with metal complexes, the reactions of 1 described herein provide the first unequivocal examples of thermal and photochemical "CO_2 splitting" to M=O and CO of *coordinated CO_2*. This process parallels the scission of other η^2-unsaturated ligands such as RN=O[17] and RNC=O[18] bound to $Cp_2Nb{-}X$ units. It is interesting to note, however, the contrasting photoinduced disproportionation (to CO and CO_3^{2-}) that is found for isoelectronic, structurally related $Cp_2Mo(\eta^2\text{-}CO_2)$[4] and for other complexes of the latter transition metals.[19] The partitioning between these two pathways appears to reflect the relative oxophilicity of early vs later transition metals. The nature of the electronic transition that gives rise to the conversion of 1 to oxo complex 2 is unclear at present, but involvement of a state (ground or excited) with character centered on the coordinated CO_2 seems imperative. Studies to address this question and to promote CO_2 insertions of 1 are underway.

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Supplementary Material Available: Tables of positional and thermal parameters and interatomic distances and angles for 2 (5 pages); a table of observed and calculated structure factors for 2 (8 pages). Ordering information is given on any current masthead page.

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Selective Metal to Carbon Bond Formation in the Synthesis of the First Rhenium Complexes with S_2CPCy_3 Ligands. X-ray Structures of $[MnRe(CO)_6(\mu\text{-}S_2CPCy_3)]$ and $[Re_2(CO)_8(\mu\text{-}S_2CPCy_3)]$

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Summary: Reactions of either $[Mn(CO)_3(S_2CPCy_3)(Br)]$ with $Na[Re(CO)_5]$ or $[Re(CO)_3(S_2CPCy_3)(Br)]$ with $Na[Mn(CO)_5]$ produce selectively the heterobimetallic complex $[MnRe(CO)_6(\mu\text{-}S_2CPCy_3)]$, which contains an unsymmetrical $\eta^2(S,S'),\eta^3(S,C,S')$-$S_2CPCy_3$ bridge donating eight electrons with the carbon atom of the S_2C group bonded to manganese; in contrast, the reaction of $[Re(CO)_3(S_2CPCy_3)(Br)]$ with $Na[Re(CO)_5]$ produces $[Re_2(CO)_8(\mu\text{-}S_2CPCy_3)]$, with a $\eta^1(S),\eta^1(S')$-S_2CPCy_3 bridge of four electrons and no carbon–rhenium bond. In apparent contradiction with previous theoretical predictions, all the experimental facts suggest a stronger ability for manganese, when compared to rhenium, to become attached to the carbon atom of the S_2CPCy_3 ligand.

The interest in complexes containing (trialkylphosphonio)dithiocarboxylato groups, S_2CPR_3, believed to be intermediates in carbon disulfide activation,[1] has produced a number of compounds in which the S_2CPR_3 adducts act as versatile ligands toward a very wide range of metals,[2,3] exhibiting a variety of coordination modes and, sometimes, new and unexpected structural types.[3,4b,c] In

