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Structure and Photochemical Isomerization of the Dinuclear Gold(I) Halide Bis(diphenylphosphanyl)ethylene Complexes: Correlation Between Quantum Yield and Aurophilicity

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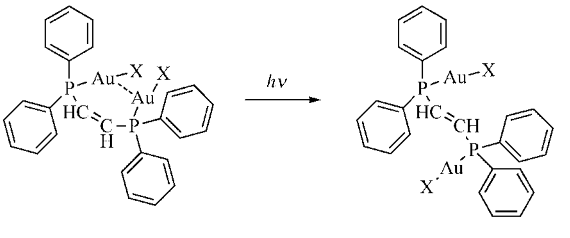
The crystal structures for *cis*-($Ph_2PCH{=}CHPPh_2$)$(AuI)_2$ and *trans*-($Ph_2PCH{=}CHPPh_2$)$(AuI)_2$ are reported. The structure of *cis*-($Ph_2PCH{=}CHPPh_2$)$(AuI)_2$ reveals a short intramolecular Au–Au distance of 2.9526(5) Å, while the structure of *trans*-($Ph_2PCH{=}CHPPh_2$)$(AuI)_2$ shows intermolecular Au–Au distances of 3.2292(7) Å. Structural data for the iodide complexes are compared to previously reported crystal structural data for *cis*- and *trans*-($Ph_2PCH{=}CHPPh_2$)$(AuCl)_2$ and dppbz$(AuCl)_2$. The quantum yields for the photochemical isomerization of *cis*-($Ph_2PCH{=}CHPPh_2$)$(AuX)_2$ with 334-nm light, $\Phi(_{cis\rightarrow trans})$, are 0.204, 0.269, and 0.363 for X = Cl, Br, and I, respectively. Prior results from ab initio calculations on the model *cis*- and *trans*-$Au_2X_2C_2H_2(PH_2)_2$ complexes aid in the interpretation of the correlation between the quantum yield for isomerization and the calculated aurophilic attraction potential $V(R_e)$.

Introduction

In the 1980s, the X-ray structures of the *cis*- and *trans* isomers of dppee$(AuCl)_2$ (dppee: $Ph_2PCH{=}CHPPh_2$) were reported by Jones,[1] and Eggleston, McArdle, and Zuber,[2] respectively. The crystal structure of *cis*-dppee$(AuCl)_2$ ($\mathbf{1}_{cis}$) reveals short intramolecular Au–Au interactions of 3.05(1) Å, whereas *trans*-dppee$(AuCl)_2$ ($\mathbf{1}_{trans}$) shows only intermolecular Au–Au interactions of 3.043(1) Å. In the structure for $\mathbf{1}_{cis}$ reported in 1980, Jones comments that "radiation damage, the exact nature of which is uncertain, causes the cell constants to increase." Subsequently, it was shown by Foley et. al that the series of *cis* complexes involving X = Cl, Br, I, and thiolate [Equation (1)] are photochemically reactive in solution, which results in a clean isomerization to the *trans* isomers.[3] In addition, the *cis* complexes show changes in crystal morphology upon exposure to room light, which suggests the interesting possibility of solid-state photochemical reactivity,[4] consistent with Jones' observations noted above.



$\mathbf{1}_{cis}$ (X = Cl)
$\mathbf{2}_{cis}$ (X = Br)
$\mathbf{3}_{cis}$ (X = I)

$\mathbf{1}_{trans}$ (X = Cl)
$\mathbf{2}_{trans}$ (X = Br)
$\mathbf{3}_{trans}$ (X = I) (1)

The photochemical conversions depicted in Equation (1) are rapid and efficient. For example, photolysis of a 2.1 mM solution of *cis*-(dppee)$(AuI)_2$ in $CDCl_3$ with a 300 W Hg arc lamp ($\lambda \geq 320$ nm) results in complete conversion of the *cis* isomer to the *trans* isomer within 3 min [as monitored by $^{31}P(^1H)$ NMR spectroscopy].[3] The quantum yields for isomerization of $\mathbf{1}_{cis}$–$\mathbf{3}_{cis}$ to the respective *trans* complexes were estimated to be greater than 0.1, and control reactions establish that the isomerization process is not thermally activated.

