Gold(III) Photooxidants. Photophysical, Photochemical Properties, and Crystal Structure of a Luminescent Cyclometalated Gold(III) Complex of 2,9-Diphenyl-1,10-Phenanthroline

Chin-Wing Chan, Wing-Tak Wong, and Chi-Ming Che*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

A luminescent cyclometalated gold(III) complex [Au(C$^\wedge$N$^\wedge$N-dpp)Cl](X) (**1a**, X = C$_7$H$_7$SO$_3$; **1b**, X = ClO$_4$; where C$^\wedge$N$^\wedge$N = C-anion of 2,9-diphenyl-1,10-phenanthroline) was prepared and characterized by X-ray crystal analysis. Crystal data for [Au(C$_{24}$H$_{15}$N$_2$)Cl](C$_7$H$_7$SO$_3$)·$^1/_2$CH$_3$OH: mol wt 950.97, triclinic, space group $P\bar{1}$ (No. 2), a = 9.690(3) Å, b = 10.799(2) Å, c = 15.934(3) Å, α = 74.20(1)°, β = 85.59(2)°, γ = 68.72(2)°, V = 1494.6 Å^3, Z = 2. In the solid state, two [Au(C$^\wedge$N$^\wedge$N-dpp)Cl]$^+$ cations stack on each other with an intermolecular Au···Au separation of 3.6 Å. Complexes **1a** and **1b** are emissive in fluid solutions with quantum yields of ~10^{-4} and lifetimes of 0.4–0.7 μs. The emission spectra of **1a** and **1b** are quite insensitive to solvents (521–670 nm) and display vibrational progression of ~1400 cm^{-1}. The small spectral red-shift (1400 cm^{-1}) of the emission of **1a** from that of free ligand (dpp) suggests a metal-perturbed intraligand emissive state. The estimated excited state reduction potential $E^{\circ *}$(Au$^{III/II}$) of 2.2 V (vs NHE) suggests that [Au(C$^\wedge$N$^\wedge$N-dpp)Cl]$^+$ is a strong photo-oxidant. This photooxidizing property has been demonstrated with the formation of the 1,4-dimethoxybenzene cation radical (DMB^{*+}) upon UV–vis irradiation of an acetonitrile solution of [Au(C$^\wedge$N$^\wedge$N-dpp)Cl]$^+$ and DMB and visible light (λ = 406 nm) induced reduction of the gold(III) complex by tetrahydrofuran.

Introduction

The chemistry of gold is strongly influenced by the relativistic effect acting on the valence orbitals.[1] The most common oxidation state of gold(I) can be stabilized by sulfur and phosphorus donors, while the gold(III) state can be stabilized by hard base donors like oxygen and nitrogen.[2]

Many efforts in photophysical and photochemical studies are concentrated on gold(I) systems, like gold(I)–phosphine oligomers[3] and monomers,[4] and the yet to be discovered imido–gold systems.[5] Gold(II) systems are starting to emerge because the unpaired-electron on gold could be stabilized by delocalization on the unsaturated ligand.[6] Metal–ligand interaction is obviously an important factor in maintaining the gold ion in some formal oxidation states.

There are numerous Au^{III}–C bonded complexes. However, most of them are unstable and undergo reductive elimination to form C–C bonds and Au^I. Exceptions are the aryl–gold complexes which are stable and useful for organic preparations.[7] Organometallic gold(III) complexes can be stabilized with the incor-

poration of π-accepting and σ-donating ligands such as 2,2′-bipyridine and 1,10-phenanthroline.[8] The relatively large Au^{III}–C bond energy[9] (157 kcal mol^{-1}) is remarkably useful for constructing catalytic gold(III) systems that may have application in organic transformations.[10] Cyclometalated gold(III) species are not unknown, but the corresponding crystal structures are scarce.[11]

Although gold(I) complexes have been applied in chemotherapy,[12] their structures as well as the metabolic mechanism are less well understood.[13] In view of the success in therapeutic application of the isoelectronic and isostructural platinum(II) compounds,[14] that of the much more electrophilic gold(III) should be prospective in inorganic drug design.[15]

In this article, the synthesis and structure of the luminescent cyclometalated gold(III) complex [Au(C$^\wedge$N$^\wedge$N-dpp)Cl]$^+$ (**1**) (where C$^\wedge$N$^\wedge$N-dpp refers to the C-anion of 2,9-diphenyl-1,-10-phenanthroline) will be presented and its excited state properties will be discussed. The [Au(C$^\wedge$N$^\wedge$N-dpp)Cl]$^+$ complex has been demonstrated to be a powerful photooxidant, capable of oxidizing 1,4-dimethoxybenzene (DMB) and tetrahydrofuran (THF) upon UV–vis irradiation.