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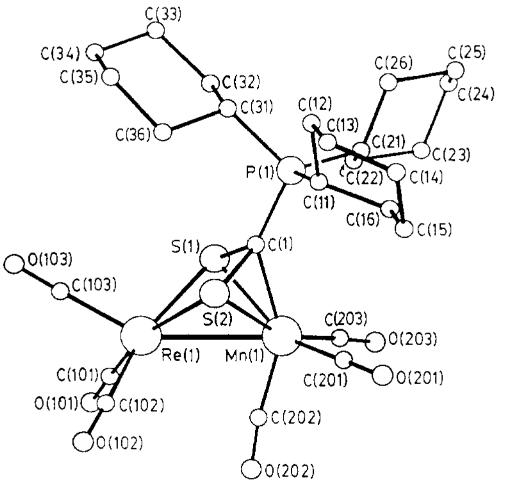
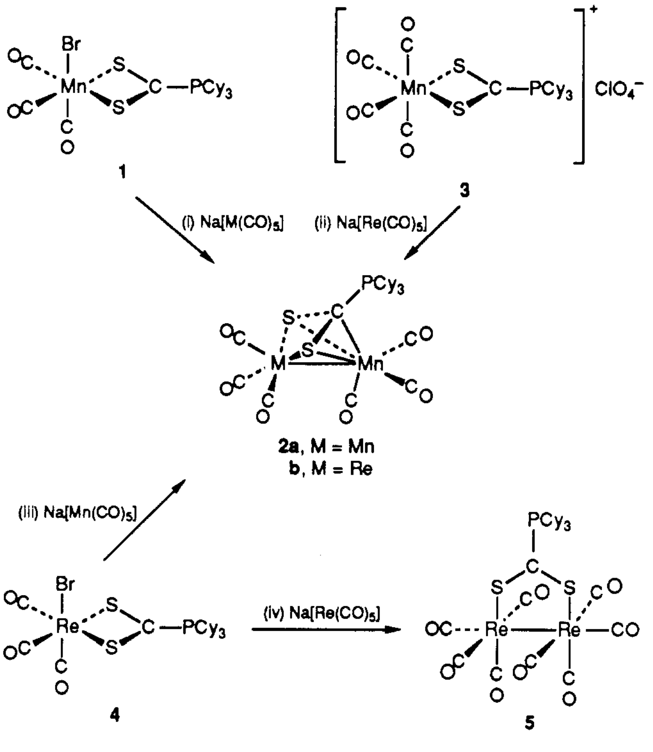


Figure 1. Perspective view of $[MnRe(CO)_6(\mu\text{-}S_2CPCy_3)]$ (**2b**) showing the atom numbering. Selected bond distance (Å) and angles (deg): Re(1)–Mn(1) = 2.830 (1), Re(1)–S(1) = 2.407 (1), Re(1)–S(2) = 2.395 (1), Mn(1)–S(1) = 2.351 2), Mn(1)–S(2) = 2.343 (2), Mn(1)–C(1) = 2.030 (5), S(1)–C(1) = 1.761 (5), S(2)–C(1) = 1.775 (5), C(1)–P(1) = 1.794 (5); S(1)–C(1)–S(2) = 105.6 (3), S(1)–Re(1)–S(2) = 71.8 (1), S(1)–Mn(1)–S(2) = 73.7 (1), Mn(1)–C(1)–P(1) = 139.7 (3), S(1)–C(1)–P(1) = 124.8 (3), S(2)–C(1)–P(1) = 120.9 (3), S(2)–Re(1)–C(101) = 161.6 (2), S(1)–Re(1)–C(102) = 163.5 (2), S(1)–Mn(1)–C(201) = 152.2 (2), C(1)–Mn(1)–C(202) = 149.5 (2), S(2)–Mn(1)–C(203) = 159.2 (2).

Scheme I



the exploration of the reactivity of coordinated S_2CPR_3 ligands in mononuclear manganese(I) complexes[4,5] we have found that hydride attack at the central carbon of S_2CPR_3 leads to the formation of products containing either dithioformate, S_2CH^-,[5a] or the phosphine adduct of dithioformate, $S_2C(H)PR_3^-$,[5b] as ligands. As an extension of this work, we have started to study the reactivity of coordinated S_2CPR_3 ligands toward carbonylmetal anions as a potential way to prepare homo- and heterobimetallic compounds containing S_2CPR_3 bridges. Here we report some preliminary results of this study, which have led to the preparation of the first complexes of rhenium with S_2CPR_3 ligands and to the observation of unexpected differences between Mn and Re in their abilities to form metal-to-carbon bonds.