In contrast, the free *cis*- and *trans*-dppee ligands do not undergo photochemical isomerization under similar conditions or when light of higher energy ($\lambda \geq 220$ nm) is used.[3] In addition, the *trans*-dppee gold complexes $\mathbf{1}_{trans}$–$\mathbf{3}_{trans}$ do not photochemically convert into the *cis*-dppee gold complexes. The photochemical reactivity of $\mathbf{3}_{trans}$ appears to be limited to a decomposition pathway that is consistent with release of I_2.[4]

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The *cis*- and *trans*-dppee ligands have been used extensively to prepare metal complexes, and examples are reported for nearly every transition metal.[5] In addition, there are a few reports of thermal isomerization processes involving dppee. For example, *cis*-dppee isomerizes to *trans*-dppee in the presence of $GaBr_3$, $GaCl_3$, and $AlBr_3$ at elevated temperatures in a catalytic process that is correlated with Lewis acidity.[6] The *cis*-dppee disulfide and *cis*-dppee dioxide also thermally isomerize to the *trans* isomers in refluxing thf in the presence of PCl_3.[7] However, photochemical reactivity for dppee is rare, and to date, as far we are aware the photoisomerization of dppee has been reported only for the gold(I) complexes **1**$_{cis}$–**3**$_{cis}$. These observations suggest a pivotal role for gold atoms in photoisomerization. In this report, we present the crystal structures for **3**$_{cis}$ and **3**$_{trans}$, details of the quantum yield measurements for the photoisomerization reactions of **1**$_{cis}$–**3**$_{cis}$ to **1**$_{trans}$–**3**$_{trans}$, and the correlation between quantum yield and aurophilicity.[8]

Results and Discussion

Structural Characterization of 3$_{cis}$ and 3$_{trans}$ Complexes

Selected bond lengths and angles for **3**$_{cis}$ and **3**$_{trans}$ are presented in Tables 1, 2, and 3, and ORTEP diagrams are shown in Figure 1. In both **3**$_{cis}$ and **3**$_{trans}$, the dppee ligands bridge two gold atoms and the Au–P (average = 2.25 Å) and Au–I (average = 2.55 Å) bond lengths are typical for gold(I).[9–13] The P–Au–I angles are approximately linear. In **3**$_{cis}$, the *cis* orientation of the rigid phosphane ligand promotes formation of an intramolecular Au–Au bond of 2.9526(5) Å. The Au–Au distance in **3**$_{cis}$ is 0.1 Å shorter than that found in the related complex **1**$_{cis}$ and 0.05 Å shorter than the intramolecular Au–Au distance in the *cis*-dppbz$(AuCl)_2$[14] (Table 3). These distances all fall within the accepted values for aurophilic interactions, which range from 2.8 Å (strong interaction) to 3.5 Å (weak interaction).[15] The two P–Au–I arms in **3**$_{cis}$ "cross" at the Au centers with an I–Au···Au–I torsion angle of 63.61°. The structure of **3**$_{trans}$ is very similar to that reported for the related complex **1**$_{trans}$.[2] Both crystallize in the centrosymmetric space group *C*2/*c* with an inversion center at the midpoint of the ethylene backbone. Only one half of each *trans* molecule is crystallographically unique. In **3**$_{trans}$, a partially disordered dichloromethane molecule is also present. The intermolecular Au–Au interactions in **3**$_{trans}$ [3.2292(7) Å] are 0.19 Å longer than in **1**$_{trans}$.

Table 1. Selected bond lengths [Å] and angles [°] for compound **3**$_{cis}$.

