Photoinduced C–C Bond Formation from Alkyl Halides catalysed by Luminescent Dinuclear Gold(I) and Copper(I) Complexes

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The photoluminescent properties of $[Au_2(\mu\text{-dppm})_2]^{2+}$ [dppm = bis(diphenylphosphino)methane], $[Au_2(\mu\text{-dmpm})_3]^{2+}$ [dmpm = bis(dimethylphosphino)methane] and $[Cu_2(\mu\text{-dppm})_2(MeCN)_4]^{2+}$ have been investigated. Irradiation of a degassed acetonitrile solution of benzyl chloride or 1-bromopentane in the presence of a sacrificial electron donor such as triethylamine and a catalytic amount of $[Au_2(\mu\text{-dppm})_2]^{2+}$ led to the formation of bibenzyl or *n*-decane. Similar photoreactions with much lower yields of the C–C bond coupling products have also been observed with $[Au_2(\mu\text{-dmpm})_3]^{2+}$ and $[Cu_2(\mu\text{-dppm})_2(MeCN)_4]^{2+}$ as catalysts. The mechanism of the photoreaction between alkyl halides and $[Au_2(\mu\text{-dppm})_2]^{2+}$ has been investigated by steady-state photolysis, Stern–Volmer quenching and flash-photolysis studies.

We have been searching for strongly luminescent inorganic complexes which find application in organic transformation reactions.[1-3] The intensely luminescent and co-ordinatively unsaturated dinuclear d^8–d^8 complex $[Pt_2(H_2P_2O_5)_4]^{4-}$ is an example which catalyses the dehydrogenation of alcohol to aldehyde/ketone and cleavage of the C–X (X = halide) bond of alkyl halides upon excitation with UV/VIS light at room temperature.[2,3] Two-co-ordinated binuclear d^{10}–d^{10} complexes such as $[Au_2(\mu\text{-dppm})_2]^{2+}$ [dppm = bis(diphenylphosphino)methane] bear some similarities to $[Pt_2(H_2P_2O_5)_4]^{4-}$ in that they also have vacant co-ordination sites for substrate-binding reactions and that their lowest electronic excited states are usually long-lived and powerful reductants.[4,5] Here we report several d^{10}–d^{10} metal complexes of this type which are photocatalysts for the conversion of benzyl chloride and 1-bromopentane into bibenzyl and *n*-decane respectively. Photoinduced C–C coupling is an important reaction in organic synthesis. Both $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine)[6] and $[Cu(mpp)_2]^+$ [mpp = 2,9-bis(*p*-methoxyphenyl)-1,10-phenanthroline][7] have been reported for photoassisted C–C coupling of benzyl bromide and its derivatives, through an electron-transfer mechanism.

Experimental

Materials.—The complexes $[Au_2(\mu\text{-dppm})_2]Cl_2$,[8] $[Au_2(\mu\text{-dmpm})_3][ClO_4]_2$ [dmpm = bis(dimethylphosphino)methane][9] and $[Cu_2(\mu\text{-dppm})_2(MeCN)_4][ClO_4]_2$[10] were prepared by published methods. The complex $[Au_2(\mu\text{-dppm})_2][CF_3SO_3]_2$ was prepared by metathesis of $[Au_2(\mu\text{-dppm})_2]Cl_2$ with $AgCF_3SO_3$ in methanol followed by precipitation with diethyl ether. It was recrystallised by diffusion of diethyl ether into an acetonitrile solution of it. All organic solvents and reagents were purified by standard procedures.[11]

Steady-state Photoreaction.—The experimental procedures and set-up for steady-state photolysis experiments were similar to those reported previously.[3] The spectral changes for the photoreaction of $[Au_2(\mu\text{-dppm})_2][CF_3SO_3]_2$ with $CHCl_3$ were followed by using a Shimadzu UV-24 spectrophotometer. In a typical preparative photochemical reaction, an acetonitrile solution (*ca.* 20 cm^3) of metal complex (15 μmol), alkyl halide (10 mmol) and triethylamine (12 mmol) was degassed by bubbling purified nitrogen through it for about 20 min and then irradiated with light of $\lambda > 300$ nm for 24 h. The volatile organic products were analysed and characterised by GC-MS methods. For bibenzyl the solution after photolysis was evaporated to dryness to give a solid residue which was loaded on a silica gel column. Elution with hexane gave bibenzyl. Quantitative analysis of an individual GC component was by a HP3394A electronic integrator. For each photoreaction the reported turnover number is the average value of three experiments.