Experimental Section

Material. 2,9-Diphenyl-1,10-phenanthroline (dpp) was prepared by literature method.[16] Acetonitrile and dichloromethane were purified by

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the standard procedure.[17] Dichloromethane was freshly distilled before use. Methanol (GR, E. Merck) was used as received. KAuCl₄ was obtained from Aldrich Chemical Co.

Physical Measurements. Infrared spectra were measured on a Nicolet 20 SXC FT-IR spectrometer. UV-visible spectra were obtained on a Milton Roy Spectronic 3000 diode-array spectrophotometer. Proton NMR spectra were obtained on Jeol GSX 270 FT-NMR spectrometer with TMS as internal reference. Elemental analysis was performed by Butterworth Laboratories Ltd.

Cyclic voltammetry was performed on a Princeton Applied Research (PAR) Model 273 potentiostate coupled to a Kipp & Zoner X-Y recorder. A conventional two-compartment cell was used in non-aqueous measurements with silver–silver nitrate (0.1 M in acetonitrile) as the reference electrode.

Photophysical Studies. Steady-state emission spectra were recorded on SPEX 1681 FLUOROLOG-2 series F111AI spectrometer equipped with 450-W xenon lamp, a rhodamine-B reference quantum counter, and a Hamamatsu R928 photomultiplier tube. The emission spectra were corrected for monochromator and photomultiplier efficiency, and for xenon lamp stability.

Quantum yield of emission was measured in a 1-cm cell and calculated with the following equation (Crosby[18]):

$$\left(\frac{\phi_s}{\phi_r}\right) = \left(\frac{B_r}{B_s}\right)\left(\frac{n_s^2}{n_r^2}\right)\left(\frac{D_s}{D_r}\right)$$

Here n and D are refractive indices of solvent and integrated emission intensities respectively, and $B = 1 - 10^{-AL}$ (A = absorbance at wavelength of excitation, L = 1 cm). The quantum yield of [Ru(bpy)₃](PF₆)₂ in degassed acetonitrile ($\phi_r = 0.062$ at room temperature[19]) was taken as reference. Sample solutions were degassed through not less than three freeze–pump–thaw cycles.

Monochromatic light ($\lambda = 406$ nm) for steady state photolysis was obtained from xenon lamp (450 W) installed on the FLUOROLOG-2 F111AI Spectrometer at 6 mm slit width. The photolyses were carried out at room temperature in a 1 cm quartz cell. Samples were degassed through three freeze–pump–thaw cycles. Progress of the photolyses was monitored by UV–vis spectrophotometry with a Perkin-Elmer Model Lambda 19 UV/vis/nearIR spectrophotometer.

Emission lifetime was measured with a conventional laser system. The excitation source was the third harmonic (355 nm) of a Quanta-Ray Q-switched DCR-3 pulsed Nd-YAG laser (10 Hz, G-resonator). Laser power was kept below 10% to avoid excited state annihilations. The emission signals were detected by a Hamamatsu R928 photomultiplier tube and recorded on a Tektronix Model 2430 digital oscilloscope. The digitized signal was interfaced to an IBM AT personal computer and analyzed with a commercial software.

Transient absorption bands after flash-photolyses were measured with DCR-3 laser system with the probe-beam from a 100-W tungsten lamp perpendicular to the laser beam. Transient signals were amplified with Tektronix AM502 differential amplifier and recorded on the Tektronix 2430 digital oscilloscope.

Characterization of Carbonyl Products. The 2,4-dinitrophenylhydrazine (DNPH) colorimetric method was adopted.[20] The sample solution (5 mL in acetonitrile) after photolysis was mixed with a DNPH solution (1 mL).[21] Solutions of pyridine (5 mL, C₅H₅N/H₂O = 4:1, v/v) and KOH (1 mL, 33% in methanol) were added after 15 min. Absorbance of the resulting solution at 526 nm was measured. The calibration curve for carbonyl concentration was prepared by measuring the absorbance at 526 nm after the acetonitrile solution (5 mL) of acetone was treated as above.