Bond lengths [Å]			
Au1–Au2	2.9526(5)	Au1–I1	2.5629(9)
Au1–P1	2.256(3)	Au2–I2	2.5385(9)
Au2–P2	2.253(2)	P1–C1	1.81(1)
P1–C11	1.81(1)	P1–C31	1.82(1)
P2–C2	1.831(11)	P2–C21	1.82(1)
P2–C41	1.832(9)	C1–C2	1.332(14)
Bond Angles [°]			
Au2–Au1–I1	90.24(2)	Au1–P1–C31	112.8(4)
Au2–Au1–P1	94.21(6)	C1–P1–C31	98.9(5)
I1–Au1–P1	174.80(7)	C11–P1–C31	107.6(4)
Au1–Au2–I2	105.40(3)	Au2–P2–C2	115.1(3)
Au1–Au2–P2	82.30(6)	Au2–P2–C21	116.3(3)
I2–Au2–P2	170.36(7)	C2–P2–C21	105.0(5)
Au1–P1–C1	119.1(3)	Au2–P2–C41	110.2(3)
Au1–P1–C11	113.3(3)	C2–P2–C41	102.0(4)
C1–P1–C11	103.7(5)	C21–P2–C41	106.9(4)

Table 2. Selected bond lengths [Å] and angles [°] for compound **3**$_{trans}$.

Bond lengths [Å]			
Au1–Au1	3.2292(7)	Au1–I1	2.5435(8)
Au1–P1	2.250(2)	P1–C1	1.811(9)
P1–C2	1.812(9)	P1–C8	1.796(9)
C1–C1	1.309(17)		
Bond Angles [°]			
Au1–Au1–I1	83.51(2)	C1–P1–C2	104.1(4)
Au1–Au1–P1	101.42(6)	Au1–P1–C8	115.9(3)
I1–Au1–P1	174.81(6)	C1–P1–C8	103.7(4)
Au1–P1–C1	113.3(3)	C2–P1–C8	104.4(4)
Au1–P1–C2	114.1(3)	P1–C1–C1	123.5(9)

Electronic Spectra of dppee Gold Complexes and Quantum Yield Measurements

The *cis*- and *trans*-dppee$(AuX)_2$ complexes (X = Cl, Br, I) exhibit featureless, broad absorptions above 300 nm. The bands for each *cis* complex are slightly redshifted relative to that of its *trans* isomer. Quantum yield measurements were carried out at 334 nm where the molar absorptivities of the *cis* complexes range from $0.9–3.0 \times 10^3\ \text{M}^{-1}\,\text{cm}^{-1}$ and those of the *trans* complexes are near zero.[3] The quantum yields for disappearance, $\Phi_{\text{disappearance}}$, of the *cis*-dppee$(AuX)_2$ complexes measured at 334 nm are: $\Phi(\mathbf{1}_{cis,\text{disappearance}}) = 0.204 \pm 0.062$; $\Phi\ (\mathbf{2}_{cis,\text{disappearance}}) = 0.269 \pm 0.092$; $\Phi(\mathbf{3}_{cis,\text{disappearance}}) = 0.363 \pm 0.055$. Because

Table 3. Selected bond lengths and angles for **3**$_{cis}$ and **3**$_{trans}$ and related phosphane gold(I) complexes.