$[Mn(CO)_3(S_2CPCy_3)(Br)]$ (**1**) reacts with $Na[Mn(CO)_5]$ (reaction i in Scheme I; M = Mn) in THF at room temperature to afford $[Mn_2(CO)_6(\mu\text{-}S_2CPCy_3)]$ (**2a**), which we had previously prepared by another route.[4b,c] Similar treatment of **1** with $Na[Re(CO)_5]$ (reaction i; M = Re)[6] produces the new heterobimetallic complex $[MnRe(CO)_6(\mu\text{-}S_2CPCy_3)]$ (**2b**). An X-ray determination (see Figure 1)[7] showed that **2b** is isostructural with **2a** and contains the S_2CPCy_3 adduct acting as an eight-electron, $\eta^2(S,S'),\eta^3(S,C,S')$ bridge, the carbon atom of the S_2C group being bonded to manganese. The distances and angles within the core $MnReS_2C$ atoms are quite similar to those found in the structure of the dimanganese compound **2a**,[4b,c] except for the longer metal–metal distance (2.830 (1) Å in **2b** vs 2.737 (1) Å in **2a**), which arises on exchanging Mn for the heavier Re atom. In accordance with this, spectroscopic data for **2b**[8] are very similar to those known for

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[6] A solution of $Na[Re(CO)_5]$ in THF (20 mL) was prepared from $Re_2(CO)_{10}$ (0.118 g, 0.182 mmol) and excess sodium amalgam (ca. 1%) and then transferred under nitrogen to a solution of **1** (0.2 g, 0.347 mmol). The mixture was stirred for 8 h at room temperature and then filtered. The solvent was evaporated in vacuo, and the residue was washed with hexane (3 × 15 mL) to extract small amounts of $Re_2(CO)_{10}$. The solid was recrystallized from CH_2Cl_2/hexane at −20 °C, giving pure microcrystals of **2b**; yield 0.144 g, 54%.

[7] Crystal and refinement data for compound **2b**: $C_{25}H_{33}MnO_6PReS_2$, $M_r = 765.77$, triclinic, space group $P\bar{1}$, $a = 11.576$ (1) Å, $b = 11.379$ (2) Å, $c = 11.061$ (1) Å, $\alpha = 85.94$ (1)°, $\beta = 77.53$ (1)°, $\gamma = 85.27$ (1)°, $V = 1415.8$ (1) Å^3, $D_c = 1.796$ g cm^{-3}, $Z = 2$, $F(000) = 756$, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu(\text{Mo K}\alpha) = 49.92$ cm^{-1}, room temperature, orange-red tabular crystal (0.36 × 0.17 × 0.13 mm). Intensities were collected on an Enraf-Nonius CAD4 diffractometer, using the $\omega-2\theta$ scan technique. A total of 4987 reflections measured in the range $0 \le \theta \le 25°$, 4469 of which with $I \ge 3\sigma(I)$ were used in the refinement. Profile analysis was applied for all reflections.[13] An empirical (ψ-scan based) absorption correction was applied. Heavy atoms were located from a Patterson synthesis and the remaining non-H atoms by DIRDIF.[14] Full-matrix least-squares refinement was made with SHELX76.[15] All non-H atoms were refined anisotropically. H atoms were geometrically positioned. The number of parameters was 367. The final R was 0.029 ($R_w = 0.033$). Crystal and refinement data for compound **5**: $C_{27}H_{33}O_8PRe_2S_2$, $M_r = 953.06$, triclinic, space group $P\bar{1}$, $a = 13.287$ (4) Å, $b = 11.401$ (4) Å, $c = 11.276$ (2) Å, $\alpha = 100.17$ (2)°, $\beta = 74.53$ (2)°, $\gamma = 96.78$ (2)°, $V = 1615.7$ (6) Å^3, $D_c = 1.959$ g cm^{-3}, $Z = 2$, $F(000) = 912$, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu(\text{Mo K}\alpha) = 78.04$ cm^{-1}, room temperature, purple tabular crystal (0.31 × 0.27 × 0.15 mm). A total of 5686 reflections were measured (same diffractometer, data collection method, limits, and corrections as for **2b**), 4769 of which with $I > 3\sigma(I)$ were used in the refinement. The structure was solved and refined by following procedures similar to those for **2b**. H atoms were geometrically positioned. The number of parameters was 371. The final R was 0.029 ($R_w = 0.031$). Drawings were made with PLUTO.[16]