Flash-photolysis Experiments and Luminescence Quenching.—Both flash photolysis and lifetime measurements were performed with a conventional laser spectrophotometer. Excitation was provided by the 355 nm output (third harmonic) of a Quanta-Ray Q-switched DCR-3 pulsed Nd-YAG laser (10 MHz, G-resonator). The luminescence decay and transient absorption signals were recorded by a R928 PMT (Hamamatsu) digitised with a Tetronix 2430 digital oscilloscope, interfaced to an IBM AT personal computer for data treatment. Transient absorption spectra of photolysed solutions were measured perpendicular to the laser beam with a 100 W tungsten lamp generating the monitoring light beam. Stern–Volmer quenching experiments were done with degassed acetonitrile solutions of metal complexes in the presence of quenchers. The bimolecular quenching rate constants k_q were obtained from Stern–Volmer plots. The solutions for flash-photolysis experiments and Stern–Volmer quenching were degassed by four freeze–pump–thaw cycles.

Results and Discussion

Photophysical Properties.—The photophysical and photoredox properties of $[Au_2(\mu\text{-dppm})_2][ClO_4]_2$ and $[Au_2(\mu\text{-dppm})_2][PF_6]_2$ have been reported previously.[4] In this work the emission lifetime and quantum yield of $[Au_2(\mu\text{-dppm})_2][CF_3SO_3]_2$ are close to those of $[Au_2(\mu\text{-dppm})_2][PF_6]_2$ as expected since both $CF_3SO_3^-$ and PF_6^- are non-co-ordinating anions. Table 1 summarises the effect of solvents on the photophysical properties of $[Au_2(\mu\text{-dppm})_2][CF_3SO_3]_2$. Changing the solvent from MeOH or MeCN to CH_2Cl_2 reduces both the emission lifetime and quantum yield significantly, but does not appear to affect the emission energy.

Table 1 Photophysical properties of d^{10} complexes in different degassed solvents at room temperature

Complex	Solvent	UV/VIS absorption λ_{max}/nm($10^{-4}\varepsilon_{max}$/dm^3 mol^{-1} cm^{-1})	Emission λ_{max}/nm	Lifetime, τ_0/μs	Quantum yield
$[Au_2(dppm)_2][CF_3SO_3]_2$	MeCN	295(2.72)	570	21	0.23
	MeOH	295(2.45)	570	19	0.10
	CH_2Cl_2	301(2.52)	570	0.8	1.5×10^{-2}
$[Cu_2(dppm)_2(MeCN)_4][ClO_4]_2$	MeCN	255(2.63)	526	7	1.5×10^{-2}
$[Au_2(dmpm)_3][ClO_4]_2$	MeCN	258(2.15) 309(0.16) 345(0.11)	588	0.8	3.5×10^{-2}

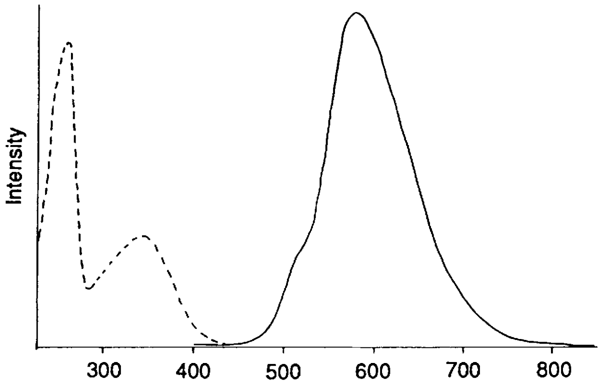


Fig. 1 Excitation (- - - -) and emission (——) spectra of a degassed acetonitrile solution of $[Au_2(dmpm)_3][ClO_4]_2$ at room temperature