Complex	Au–P [Å]	Au–X [Å]	P–Au–X [°]	X–Au···Au–X Torsion [°]	Intramolecular Au···Au [Å] (≤ 3.5 Å)	Intermolecular Au···Au [Å] (≤ 3.5 Å)	Ref.
cis-dppee$(AuI)_2$ (**3**$_{cis}$)	2.256(3), 2.253(2)	2.5629(9), 2.5385(9)	174.80(7), 170.36(7)	63.61	2.9526(5)	*none*	this work
cis-dppee$(AuCl)_2$ (**1**$_{cis}$)	2.226(4), 2.239(5)	2.299(5), 2.289(5)	172.5(2), 173.3(2)	52.49	3.05(1)	*none*	[1]
cis-dppbz$(AuCl)_2$	2.2408(15), 2.2360(16)	2.2921(16), 2.2925(16)	173.07(6), 173.21(6)	–63.92	2.996(1)	*none*	[12]
trans-dppee$(AuI)_2$ (**3**$_{trans}$)	2.250(2)	2.5435(9)	174.81(6)	180.00	*none*	3.2292(7)	this work
trans-dppee$(AuCl)_2$ (**1**$_{trans}$)	2.235(2)	2.291(2)	173.5(1)	180.00	*none*	3.043(1)	[2]

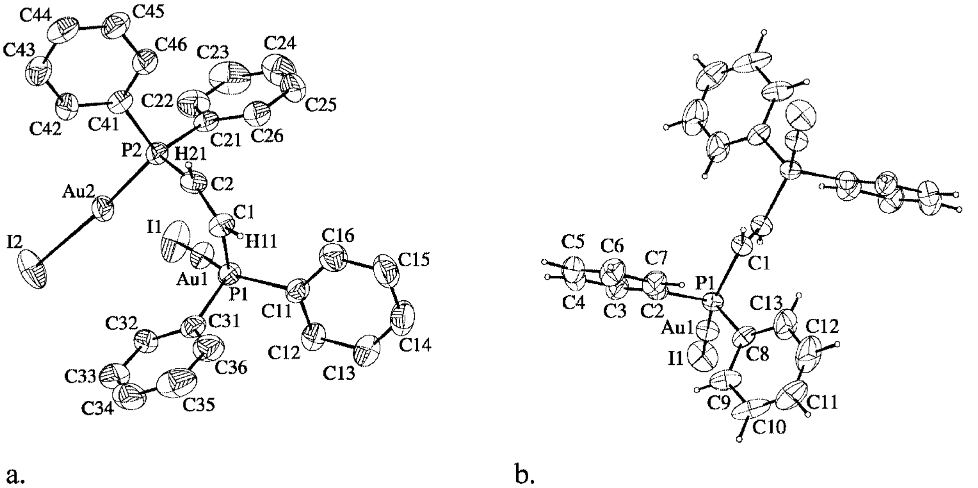


Figure 1. ORTEP drawings of a) $\mathbf{3}_{cis}$ and b) $\mathbf{3}_{trans}$ at the 50% probability level.

the photochemical isomerization processes are clean and appear to be irreversible, the quantum yields are reasonable estimates of the relative photoefficiencies of the *cis* to *trans* isomerizations, e.g. $\Phi(\mathbf{1}_{cis,\text{disappearance}}) = \Phi(\mathbf{1}_{cis} \rightarrow \mathbf{1}_{trans})$.

It is interesting to note that the increase in quantum yield in this series is correlated with an increase in the aurophilic attraction potential[16] (Figure 2). The quantum yield is also correlated with a decrease in electronegativity of the halide ligand X[16] (not shown). Both correlations give linear correlation coefficients above 0.99. The aurophilic attraction potential is a measure of the energy of interaction between a dimer and a pair of monomers and has been calculated[16] as well as estimated experimentally. Experimental values for the aurophilic attraction potential, $V(R_e)$, have been reported in the range 29–42 kJ mol^{-1}.[15,17–22] The ligand dependence on aurophilic attraction has been studied on the interacting, perpendicular X–Au–PH$_3$ monomer by using 19-valence electron quasirelativistic pseudopotentials for gold.[16] The study estimates that in interacting X–Au–PH$_3$ monomers, the aurophilic potentials, $V(R_e)$, are 16.7, 19.3, and 22.5 kJmol^{-1} for X = Cl, Br, and I, respectively. Thus, the aurophilic potential increases as the electronegativity of X decreases.