[8] Analytical and spectroscopic data for the compounds. $^{31}P\{^1H\}$ NMR (121.5 MHz) chemical shifts are in ppm to higher frequency of external 85% H_3PO_4. $^{13}C\{^1H\}$ NMR (75.5 MHz) chemical shifts are in ppm to higher frequency of internal TMS. **2a**:[4b,c] $\nu(CO)$ (cm^{-1}, THF solution) 2022 s, 1980 vs, 1928 s, 1918 s, 1900 m; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 30.9. **2b**: $\nu(CO)$ (cm^{-1}, THF solution) 2024 s, 1987 vs, 1925 vs, 1915 (sh), 1896 m; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 41.23. Anal. Calcd for $C_{25}H_{33}MnO_6PReS_2$: C, 39.21; H, 4.34. Found: C, 39.37; H, 4.37. **4**: $\nu(CO)$ (cm^{-1}, CH_2Cl_2 solution) 2023 s, 1924 s, 1901 s; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 35.1. Anal. Calcd for $C_{22}H_{33}BrO_3PReS_2$: C, 37.39; H, 4.71. Found: C, 37.70; H, 4.72. **5**: $\nu(CO)$ (cm^{-1}, THF solution) 2064 m, 2007 s, 1969 vs, 1939 m, 1908 s; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 43.9; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$) 215.28 [d, $J(PC) = 40$ Hz, S_2CPCy_3], 207.67 [s, 4 CO], 199.80 [s, 2 CO], 193.14 [s, 2 CO], 32.33 [d, $J(PC) = 33$ Hz, 3 C^1 of cyclo-C_6H_{11}], 26.91 [d, $J(PC) = 11$ Hz, 3 × (C^2, C^6) of cyclo-C_6H_{11}], 26.84 [s, 3 × (C^3, C^5) of cyclo-C_6H_{11}], 25.47 [s, 3 C^4 of cyclo-C_6H_{11}]. Anal. Calcd for $C_{27}H_{33}O_8PRe_2S_2$: C, 34.03; H, 3.49. Found: C, 34.16; H, 3.51.

2a. However, they are different enough to permit an easy and unambiguous spectroscopic identification, especially by their ^{31}P NMR signals and ν(CO) IR frequencies. No significant amount of the other possible isomer of **2b** with the central carbon of the S_2CPCy_3 bridge bonded to rhenium was found. Treatment of the cation $[Mn(CO)_4(S_2CPCy_3)]^+$ (**3**) with $Na[Re(CO)_5]$ (reaction ii in Scheme I) also gives **2b**. As in reaction i (M = Re), the isomer containing a Re–C bond was not detected.

It was thought that the selective Mn–C bond formation in reactions i and ii could be kinetically induced by the fact that S_2CPCy_3 was initially bonded to the Mn atom in the starting compounds **1** and **3**. To clarify this point, the new complex $[Re(CO)_3(S_2CPCy_3)(Br)]$ (**4**), analogous to **1**, was prepared by refluxing $[Re(CO)_5(Br)]$ and S_2CPCy_3 in toluene/CS_2.[9] Treatment of **4** with $Na[Mn(CO)_5]$ at room temperature (reaction iv)[10] gave a product whose spectroscopic data[8] were identical with those observed for **2b**. Again, the final product contains a Mn–C bond and the existence of the isomer with a Re–C bond was not detected in the IR or ^{31}P NMR spectra of the reaction mixtures. It can be considered, therefore, that reactions i–iii lead selectively to the formation of a Mn–C rather than to a Re–C bond, thus revealing a stronger preference for manganese to form a metal–carbon bond in this type of complexes. This is remarkable, since in the structure of **2b** the rhenium atom is hexacoordinated while manganese is heptacoordinated and, for steric reasons, we would predict a stronger preference for the heaviest atom to achieve the highest coordination number.