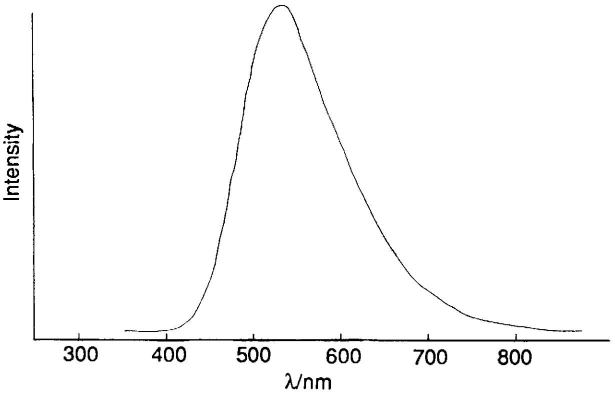


Fig. 2 Emission (——) spectrum of a degassed acetonitrile solution of $[Cu_2(dppm)_2(MeCN)_4][ClO_4]_2$ at room temperature

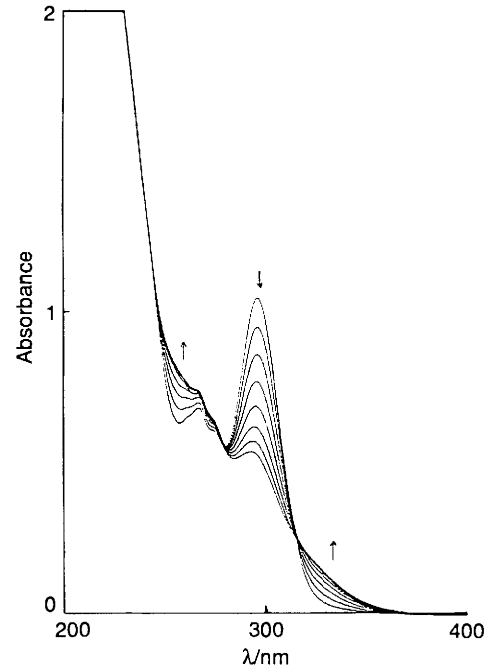


Fig. 3 Spectral changes of $[Au_2(dppm)_2][CF_3SO_3]_2$ (*ca.* 5×10^{-5} mol dm^{-3}) in a $CHCl_3$–MeCN (1 : 1) degassed solution upon excitation at $\lambda > 300$ nm. Spectral scans at 10 min intervals

The spectroscopic properties of the three-co-ordinated complex $[Au_2(\mu\text{-dmpm})_3][ClO_4]_2$ have been reported and discussed by Mason and co-workers.[9] This complex shows an intense absorption band with λ_{max} at 260 nm which is assigned to the $^1(p_\sigma \longleftarrow d_{\sigma^*})$ transition. There is a weak and broad absorption band at 311 and a shoulder at 341 nm. Here, we find that $[Au_2(\mu\text{-dmpm})_3]^{2+}$ exhibits room-temperature photoluminescence at similar energy to that for $[Au_2(\mu\text{-dppm})_2][CF_3SO_3]_2$ but with a smaller quantum yield (Fig. 1). The excitation spectrum of the emission shows a broad absorption band at 345 nm. With reference to previous studies by Mason and co-workers,[9] the excitation band at 345 nm was suggested to arise from the $d_{\delta^*} \longrightarrow p_\sigma$ transition. We tentatively assign the emission of $[Au_2(\mu\text{-dmpm})_3]^{2+}$ to one of the spin–orbit states of the $d_{\delta^*}p_\sigma$ triplet. This assignment would imply that the d_{δ^*} is higher in energy than the d_{σ^*} orbital in the three-co-ordinated binuclear gold(I) complexes. Harvey and Gray[12] made a similar suggestion for the isoelectronic $[Pt_2(\mu\text{-dppm})_3]$ system.