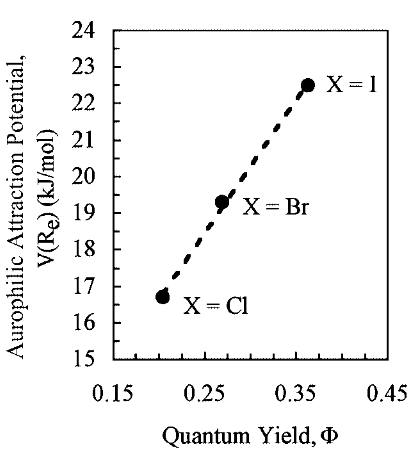


Figure 2. Correlation between aurophilic attraction potential[14] and quantum yield for isomerization of $\mathbf{1}$–$\mathbf{3}_{cis}$ to $\mathbf{1}$–$\mathbf{3}_{trans}$.

Photochemical Isomerization of Alkenes – Direct and Photosensitized

The direct and triplet sensitized photochemical isomerization of alkenes and polyenes has been extensively studied and reviewed. The ground state of the *cis* olefin is usually slightly higher in energy than that of the *trans* isomer, and photochemical processes have been shown to proceed through either discrete singlet or triplet pathways. For many organic dienes, e.g. stilbenes or 1,2-diphenylpropenes, photoisomerization originating from either the *cis* or *trans* isomer produces a photostationary state as a result of direct photolysis or photolysis with the addition of a triplet sensitizer.[23]

While the molar absorptivity of the two isomers at a particular wavelength affects the direct population of the *cis** and *trans** excited states, it is the shape of the excited state potential surface that is often critical for understanding the mechanism and photoefficiency of isomerization.[24–29] The research of Hammond and coworkers in the 1960s laid the groundwork for an explosion of interest in this field by illustrating how suitable photosensitizers could be used to understand reactivity that ensues after photoexcitation.[28]

To explain the basic photochemical phenomena, we have included Figure 3, which shows *cis* and *trans* olefin ground states, and an excited state potential surface reached by photoexcitation. This is a generic diagram similar to many diagrams used to discuss olefin photoisomerization,[26–28] and precise details of energy changes of the ground state as a function of olefin twist angle have been omitted. Excitation, according to the Franck–Condon principle, produces vertical transitions and initial excited states possess identical geometries as in the ground state. Three critical points are important to keep in mind: (a) excitation of either isomer populates a common potential surface, (b) the energy of the excited state is a function of the degree of olefin twist, and (c) deactivation pathways (e.g. thermal relaxation, luminescence) as well as the lifetime of the excited state dictate how far the excited state travels along the excited state potential surface. The excited state perpendicular geometry, *p**, with a twist angle of 90° may be thought of ideally as the state from which it is equally possible to convert to either isomer (see Figure 3). In the diagram in Figure 3, the excited states *trans** or *p** occur at local minima while *cis** is found at a transient position. However, the actual shape of the process under consideration varies and has a significant effect on the ensuing chemistry.

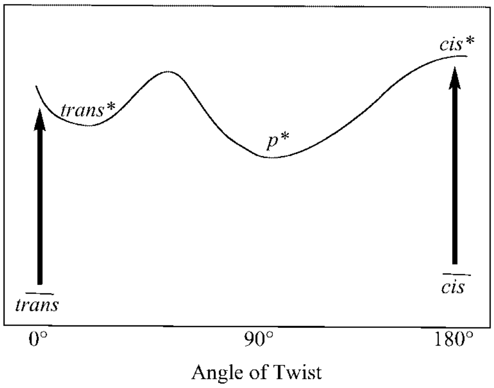


Figure 3. Relative energy of ground and excited states as a function of the angle of twist around the C–C olefin bond.