Preparation of [Au(C^N^N-dpp)Cl](X) (1a, X = 4-CH₃C₆H₄SO₃; 1b, X = ClO₄). A mixture of 2,9-diphenyl-1,10-phenanthroline (100 mg, 0.3 mmol), KAuCl₄·¹/₂H₂O (116 mg, 0.3 mmol), and silver p-toluenesulfonate (336 mg, 2 equiv) in acetonitrile (50 mL) was refluxed for 72 h. The resulting suspension was concentrated to about 20 mL and filtered. The

Table 1. Crystallographic Data for [Au(C₂₄H₁₅N₂)Cl]C₇H₇SO₃·¹/₂CH₃OH

formula	[Au(C₂₄H₁₅N₂)Cl]-C₇H₇SO₃·¹/₂CH₃OH
fw	734.97 (750.97)
cryst syst	triclinic
space group	$P\bar{1}$ (no. 2)
λ(Mo Kα), Å	0.71073
data collecn temp, K	293
a, Å	9.690(3)
b, Å	10.799(2)
c, Å	15.934(3)
α, deg	74.20(1)
β, deg	85.59(2)
γ, deg	68.73(2)
V, Å³	1494.6
Z	2
ρ(calcd), g·cm⁻³	1.668
abs coeff (μ), cm⁻¹	51.0
R^a	0.041
R_w^b	0.061

$^a R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $^b R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. $w = 4F_o^2/[\sigma^2(F_o)^2 + (0.075F_o^2)^2]$.

slightly colored precipitate was then extracted with boiling acetonitrile. Diffusion of diethyl ether into the yellowish-green solution obtained above gave yellowish-green prisms of **1a** in 14% yield. The perchlorate salt (**1b**) was similarly prepared except AgClO₄ was used. Anal. Calcd for **1a**, C₃₁H₂₂N₂AuClSO₃: C, 50.66; H, 3.02; N, 3.81. Found: C, 50.78; H, 2.98; N, 4.07. ¹H NMR in DMSO-d₆: δ 9.22 (d, H8), 9.10 (d, H13), 8.77 (d, H9), 8.40 (d, H12), 8.40 (dd, H10, 11), 8.12 (dd, H5), 7.89 (m, H16, 20), 7.64 (m, H17, 18, 19), 7.64 (m, H3, 4), 7.42 (td, H2), 7.47 (d, H_X), 7.10 (d, H_A), and 2.28 (s, CH₃). UV–vis in CH₃CN (λ_{max}, nm/(10⁻³ϵ)): 222 (50), 244 (29.2), 274 (18.2), 310 (17.6), 384 (3.9), 406 (3.1).

X-ray Crystal Structure Determination. A yellowish-green crystal of [Au(C^N^N-dpp)Cl](CH₃C₆H₄SO₃) (**1a**) with dimensions 0.22 × 0.24 × 0.24 mm³ was obtained from acetonitrile solution. Diffraction data (5187 unique) were collected on an Enraf-Nonius diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710$ 73 Å) at 293 K. The ω–2θ scan method with 2θ of 2–50°, scan width (deg in ω) = 0.55 + 0.34 (tan θ), and scan speed of 1.27–8.24 deg/min was employed. Empirical absorption was corrected with the ψ-scan method. Atomic scattering factors were taken from ref 22a, and all calculations were carried out on a Micro Vax II computer with the Enraf-Nonius structure determination package, SDP.²²ᵇ The structure was solved with Patterson and Fourier methods. Refinements were carried out on 4720 data ($F_o > 3\sigma(F_o)$) and 195 parameters with full-matrix least-squares methods. All of the non-hydrogen atoms were refined isotropically, and the hydrogen atoms at calculated positions with assigned isotropic temperature factors were not refined. The final agreement factors were $R = 0.041$, $R_W = 0.061$, and $S = 1.393$. The residual extrema in the final difference map ranged from –1.09 to +1.89 e Å⁻³ and were close to the gold atom. The crystallographic data are summarized in Table 1, and the fractional atomic coordinates for all non-hydrogen atoms are given in Table 2. Selected bond distances and bond angles are listed in Table 3.