The synthesis and crystal structure of $[Cu_2(\mu\text{-dppm})_2(MeCN)_4][ClO_4]_2$ have been reported.[10] The two Cu atoms are bridged by two dppm ligands at a separation of 3.757(3) Å indicating that there is no metal–metal interaction. This complex also exhibits room-temperature photoluminescence. Fig. 2 shows its emission spectrum in degassed acetonitrile at room temperature. The excitation spectrum of the emission is featureless, showing broad absorptions in the range 350–280 nm. The emission centred at 526 nm, which is similar to that for $[Cu(L\text{–}L)(PPh_3)_2]^+$ (L–L = 2,2′-bipyridine or 1,10-phenanthroline),[13] is tentatively assigned to be m.l.c.t. in nature (m.l.c.t. = metal to ligand charge transfer).[3] A direct comparison of the three complexes $[Au_2(\mu\text{-dppm})_2]^{2+}$, $[Au_2(\mu\text{-dmpm})_3]^{2+}$ and $[Cu_2(\mu\text{-dppm})_2(MeCN)_4]^{2+}$ (Table 1) indicates that $[Au_2(\mu\text{-dppm})_2]^{2+}$ is likely to be the best photosensitiser since it has the longest excited-state lifetime.

Photoreaction of Au_2 *Complexes with Alkyl Halides.*—Only the photoreactions of $[Au_2(\mu\text{-dppm})_2]^{2+}$ with halogenocarbons have been investigated in detail. Fig. 3 shows the spectral changes of a $CHCl_3$–MeCN (1 : 1) degassed solution of $[Au_2(\mu\text{-dppm})_2][CF_3SO_3]_2$ upon excitation at $\lambda > 300$ nm. The spectrum shows clean isosbestic points. Under the experimental conditions employed the solution is stable in the absence of light. The inorganic product after photolysis has been identified as $[Au_2(\mu\text{-dppm})_2Cl_2]$[8] by UV/VIS and ^{31}P NMR spectroscopy. We have found that $[Au_2(\mu\text{-dmpm})_3]^{2+}$ easily undergoes dissociation of dmpm ligand upon photolysis in acetonitrile. For this reason its photoreaction with halogenocarbons has not been studied in detail.

Table 2 Product yields of photocatalysis reactions

Run	Photocatalyst	Alkyl halide	Product	Yield (%)	Turnover number[a]
1	$[Au_2(dppm)_2][CF_3SO_3]_2$	$PhCH_2Cl$	Bibenzyl	22	172
			$[NEt_3(CH_2Ph)]Cl$	70	
2[b]		$PhCH_2Cl$	Bibenzyl	16	108
			Toluene	0.4	3
			$[NEt_3(CH_2Ph)]Cl$	64	
3		$CH_3(CH_2)_4Br$	*n*-Decane	10	68
			$[NEt_3\{(CH_2)_4CH_3\}]Br$	57	
4	$[Cu_2(dppm)_2(MeCN)_4][ClO_4]_2$	$PhCH_2Cl$	Bibenzyl	5	37
			$[NEt_3(CH_2Ph)]Cl$	78	
5	$[Au_2(dmpm)_3][ClO_4]_2$	$PhCH_2Cl$	Bibenzyl	6	42
			$[NEt_3(CH_2Ph)]Cl$	74	
6[c]	Blank	$PhCH_2Cl$	Bibenzyl	1	—
			$[NEt_3(CH_2Ph)]Cl$	89	

[a] The turnover number is the moles of product per moles of catalyst. [b] In the presence of Pr^iOH. [c] The blank test was done in the absence of metal complex.