We may also consider photolysis of a system that contains a photosensitizer. In this case, photolysis produces an excited state sensitizer that must either become covalently attached or is pre-complexed to the olefin in order for photoisomerization to occur. Examples of sensitizers in both categories exist. In order for the sensitizer to influence the olefin, energy transfer must occur. If the excited state lifetimes are short compared to processes involving rotation about the carbon–carbon double bond or if rotation is hindered, the excited state will undoubtedly relax with little or no photoisomerization. However, if the lifetime is sufficiently long for either a system involving a sensitizer or for direct photolysis of an olefin, then the shape of the excited state potential surface and the energy available to the excited state complexes will dictate the process that occurs.

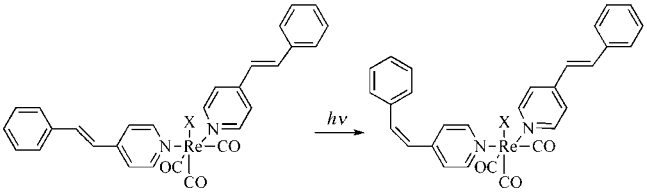
The Photochemical Process and Quantum Efficiency

To consider why the quantum yield for photoisomerization of $\mathbf{1}_{cis}$–$\mathbf{3}_{cis}$ is correlated with the aurophilic potential, it is useful to consider the overall photoisomerization as occurring in distinct steps involving absorption of a photon by a ground state molecule, the creation of an excited state complex, rotation about the C=C bond, and relaxation to various isomers. The gold complexes may be thought of as an assembly involving a chromophore (X–Au) that is covalently attached to the olefin through phosphorus atoms in the dppee ligand [see Equation (1)]. Thus, the ground state, excited state, and mixing of X, Au, and C=C orbitals all play important roles in the observed photoisomerization reaction.

Ab initio MP2 calculations on the model complexes *cis*- and *trans*-$Au_2X_2C_2H_2(PH_2)_2$ were previously reported and the excited states were investigated by the CIS (configuration interaction with single excitations only) and CAS-LMP2 procedures.[30] The results show that in the *cis* compounds the degree of aurophilic interaction increases with an increase in the softness of the ligand. Thus, $\mathbf{3}_{cis}$ would be expected to have a greater aurophilic interaction than $\mathbf{1}_{cis}$. The aurophilic interactions stabilize the ground state of the *cis* complexes relative to that of the *trans* complexes. In addition, the aurophilic interactions stabilize the first excited state, which leads to a red shift and an increased transition moment for the *cis* complexes, in contrast to that observed for the *trans* complexes. While the overall effect lowers the energy needed for promotion into the first excited state of the $\mathbf{1}_{cis}$–$\mathbf{3}_{cis}$ complexes (i.e. the red shift), it does not explain the increase in photoefficiency, since quantum yield measures the ratio of the number of *cis* molecules that isomerize relative to those that absorb light, regardless of what the energy gap is at 334 nm.

The stabilization of the first excited state was found to be critically dependent on the intramolecular Au–Au distance. The CIS calculations produce results that suggest that the HOMO–LUMO transitions (as well as the first few singlet excitations) are primarily halide to gold [Au(5d6s6p)] charge transfer transitions. However, there were significant admixtures from a variety of other orbitals. For both the *cis* and *trans* complexes, phosphorus p orbital character is found in the LUMO orbitals. In addition, for the *cis* complexes, the HOMO has some gold character, and in the LUMO, there is significant ethylene π* character. Population of an orbital with ethylene π* character in the *cis* complexes would be predicted to weaken the carbon–carbon double bond. The shorter Au–Au bond length in $\mathbf{3}_{cis}$ than in $\mathbf{1}_{cis}$ may indicate a higher degree of aurophilic interaction. Although the ab initio calculations do not easily permit quantification of orbital mixing, it seems reasonable to suggest that the aurophilic interaction in the *cis* complexes facilitates mixing of ethylene π* character in the excited states. Thus, it may be inferred that $\mathbf{3}_{cis}$ would have a greater degree of ethylene π* character in the excited state than $\mathbf{1}_{cis}$.