In fact, the structures of compounds **2a**[4b,c] and **2b** pose several questions on the grounds of our current theoretical understanding of the bonding features in bimetallic systems, mainly concerning the factors that compel the S_2CPCy_3 ligand to adopt an unsymmetrical bonding mode of the type $\eta^2(S,S')$,$\eta^3(S,C,S')$ instead of a symmetrical disposition of type $\eta^2(S,S')$,$\eta^2(S,S')$, especially in the case (as in compound **2a**) in which both sides of the bimetallic system are identical. Thus, from the results of several MO calculations on molecules in which three-atom groups such as C_3R_3,[11a] S_2CS, and S_2CSMe[11b] form bridges straddling a metal–metal bond, it has been concluded that the ligands tilt toward one of the metals predominantly due to electronic factors and that the bridge tilts toward the metal which provides the more diffuse orbitals. When the metal environment is symmetrical, the ligand would tilt only if the terminal ligands were not free to pyramidalize, i.e., if the metals were not free to reorganize the disposition of their terminal ligands in order to direct their orbitals toward the symmetric bridge. In our results, both structures (**2a** and **2b**) are in apparent contradiction with those theoretical predictions: in **2a** the bimetallic fragment $(CO)_3MnMn(CO)_3$ is symmetrical and the six terminal carbonyl groups have no restriction to pyramidalize, while in **2b** the rhenium atom would offer the most diffuse orbitals to the central carbon of the S_2CPCy_3 ligand. We have started to perform extended Hückel calculations on the structures of **2a** and **2b**, in an attempt to obtain some insight into the factors that govern the behavior of these systems.

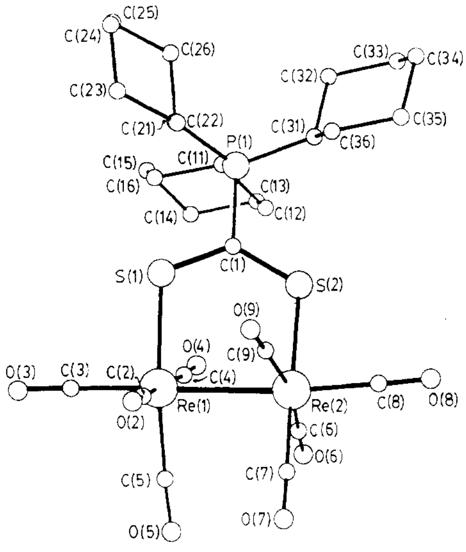

Figure 2. Perspective view of $[Re_2(CO)_8(\mu\text{-}S_2CPCy_3)]$ (**5**) showing the atom numbering. Selected bond distances (Å) and angles (deg): Re(1)–Re(2) = 2.987 (1), Re(1)–S(1) = 2.462 (1), Re(2)–S(2) = 2.442 (2), S(1)–C(1) = 1.690 (5), S(2)–C(1) = 1.666 (5), C(1)–P(1) = 1.830 (6), Re(1)–C(2) = 1.957 (7), Re(1)–C(3) = 1.925 (7), Re(1)–C(4) = 1.990 (7), Re(1)–C(5) = 1.945 (7), Re(2)–C(6) = 2.003 (7), Re(2)–C(7) = 1.938 (7), Re(2)–C(8) = 1.930 (7), Re(2)–C(9) = 1.971 (7); Re(2)–Re(1)–S(1) = 88.4 (1), Re(1)–Re(2)–S(2) = 87.5 (1), S(1)–C(1)–S(2) = 129.0 (3), S(1)–Re(1)–C(5) = 173.6 (2), S(2)–Re(2)–C(7) = 176.8 (2), S(1)–Re(1)–C(2) = 91.7 (2), S(1)–Re(1)–C(2) = 92.1 (3), S(1)–Re(1)–C(4) = 84.9 (2). Angles S(2)–Re(2)–C(carbonyl) are similar to those of Re(1).

It was reasonable to expect that the reaction of **4** with $Na[Re(CO)_5]$ (reaction iv in Scheme I)[12] would give the dirhenium hexacarbonyl complex analogous to **2a** and **2b**. However, quite unexpectedly, the product of reaction iv was characterized by analytical and spectroscopic methods, and by an X-ray determination[7] (Figure 2), as being $[Re_2(CO)_8(\mu\text{-}S_2CPCy_3)]$ (**5**), in which the S_2CPCy_3 ligand serves as a $\eta^1(S)$,$\eta^1(S')$ bridge between the two rhenium atoms and donates four electrons. The production of **5** in reaction iv confirms again the reluctance of rhenium to interact with the central carbon of the S_2CPCy_3 moiety, in contrast with the stronger preference shown by manganese in the previous reactions.