Table 3 Rate constants for the quenching of $[Au_2(dppm)_2]^{2+}$ by alkyl halides in acetonitrile at room temperature

Alkyl halide (RX)	$-E^\circ(RX\text{–}RX^{\bullet-})$[a]/V	k_q/dm^3 mol^{-1} s^{-1}
CBr_4	0.30[b]	8.90×10^9
$CHBr_3$	0.64[b]	8.70×10^9
CCl_4	0.78[b]	3.37×10^9
4-Nitrobenzyl bromide	0.80[b]	9.06×10^9
Allyl bromide	1.21[b]	7.58×10^8
MeI	1.63[b]	1.00×10^9
EtI	1.67[b]	1.73×10^9
$CHCl_3$	1.67[b]	4.59×10^7
$PhCH_2Cl$	1.94[b]	1.85×10^6
1-Bromobutane	2.27[b]	2.85×10^6
1-Bromopentane	—	3.96×10^6
CH_2Cl_2	—	4.40×10^4

[a] Half-wave potentials were measured in 75% dioxane–25% water against the SCE. [b] From ref. 14.

Organic Products of Photocatalysis Reaction.—Irradiation of a degassed acetonitrile solution containing benzyl chloride or 1-bromopentane, metal complex and triethylamine gave the C–C coupling product. The results are summarised in Table 2. Based on the turnover numbers for bibenzyl, $[Au_2(\mu\text{-dppm})_2][CF_3SO_3]_2$ is the best photosensitiser (runs 1, 2, 4, 5) among the three complexes studied. Interestingly, the C–Br bond of saturated halogenocarbon could also be cleaved leading to C–C bond formation (run 3). In the presence of a hydrogen-atom donor such as Pr^iOH a small amount of toluene is found (run 2). The quaternary ammonium salt $[NEt_3(CH_2Ph)]Cl$, identified by NMR and IR spectroscopy and its melting point, was also found in high yields in all runs. It is likely that this was formed from the thermal reaction of benzyl chloride with triethylamine, thus accounting for the relatively low yield of bibenzyl.

Quenching and Flash-photolysis Studies.—The quenching of the phosphorescence of $[Au_2(\mu\text{-dppm})_2]^{2+}$ by alkyl halides in acetonitrile has previously been communicated.[5d] The quenching rate constants are listed in Table 3. The emissions of $[Cu_2(\mu\text{-dppm})_2(MeCN)_4]^{2+}$ and $[Au_2(\mu\text{-dmpm})_3]^{2+}$ are also quenched by benzyl chloride with rate constants of 2.74×10^6 and 3.27×10^6 dm^3 mol^{-1} s^{-1} respectively, which are comparable to the values of 1.85×10^6 and 5×10^6 dm^3 mol^{-1} s^{-1} found for the $[Au_2(\mu\text{-dppm})_2]^{2+}$ and $[Cu(mpp)_2]^+$ (ref. 7) systems respectively. This suggests that the rates of photoreaction are primarily governed by the homolysis of the C–Cl bond.

Fig. 4 shows the transient difference absorption spectrum recorded 5 μs after flashing a degassed acetonitrile solution of $[Au_2(\mu\text{-dppm})_2]^{2+}$ and *cis*-$[Os^{VI}LO_2]^{2+}$ (L = *N,N,N′,N′*,3,6-hexamethyl-3,6-diazaoctane-1,8-diamine).[15] As the latter complex is a one-electron oxidant with $E^\circ = 0.06$ V *vs.* Ag–$AgNO_3$, the excited state of $[Au_2(\mu\text{-dppm})_2]^{2+}$, which is a powerful one-electron reductant, reacts with it through an electron-transfer mechanism [equation (1)]. The broad band centred at about 380 nm in Fig. 4 is believed to be due to $[Au_2(\mu\text{-dppm})_2]^{3+}$ because *cis*-$[Os^{V}LO_2]^+$ does not show any significant absorption in this region.[15]