The relatively high quantum yield for photoisomerization of $\mathbf{1}_{cis}$–$\mathbf{3}_{cis}$ suggests that the HOMO–LUMO transition directly populates an orbital with sufficient ethylene π* character to weaken the C=C bond and permit rotation. Our results can be compared to the $ReX(CO)_3L_2$ complexes {see [Equation (2)]; X = Cl, Br; L = *trans*-4-styrylpyridine} whose IL transitions involve a spin-allowed π–π* transition, which directly weakens the C=C bond, permitting rotation and high quantum yields ($\Phi = 0.49$–0.64). In this case, the quantum yields are very similar to that of the free ligand.[31] In contrast, the quantum yield for photoisomerzation of *cis*-styrylferrocene [Equation (3)] is ca. 0.001. The inefficiency of this isomerization is attributed to rapid deactivation of the triplet *cis* excited state by the heavy atom effect.[26,32]



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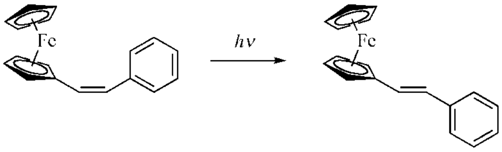

(3)

We are continuing to explore the correlation between quantum yield and aurophilic potential as a function of the ligands attached to gold. Preliminary results indicate that substitution of thiolate ligands for halides increases the photoefficiency, while substitution of arsenic for phosphorus in dppee decreases the photoefficiency.

Summary

The crystal structure of the *cis*-$(AuI)_2$dppee shows a shorter gold–gold distance than the analogous chloride and bromide complexes. This is consistent with the assertion, made by Pyykkö and others, that soft ligands should increase the gold–gold interaction. We have demonstrated that the quantum yield for the photoisomerization of *cis*-$(AuX)_2$dppee to the *trans*-$(AuX)_2$dppee [X = Cl(Φ = 0.204); Br(Φ = 0.269); I(Φ = 0.363)] increases as the aurophilic attraction potential increases. We suggest that the increase in quantum yield is indicative of increased ethylene π* character in the first excited state of the iodide complex ($\mathbf{3}_{cis}$) relative to that in the chloride complex ($\mathbf{1}_{cis}$). This experimental approach allows a quantitative comparison of the effect of different ligands on the strength of gold–gold interactions.

Experimental Section

General Procedures: Methylene chloride (spectral grade) was obtained from Aldrich and used as received. Complexes $\mathbf{1}_{cis}$–$\mathbf{3}_{cis}$ and $\mathbf{3}_{trans}$ were synthesized and purified as previously reported.[3,4] The following abbreviations are used: dppee = 1,2-bis(diphenylphosphanyl)ethylene; dppbz = 1,2-bis(diphenylphosphanyl)benzene.

Quantum Yield Measurements: A 200-W Oriel mercury arc lamp was used for quantum yield measurements. The wavelengths for the experiments were isolated by using a model 77250 Oriel monochrometer with 6-mm gratings. Ferrioxalate actinometry was used for determining lamp flux for quantum yield calculations.[33] The flux for the 200-W lamp had an average value of 6.12×10^{15} photons/Ls. Gold(I) complexes were dissolved in dichloromethane, and the solutions were protected from light while transferring them to a dark room for quantum yield experiments. No attempts were made to exclude oxygen from the solutions. Previous studies confirmed that the presence of oxygen does not affect the photochemical isomerization reaction.[4] Solutions were irradiated at room temperature in 1-cm quartz cells and were stirred during irradiation. Absolute quantum yield measurements for the *cis* to *trans* isomerization were made by monitoring the decrease in absorbance for the *cis* complexes at 334 nm (X = I, Br, Cl). Absorbances were measured by using a Beckman DU spectrophotometer. Quantum yield measurements were replicated 4–6 times for each complex.