In addition to their connection with the study of the carbon–metal bond formation, the new rhenium complexes described here present other features of interest. As far as we know, **2b**, **4**, and **5** are the first complexes of rhenium containing S_2CPR_3 ligands, **2b** is the first complex containing an S_2CPR_3 ligand as a bridge between two different metals (and indeed acting as an eight-electron donor) and **5** contains the first example of a four-electron $\eta^1(S)$,$\eta^1(S')$-S_2CPR_3 bridge between two singly bonded metals.

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(9) To a suspension of $Re(CO)_5Br$ (0.472 g, 1.162 mmol) in a mixture of toluene (20 mL) and CS_2 (3 mL) was added S_2CPCy_3 (0.414 g, 1.162 mmol), and the mixture was heated at reflux temperature for 8 h. **4** precipitated as a purple-red solid, which was collected in a filter, washed with Et_2O (3 × 10 mL), and dried in vacuo; yield 0.408 g, 50%.

(10) The reaction was carried out as described in ref 6 with **4** (0.2 g, 0.283 mmol) and a solution of $Na[Mn(CO)_5]$ (from $Mn_2(CO)_{10}$ (0.066 g, 0.17 mmol) and excess sodium amalgam). The stirring time was 4 h; yield of **2b** 0.176 g, 81%.

(11) (a) Jemmis, E. D.; Prasad, B. V. *J. Organomet. Chem.* **1988**, *347*, 401. (b) Prasad, B. V.; Reddy, C. S.; Jemmis, E. D. *Inorg. Chim. Acta* **1989**, *162*, 281.

(12) **4** (0.2 g, 0.283 mmol) was reacted with $Na[Re(CO)_5]$ (ca. 0.320 mmol) in THF for 10 h at room temperature. The workup was as in ref 6. Recrystallization from CH_2Cl_2/hexane at −20 °C gave **5** as dark red crystals; yield 0.22 g, 78%.

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

Acknowledgment. We thank the Spanish Dirección General de Investigación Científica y Técnica for financial support (Project No. PB88-0467) and the Fundación Santa María for a grant (to B.A.).

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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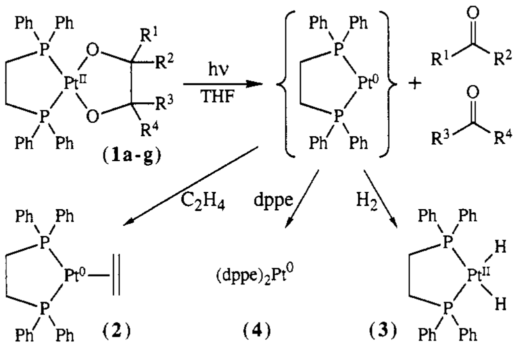
Summary: Photolysis of thermally stable (1,2-bis(diphenylphosphino)ethane)platinum(II) glycolate complexes causes a facile net [2 + 2 + 2] cycloreversion of the 2,5-dioxaplatinacyclopentane moiety to give two organic carbonyl compounds and a reactive (dppe)Pt^0 intermediate, as shown by trapping with 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.

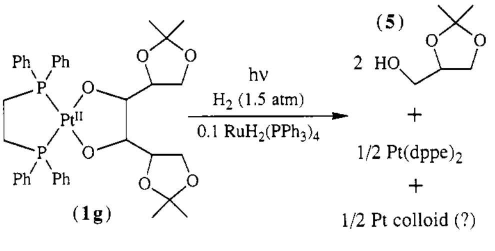
Several recent findings have described the photoinduced retrocyclization of heterometallacycles to give reactive organometallic species.[1-4] We predict that this will prove to be a very general and valuable reactivity pattern. In support of this, we report here a new example, the first demonstration 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]

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