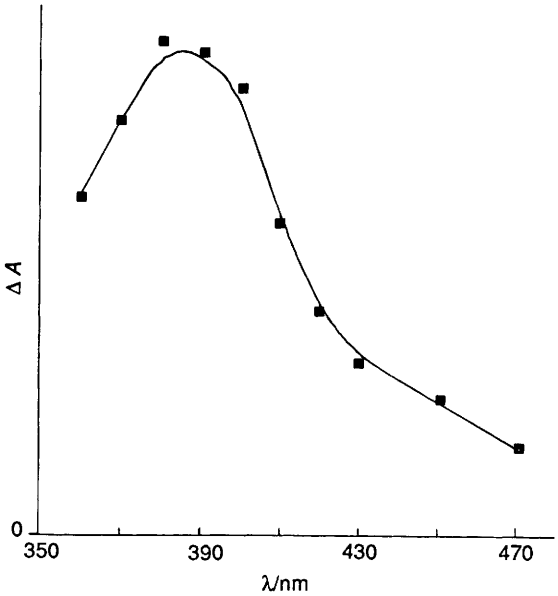


Fig. 4 Transient difference absorption spectrum recorded 5 μs after the laser flash (355 nm) of a degassed acetonitrile solution of $[Au_2(dppm)_2][CF_3SO_3]_2$ (10^{-4} mol dm^{-3}) and *cis*-$[Os^{VI}LO_2]^{2+}$ (10^{-3} mol dm^{-3})

$$[Au_2(\mu\text{-dppm})_2]^{2+} + cis\text{-}[Os^{VI}LO_2]^{2+} \longrightarrow [Au_2(\mu\text{-dppm})_2]^{3+} + cis\text{-}[Os^{V}LO_2]^{+} \quad (1)$$

Fig. 5(*a*)–(*c*) show the transient difference absorption spectra recorded 5 μs after flashing acetonitrile solutions containing $[Au_2(\mu\text{-dppm})_2]^{2+}$ and ethyl iodide, 1-bromopentane and chloroform respectively. In each case long-lived transient species with similar spectra to each other but red-shifts from that of $[Au_2(\mu\text{-dppm})_2]^{3+}$ (Fig. 4) are obtained. The decay of the transient species is complex as neither first- nor second-order kinetics is observed. In the photoreaction of $[Au_2(\mu\text{-dppm})_2]^{2+}$ with benzyl chloride the transient difference spectrum recorded 2 μs after the laser flash shows a broad

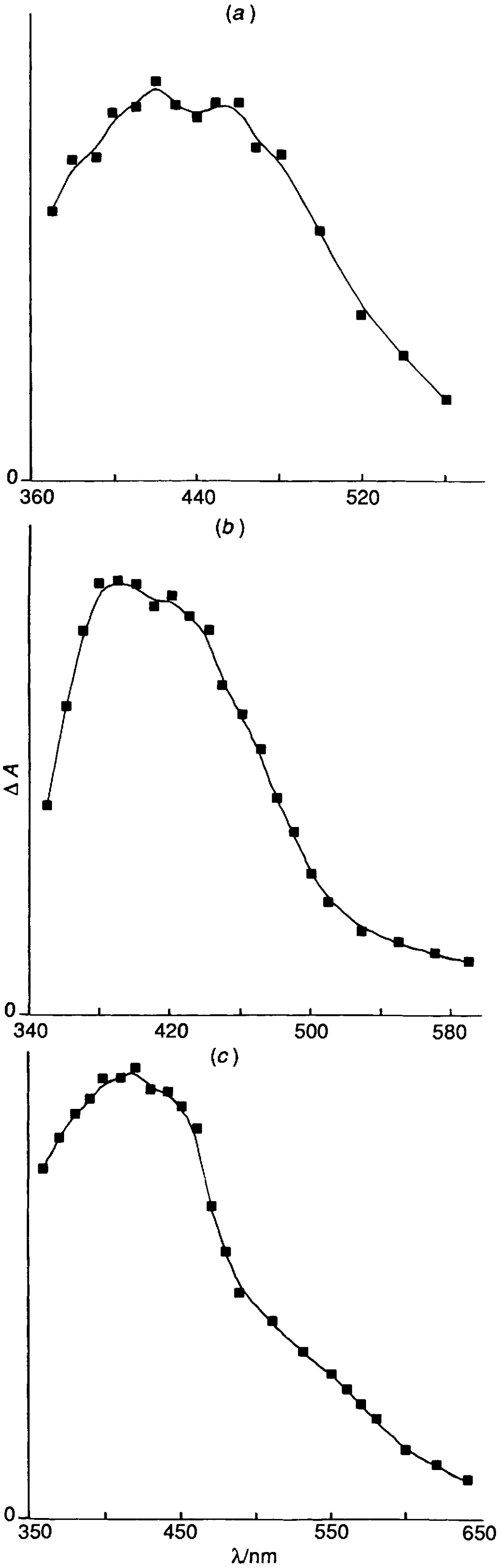
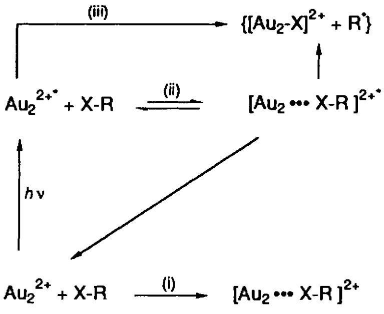