Crystal Structure Determination: Details of the X-ray experiments and crystal data for $\mathbf{3}_{cis}$ and $\mathbf{3}_{trans}$ are summarized in Table 4. Crystals of $\mathbf{3}_{cis}$ and $\mathbf{3}_{trans}$ were grown from CH_2Cl_2/Et_2O. Crystals of $\mathbf{3}_{trans}$ turned opaque when exposed to the atmosphere owing to loss of solvent, and no longer diffract X-rays. In order to prevent loss of solvent, crystals of $\mathbf{3}_{trans}$ were coated with a thin film of epoxy. Crystals of $\mathbf{3}_{cis}$ did not require any special treatment.

Table 4. Crystallographic data for compounds $\mathbf{3}_{cis}$ and $\mathbf{3}_{trans}\cdot 2CH_2Cl_2$.

	$\mathbf{3}_{cis}$	$\mathbf{3}_{trans}\cdot 2CH_2Cl_2$
Chemical formula	$C_{26}H_{22}Au_2I_2P_2$	$C_{28}H_{26}Au_2Cl_4I_2P_2$
Formula mass	1044.15	1214.02
Space group	P1 21/*n* 1	C 1 2/*c* 1
a [Å]	12.6165(15)	11.7391(14)
b [Å]	14.505(1)	20.3363(16)
c [Å]	15.2955(9)	15.634(3)
β [°]	103.457(7)	108.255(17)
V [Å^3]	2722.3(4)	3544.6(9)
Z	4	4
T [°C]	21	21
λ [Å]	0.71073	0.71073
$\rho_{calcd.}$ [g cm^{-1}]	2.547	2.267
μ [cm^{-1}]	13.164	10.419
$R^{[a]}$	0.0476	0.0380
$R_w^{[b]}$	0.0548	0.0379

[a] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Data on $\mathbf{3}_{cis}$ and $\mathbf{3}_{trans}$ were collected with an Enraf–Nonius CAD4-Turbo diffractometer at Brandeis University by using the Enraf–Nonius EXPRESS program with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods by using SHELXS-86 and refined with the Oxford CRYSTALS package. Drawings were made (50% probability ellipsoids) with the Oxford CAMERON program. All non-hydrogen atoms were located from successive difference-Fourier syntheses for both structures. Final refinement of positional and anisotropic displacement parameters for all non-hydrogen atoms in compound $\mathbf{3}_{cis}$ led to R = 0.0476 and R_w = 0.0548 by using 4602 data for which $I > 1.96\sigma(I)$. For compound $\mathbf{3}_{trans}$, final refinement of positional and isotropic displacement parameters for all non-hydrogen atoms [anisotropic displacement parameters for Au, P, I, C(1), C(2), and C(8), a total of 77 parameters] led to R = 0.0380 and R_w = 0.0379 by using 2272 data for which $I > 1.96\sigma(I)$. Attempts to refine all non-hydrogen atoms by using anisotropic displacement parameters led to unsatisfactory values. Hence the non-*ipso* carbon atoms in each of the phenyl rings were refined by using isotropic displacement parameters. The hydrogen atoms were placed in calculated positions ($d_{C–H}$ = 0.95 Å) in both structures.

For the solvent molecule present in $\mathbf{3}_{trans}$, only atom Cl(1) was refined by using an anisotropic displacement parameter, while the other atoms in the solvent molecule were refined by using isotropic displacement parameters. The CH_2Cl_2 solvent was found to be partially disordered over two sites with the major component occupancy equal to 0.67(2). The Cl–C distances and the Cl–C–Cl angles were restrained to be at 1.75(5) Å and 111.0(5)°. Occupancy constraints were also applied to the disordered atoms in the solvent molecule.

Supplementary Crystallographic Data: CCDC-646580 and -646581 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data_request/cif.

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