An Unprecedented Photochemical *Cis* to *Trans* Isomerization of Dinuclear Gold(I) Bis(diphenylphosphino)ethylene Complexes

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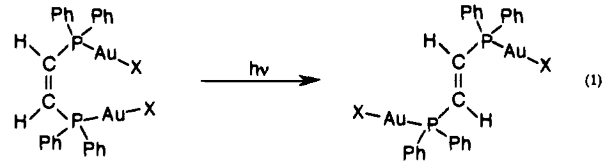
The implicit rigidity imparted by the alkene backbone in *cis*- and *trans*-1,2-bis(diphenylphosphino)ethylene (dppee) has made these bisphosphines valuable additions to the arsenal of phosphine ligands used in transition metal chemistry. Since their syntheses more than 25 years ago, over 100 studies have been published, with examples of dppee complexes now reported for nearly every d-block transition metal.^{1} Bonding to the phosphine lone pairs dominates the mode of metal complexation; however, coordination of the π-bond in *cis*-dppee has recently been observed in a gold complex.^{1i} Consideration of the olefin character of the dppee ligands in light of the extensive photochemistry of olefins^{2} suggests the intriguing possibility of photochemical reactivity for *cis*- and *trans*-dppee. Although there are examples of photochemical reactions of transition metal complexes containing the *cis*-dppee ligand,^{1a,b,f} to our knowledge, photochemical isomerization of free or coordinated *cis*- and *trans*-dppee has not been reported. We now report on the unprecedented photochemical reactivity of the series of dinuclear gold(I) complexes, Au_2X_2(*cis*-dppee) (X = Cl, Br, I, *p*-$SC_6H_4CH_3$), which cleanly isomerize to the *trans* isomers, Au_2X_2(*trans*-dppee), upon photolysis (eq 1).



(1)

1 **2**

X = Cl (a), Br (b), I (c), *p*-$SC_6H_4CH_3$ (d)

We have been investigating dinuclear gold(I) complexes such as $Au_2(p\text{-}SC_6H_4CH_3)_2(LL)$ and $Au_2(SCH_2CH_2CH_2S)(LL)$, where LL is a flexible bisphosphine ligand varying from 1,1-bis(diphenylphosphino)methane to 1,5-bis(diphenylphosphino)pentane.^{3} These complexes exhibit S → Au charge transfer transitions in the UV−visible region (330−360 nm) that appear to be perturbed by gold(I)−gold(I) interactions.^{3a} We recently began investigating the dinuclear gold(I) complexes employing *cis*- and *trans*-dppee ligands, Au_2X_2(*cis*-dppee) and Au_2X_2(*trans*-dppee) (X = Cl, Br, I, *p*-$SC_6H_4CH_3$). These two series offer the opportunity to examine and compare electronic structure and reactivity of conformations in which the two gold atoms are constrained to be within bonding distance (**1a**−**d**)^{4a} *vs* those in which intramolecular approach of the two golds is precluded (**2a**−**d**).^{4b}

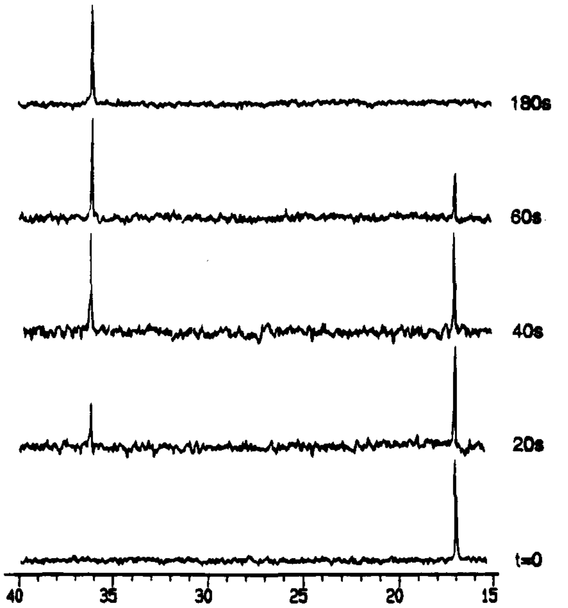


Figure 1. Photolysis experiment of a 2.1 mM solution of Au_2I_2(*cis*-dppee) (**1c**) in $CDCl_3$, monitored by $^{31}P\{^1H\}$ NMR. The peak at 17.0 ppm is for **1c**, and the peak at 35.9 ppm is for **2c** (cumulative irradiation times are indicated on the stacked spectra).