Fig. 5 Transient difference absorption spectra recorded 5 μs after the laser flash (355 nm) for a degassed acetonitrile solution of $[Au_2(dppm)_2][CF_3SO_3]_2$ (10^{-4} mol dm^{-3}) and (*a*) ethyl iodide (0.6 mol dm^{-3}), (*b*) 1-bromopentane (1 mol dm^{-3}) and (*c*) chloroform (0.5 mol dm^{-3})

absorption ranging from 380 to 500 nm (λ_{max} 380 and 440 nm). When monitoring at 440 nm the absorbance decayed through a second-order kinetics. We suggest that the photoreactions (2)



Scheme 1

$$[Au_2(\mu\text{-dppm})_2]^{2+*} + RX \longrightarrow [Au_2(\mu\text{-dppm})_2X]^{2+} + R^{\bullet} \quad (2)$$

occur. Since the spectrum of $[Au_2(\mu\text{-dppm})_2X]^{2+}$ would not be the same as that of $[Au_2(\mu\text{-dppm})_2]^{3+}$, equation (2) may explain the different absorption spectra shown in Figs. 4 and 5(*a*)–(*c*).

General Remarks

Photoinduced C–C bond formation from alkyl halides catalysed by luminescent inorganic complexes has previously been reported.[6,7] Examples include $[Ru(bipy)_3]^{2+}$ (ref. 6) and $[Cu(mpp)_2]^+$.[7] Here, $[Au_2(\mu\text{-dppm})_2]^{2+}$ serves as a prototype example illustrating that luminescent dinuclear metal complexes are potent new photocatalysts for such transformations. Compared with $[Ru(bipy)_3]^{2+}$ and $[Cu(mpp)_2]^+$, $[Au_2(\mu\text{-dppm})_2]^{2+}$ should be a better photocatalyst because it has the longest excited-state lifetime and the most negative E° value for the couple $M^+ + e^- \longrightarrow M^*$ [$E^\circ(Ru^{3+}\text{-}Ru^{2+*}) = -0.82$ V *vs.* normal hydrogen electrode in water,[16] $E^\circ(Cu^{2+}\text{-}Cu^{+*}) = -1.43$ V *vs.* sodium chloride saturated calomel electrode (SSCE) in acetonitrile,[7] and $E^\circ(Au_2^{3+}\text{-}Au_2^{2+*}) = -1.6$ V *vs.* SSCE in acetonitrile[4a]].

