished preliminary results.

(32) A detailed investigation of the photophysics and photochemistry of the glycolate complexes is currently being carried out in collaboration with Professor Cliff Kubiak (Purdue University).

(33) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, Germany, 1970; p 152.

(34) Cf.: McKinney, R. J.; Thorn, D. L.; Hoffmann, R.; Stockis, A. *J. Am. Chem. Soc.* **1981**, *103*, 2595–2603.

(35) We see no spectroscopic evidence for bound aldehyde or ketone complexes (cf. L$_2$Pt formaldehyde complexes[27]), even in the absence of trapping ligands.

(36) We have also observed glycol cleavage reactions upon chemical (ferrocenium hexafluorophosphate) and electrochemical oxidation of the glycolate complexes. These reactions are rather complicated and will be detailed in a future publication.

dioxide and L_2Pt^0 on photolysis.[1,37] There are, however, some very significant differences. On the basis of model reactions (eqs 1 and 2),[38] it is clear that the thermodynamics of glycolate cycloreversion should be much less favorable than for oxalate cycloreversion. In fact, glycolate photoreversion may result in a significant net storage of photochemical energy. In addition, alteration of the glycol substituents provides a means to increase complex solubility and to probe details of the reaction photochemistry, options that are simply not possible with metal oxalates.

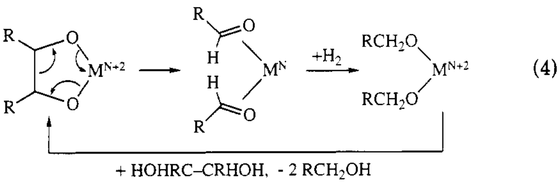
$$HOCH_2CH_2OH \rightarrow 2HCHO + H_2 \qquad \Delta G^\circ = +24.5 \text{ kcal/mol} \tag{1}$$

$$HO_2CCO_2H \rightarrow 2CO_2 + H_2 \qquad \Delta G^\circ = -21.7 \text{ kcal/mol} \tag{2}$$

In the course of our trapping studies, we discovered that dihydride monomer **3**, which has been reported to readily lose hydrogen to form the neutral dihydride dimer $(dppe)Pt(\mu\text{-}H)_2Pt(dppe)$[39,40] (eq 3), actually exists in facile, nearly thermoneutral equilibrium with the dimer under hydrogen: $K_{eq} = 1.7$ at 22 °C (^1H NMR, THF-d_8).

$$2(dppe)PtH_2 \rightleftharpoons (dppe)Pt(\mu\text{-}H)_2Pt(dppe) + H_2 \tag{3}$$

The formation of these platinum hydrides suggests that it might be possible to convert the observed oxidative cleavage[41] into a reductive cleavage. This could serve as a basis for the development of a catalytic cycle for effecting the hydrocracking of carbohydrate C–C bonds (eq 4). In fact, no aldehyde or ketone hydrogenation products were observed in photolyses of the platinum glycolate complexes under hydrogen, even when substantial amounts of the platinum hydrides were present. We therefore carried out



(4)

Net Proposed Reaction: $(CHOH)_n + nH_2 \longrightarrow nCH_3OH$

the photolysis of carbohydrate model complex **1g** in the presence of the known aldehyde hydrogenation catalyst $(PPh_3)_4RuH_2$[42,43] (0.15 equiv, THF, 1.5 atm of H_2). The sole organic product observed (Scheme II) was 1,2-isopropylideneglycerol (**5**; 84% by GC, identified by ^1H NMR spectroscopy and comparison of the GC–MS pattern with that of an authentic sample).[44] Glycerol **5** is postulated to originate from initial photolytic cleavage of the dioxaplatinacycle **1g** to give 2 equiv of 2,3-isopropylideneglyceraldehyde, which is subsequently hydrogenated by the Ru catalyst. Studies are now being directed at the chemistry of new metal glycolate systems, with the goal of finding a single metal system capable of catalytically effecting the complete net reaction shown in eq 4 under thermal conditions.

Acknowledgment. We thank Drs. Morris Bullock, Fred Lemke, Carol Creutz, and Bruce Brunschwig for helpful discussions and Professor Robert Bergman for details of work in progress by David Glueck, Robert Simpson, and M. D. Sponsler in this group. This research was carried out at Brookhaven National Laboratory under Contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

Supplementary Material Available: Synthetic, spectroscopic, and analytical details for **1a–g**, additional experimental details of the photolyses, and a figure giving the UV–vis spectra of **1a,e** (9 pages). Ordering information is given on any current masthead page.

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(38) Although the model reactions do not accurately correspond to the reactions of interest, the binding strengths of the two ligands to Pt(II) should not be sufficiently different to alter the conclusion that glycolate cycloreversion should be much less favorable than oxalate cycloreversion.

(39) Carmichael, D.; Hitchcock, P. B.; Nixon, J. F.; Pidcock, A. *J. Chem. Soc., Chem. Commun.* **1988,** 1554–1556.

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(41) The oxidative glycol cleavage reaction observed here is analogous in terms of the products formed to those commonly carried out with periodate and lead tetraacetate: Perlin, A. S. In *The Carbohydrates: Chemistry and Biochemistry,* 2nd ed.; Pigman, W. W., Horton, D., Eds.; Academic Press: New York, 1980; Vol. IB, pp 1167–1215.

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(43) Linn, D. E., Jr.; Halpern, J. *J. Am. Chem. Soc.* **1987,** *109,* 2969–2974.

(44) The primary Pt–P product formed under these conditions is $(dppe)_2Pt$ (**4**), apparently resulting from disproportionation of the $(dppe)Pt^0$ intermediate to give **4** and what appears to be colloidal platinum.

Vinylidene Complexes by M=C/N=C Metathesis from Benzylidene Complexes and Ketenimines

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Summary: Pentacarbonylbenzylidenetungsten adds triphenylketenimine to produce, after rearrangement, the imine adduct of pentacarbonyl(diphenylvinylidene)tungsten, which on thermolysis gives either an azetidinylidene complex or/and pentacarbonyl(diphenylvinylidene)tungsten.

Electrophilic transition-metal carbene complexes react with N=C double-bond systems (imines, carbodiimides, diaza dienes) in different ways. On photolysis of $(CO)_5M\text{-}[C(R)R']$ in the presence of imines β-lactams are formed.[1,2] Hegedus et al. proposed that the reaction is initiated by a photoinduced CO/carbene ligand coupling. The resulting ketene complex then reacts with imines to give the β-lactams. In contrast, the thermal reaction of alkoxy-

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(2) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M.; Yijun, C.; Anderson, O. P. *J. Am. Chem. Soc.* **1984,** *106,* 2680.