The *cis* and *trans* complexes were synthesized by ligand substitution reactions of the chloride complexes **1a** and **2a**, respectively.^{4c} After recrystallization, all complexes gave satisfactory elemental analyses and ^1H and $^{31}P\{^1H\}$ NMR spectra (see supporting information). The eight purified complexes each show a sharp singlet in the room temperature $^{31}P\{^1H\}$ NMR spectra, indicating the equivalence of all phosphorus atoms in solution. The syntheses of all *trans*-dppee complexes are straightforward and occur in high yield. However, initial attempts to make **1c,d** repeatedly yielded some *trans* isomers (**2c,d**). Protecting the reaction vessel from exposure to room light dramatically decreased the amount of **2c,d** produced. Photochemical experiments using a 300 W Hg arc lamp (Oriel) and a Pyrex filter ($\lambda \geq 320$ nm)^{5} confirm that a facile, photochemical isomerization (eq 1) occurs for all *cis* complexes, **1a**−**d**. For example, isomerization of **1c** to **2c** is complete within 3 min of photolysis (Figure 1). No visible precipitate forms during the photochemical experiment. Similar photochemical reactivity is observed for all Au_2X_2(*cis*-dppee) complexes. Dark reaction control experiments establish that the *cis*−*trans* isomerization is not a thermal process. Initiation of the isomerization by radicals formed from homolytic cleavage of the Au−X bond (when X = SR, I, or Br) is unlikely because, when the photolysis is conducted in chloroform, no chlorine atom abstraction products such as Au_2Cl_2(dppee) are observed.

The UV−vis spectra of free *cis*- and *trans*-1,2-dppee each show a broad UV absorption band (λ_{max} = 260 nm) that tails

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(4) (a) In **1a**, the intramolecular Au−Au distance is 3.05 Å: Jones, P. G. *Acta Crystallogr.* **1980**, *B36*, 2775. (b) In **2a**, the intramolecular Au−Au separation is 7.74 Å: Eggleston, D. S.; McArdle, J. V.; Zuber, G. E. *J. Chem. Soc., Dalton Trans.* **1987**, 677. (c) In addition to **1a** and **2a**, the synthesis and elemental analysis for **1b** were previously reported: McAuliffe, C. A.; Parish, R. V.; Randall, P. D. *J. Chem. Soc., Dalton Trans.* **1979**, 1730.

(5) The absorbance of the Pyrex filter is ≤1.0 at wavelengths greater than 320 nm.

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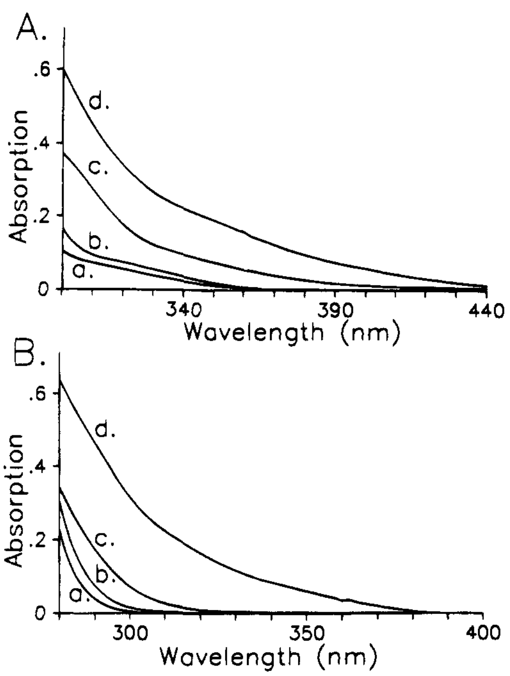

Figure 2. UV–visible spectra in $CHCl_3$ solution. (A) Au_2X_2(*cis*-dppee): a, X = Cl, 4.1 × 10^{-5} M; b, X = Br, 4.8 × 10^{-5} M; c, X = I, 3.2 × 10^{-5} M; d, X = *p*-$SC_6H_4CH_3$, 4.1 × 10^{-5} M. (B) Au_2X_2(*trans*-dppee): a, X = Cl, 7.1 × 10^{-5} M; b, X = Br, 5.6 × 10^{-5} M; c, X = I, 3.3 × 10^{-5} M; d, X = *p*-$SC_6H_4CH_3$, 3.0 × 10^{-5} M.

into the near-visible, with little absorption at $\lambda \geq 350$ nm.[6] The UV–vis spectra for **1a–d** and **2a–d** (Figure 2) show a red shift in the onset of the manifold of low-energy transitions going from X = Cl (a) to X = SR (d), which correlates with the softness of X. This trend indicates a significant contribution of the ligand X in the lowest energy transitions.