There are several pathways by which alkyl halides could interact with the ground and excited states of $[Au_2(\mu\text{-dppm})_2]^{2+}$ and these are depicted in Scheme 1. Pathway (i) involves co-ordination of alkyl halide to Au_2^{2+} to give a non-emissive $[Au_2 \cdots X\text{–}R]^{2+}$ species. We have no direct evidence to prove or disprove this pathway despite the fact that halogenocarbon complexes of d^{10} metal ions such as that of Ag^I are known.[17] However, the ^{31}P NMR chemical shifts of the dppm ligand of $[Au_2(\mu\text{-dppm})_2]^{2+}$ in $CHCl_3$, $Pr^iI\text{–}CHCl_3$ (1:10), MeCN, MeOH, pyridine–methanol (2:5) and CH_2Cl_2 are δ 36.3, 36.1, 36.9, 36.9, 36.7 and 35.9 respectively, which are very similar. Furthermore, the UV/VIS absorption spectra of $[Au_2(\mu\text{-dppm})_2]^{2+}$ in MeCN, MeOH or CH_2Cl_2 are also very similar (Table 1). These point to no significant metal–solvent and/or alkyl halide interaction in the ground state and hence pathway (i) is unlikely to play any significant role in the photoreactions. Pathway (ii) involves the formation of an exciplex which may or may not be emissive. Formation of a metal complex–solvent exciplex has previously been suggested by McMillin *et al.*[13] to account for the solvent-induced quenching of the emission of mononuclear copper(I) complexes of π-aromatic diimines. We have found that the emission spectra of $[Au_2(\mu\text{-dppm})_2][CF_3SO_3]_2$ in dichloromethane, methanol and acetonitrile are very similar to each other, thus disproving the formation of an emissive exciplex in these solvents. However, this does not necessarily rule out the formation of a non-emissive exciplex. The dramatic decrease in both the emission lifetime and emission quantum yield on going from methanol or acetonitrile to dichloromethane is due to the reaction occurring between the excited state of $[Au_2(\mu\text{-dppm})_2]^{2+}$ and CH_2Cl_2. Given that the measured quenching rate constant by CH_2Cl_2 in MeCN is 4.4×10^4 dm^3 mol^{-1} s^{-1}, the calculated emission lifetime of $[Au_2(\mu\text{-dppm})_2]^{2+}$ in CH_2Cl_2 is 1.36 μs, a value which is not far off the experimentally determined lifetime (0.8 μs). The fact that no saturation kinetics has been observed in the Stern–Volmer quenching of the emission by RX argues against the formation of exciplexes. We therefore suggest that pathway (ii) is unlikely to be important for the photoreactions.

Pathway (iii) is the collisional reaction between the excited state of $[Au_2(\mu\text{-dppm})_2]^{2+}$ and RX. Two kinds of mechanism are feasible, namely direct halogen-atom transfer (a.t.) to $[Au_2(\mu\text{-dppm})_2]^{2+*}$ and electron transfer (e.t.) $\{[Au_2(\mu\text{-dppm})_2]^{2+*}$ to RX$\}$ followed by RX^- fragmentation (Scheme 2). Since both a.t. and e.t. pathways involve charge transfer from $[Au_2(\mu\text{-dppm})_2]^{2+*}$ to RX, it is not surprising to find nearly diffusion-controlled quenching rate constants for those alkyl halides having low reduction potentials. The fact that the quenching rate constants follow the order methyl iodide > allyl bromide > chloroform suggests that the C–X bond energy rather than the $E°(RX\text{–}RX^{\bullet -})$ value governs the quenching of $[Au_2(\mu\text{-dppm})_2]^{2+*}$ by RX. Results of flash-photolysis experiments also provide spectroscopic evidence that $[Au_2(\mu\text{-dppm})_2X]^{2+}$ was immediately formed at the very early stage of the photoreactions (*ca.* several μs after the laser flash). We therefore conclude that the a.t. pathway is likely to be the mechanism for the photoreactions.

$$\text{a.t.: } [Au_2(\mu\text{-dppm})_2]^{2+*} + RX \longrightarrow \{[Au_2(\mu\text{-dppm})_2X]^{2+}, R^\bullet\}$$

$$\text{e.t.: } [Au_2(\mu\text{-dppm})_2]^{2+*} + RX \longrightarrow \{[Au_2(\mu\text{-dppm})_2]^{3+} + RX^-\}$$

$$RX^- \xrightarrow{\text{fast}} R^\bullet + X^-$$

$$[Au_2(\mu\text{-dppm})_2]^{3+} + X^- \longrightarrow [Au_2(\mu\text{-dppm})_2X]^{2+}$$

Scheme 2

Acknowledgements

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