The photochemical *cis–trans* isomerization of uncoordinated olefins has been extensively investigated.[2] Photostationary states are typically achieved because each isomer is photochemically active and each has a similar molar absorptivity in the region of photolysis. In contrast, the uncoordinated *cis*- and *trans*-dppee ligands do not isomerize, even when higher energy light ($\lambda \geq 220$ nm) is used.[7] The extent of conversion of **1** to **2** (see Figure 1) suggests that reaction 1 is irreversible, i.e., the *trans* complexes do not photochemically isomerize. This conclusion is supported by separate photochemical experiments which demonstrate that irradiation of **2c** (1.9 mM in $CDCl_3$, 20 min at $\lambda \geq 220$ nm) or **2d** (2.4 mM in $CDCl_3$, 10 min at $\lambda \geq 320$ nm) does not produce detectable amounts of the *cis* isomers **1c**,**d**, respectively.[8] The photochemistry of series **1** is striking for several reasons. First, coordination of *cis*-dppee to two golds activates the ligand toward photochemical isomerization. Second, the *trans* ligand is not similarly activated. Third, photolysis of series **1** occurs without decomposition, whereas photolysis of gold complexes typically leads to deposition of colloidal or metallic gold.[9]

An explanation for the photochemical reactivity of series **1** is likely to include steric and electronic contributions. The *trans* isomer of the *uncoordinated* ligand is calculated by semiempirical methods to be 23 kJ/mol more stable than *cis*-dppee.[10a] Molecular mechanics calculations also indicate that steric interactions in *cis*-dppee are slightly greater than those in the *trans* isomer.[10b] Thus, a driving force for the photochemical isomerization of the gold complexes **1a–d** may be the relief of steric strain and the thermodynamic stability of the *trans* complexes. The important point is that coordination of gold is essential for interconversion of *cis*-dppee to *trans*-dppee. Transition metal phosphine complexes with d^{10} electronic configurations have been used as photosensitizers for olefin isomerization.[11] For example, Cu(dppe)BH_4 (dppe = diphenylphosphinoethane) sensitizes isomerization of both *cis*- and *trans*-piperylene, and photostationary states are achieved.[12] In the case of the d^{10} complexes, **1a–d**, the Au–X moiety may act as both chromophore and photosensitizer for the coordinated *cis*-dppee ligand. The difference in photochemistry for the two series suggests that the proximity of golds in **1a–d** is critical to the excited state reactivity. The fact that series **1** isomerizes while series **2** does not suggests that the *cis* complexes possess a low-lying excited state with significant C=C π^* character which is populated directly upon photolysis or by intramolecular energy transfer. A full explanation for the photochemical reactivity must await further experimental details.

Finally, it is noteworthy that photochemical isomerization of series **1** also occurs in the solid state. Exposure of solid **1c** to room light for 4 days results in ~50% conversion to **2c**. Luminescence, electrochemical, and mechanistic photochemical studies are now underway to explore the interesting electronic structure of transition metal–dppee complexes.

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Supporting Information Available: Experimental details on the preparation and characterization of **1a–d** and **2a–d** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[6] Spectra recorded in chloroform: 5 × 10^{-5} M *cis*-dppee; 8 × 10^{-5} M *trans*-dppee.

[7] A 4.8 mM solution of *cis*-dppee in $CDCl_3$ (−22.0 ppm) was irradiated in a quartz vessel, and aliquots were withdrawn for ^{31}P NMR analysis. After 24 min of photolysis, no peak due to *trans*-dppee (−6.3 ppm) was detected. A small, unidentified peak at ~22 ppm was observed after 14 min of photolysis. Similar experiments establish that there is no photochemical isomerization for *trans*-dppee.

[8] Reactions were monitored by $^{31}P\{^1H\}$ NMR. If any *trans* to *cis* isomerization occurs, the ratio of *trans–cis* must be >25:1. There is some photochemical reactivity for **2c**,**d**, but the process is slow, and the products have not yet been identified.

[9] Horvath, O.; Stevenson, K. L *Charge Transfer Photochemistry of Coordination Compounds*; VCH Publishers: New York, 1993; p 64.

[10] (a) Semiempirical calculations of the heats of formation were performed using the AM1 Hamiltonian within the Spartan group of molecular orbital programs by Wavefunction, Inc.: *trans*-dppee, 653 kJ/mol; *cis*-dppee, 676 kJ/mol. These calculations also indicate that the LUMO of *cis*-dppee has C=C π^* character, while that of the *trans* isomer does not. (b) Molecular mechanics calculations were performed using PCModel by Serena Software: *trans*-dppee, 152 kJ/mol; *cis*-dppee, 160 kJ/mol.

[11] Kutal, C. *Coord. Chem. Rev.* **1990**, *99*, 213.

[12] (a) Liaw, B.; Orchard, S. W.; Kutal, C. *Inorg. Chem.* **1988**, *27*, 1311. (b) Fife, D. J.; Moore, W. M.; Morse, K. W. *Inorg. Chem.* **1984**, *23*, 1545.