Results and Discussion

Synthesis and Characterization. Cyclometalated gold(III) complexes are not unprecedented.²³ In this work, metalation of dpp by gold(III) gave the cyclometalated [Au(C^N^N-dpp)-Cl]⁺.

$$AuCl_4^- + 2dpp + 2Ag^+ \rightarrow [Au(C^\wedge N^\wedge N\text{-dpp})Cl]^+ +$$
$$Hdpp^+ + Cl^- + 2AgCl(s)$$
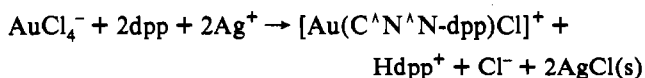
In this case, silver(I) p-toluenesulfonate was added to the reaction mixture to remove the coordinated chloride from AuCl₄⁻,

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Table 2. Positional Parameters and Their Estimated Standard Deviations for [Au(C$_{24}$H$_{15}$N$_2$)Cl]C$_7$H$_7$SO$_3$·$^1/_2$CH$_3$OH

atoms	x	x	z	$B,^a$ Å^2
Au	0.16513(2)	0.47824(2)	0.43311(1)	3.233(5)
Cl	0.1205(2)	0.7008(2)	0.4323(1)	4.65(4)
S	0.4417(2)	0.2999(2)	0.2534(1)	4.17(4)
O(1)	0.3508(7)	0.4251(6)	0.2754(4)	6.3(2)
O(2)	0.5704(6)	0.3101(6)	0.2052(4)	6.5(2)
O(3)	0.4777(9)	0.1805(7)	0.3273(5)	7.8(2)
N(1)	0.1961(6)	0.2825(5)	0.4484(3)	3.44(9)*
N(2)	0.0098(6)	0.4930(5)	0.3327(4)	3.6(1)*
C(1)	0.3178(7)	0.3920(6)	0.5314(5)	3.8(1)*
C(2)	0.3818(9)	0.4581(8)	0.5704(5)	4.9(2)*
C(3)	0.488(1)	0.3820(9)	0.6356(6)	5.6(2)*
C(4)	0.537(1)	0.2373(9)	0.6591(6)	6.0(2)*
C(5)	0.4765(9)	0.1697(8)	0.6184(5)	4.9(2)*
C(6)	0.3665(8)	0.2489(7)	0.5549(5)	3.9(1)*
C(7)	0.2929(8)	0.1875(7)	0.5104(5)	3.9(1)*
C(8)	0.3086(9)	0.0458(8)	0.5247(6)	4.9(2)*
C(9)	0.2179(9)	0.0157(8)	0.4769(5)	4.9(2)*
C(10)	0.1126(8)	0.1186(7)	0.4153(5)	4.1(1)*
C(11)	0.1063(7)	0.2543(6)	0.4027(4)	3.6(1)*
C(12)	0.0035(7)	0.3655(6)	0.3440(4)	3.7(1)*
C(13)	-0.0985(8)	0.3402(7)	0.2997(5)	4.2(1)*
C(14)	-0.0945(9)	0.2030(8)	0.3135(5)	4.8(2)*
C(15)	0.0068(9)	0.0953(8)	0.3679(5)	4.7(2)*
C(16)	-0.2014(8)	0.4539(7)	0.2440(5)	4.5(1)*
C(17)	-0.1910(8)	0.5824(7)	0.2284(5)	4.3(1)*
C(18)	-0.0818(7)	0.6008(6)	0.2718(4)	3.7(1)*
C(19)	-0.0608(7)	0.7348(6)	0.2464(4)	3.6(1)*
C(20)	-0.1804(8)	0.8534(7)	0.2359(5)	4.5(1)*
C(21)	-0.1618(9)	0.9839(8)	0.2043(5)	4.9(2)*
C(22)	-0.020(1)	0.9855(8)	0.1825(6)	5.3(2)*
C(23)	0.0978(8)	0.8661(7)	0.1912(5)	4.6(1)*
C(24)	0.0805(8)	0.7360(7)	0.2261(5)	3.9(1)*
C(25)	0.3338(9)	0.2688(7)	0.1827(5)	4.7(1)*
C(26)	0.200(1)	0.368(1)	0.1498(7)	6.8(2)*
C(27)	0.113(2)	0.340(1)	0.0911(9)	9.3(3)*
C(28)	0.184(2)	0.215(1)	0.0689(9)	9.1(3)*
C(29)	0.314(2)	0.118(1)	0.0964(9)	9.2(3)*
C(30)	0.394(1)	0.143(1)	0.1588(8)	7.4(2)*
C(31)	0.098(2)	0.188(2)	-0.011(1)	11.5(5)*
O(4)	0.469(2)	0.726(2)	0.088(1)	10.9(5)*
C(32)	0.396(4)	0.674(3)	0.029(2)	11.7(9)*

^{a} Starred values denote atoms that were refined isotropically. Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for [Au(C$_{24}$H$_{15}$N$_2$)(Cl)](C$_7$H$_7$SO$_3$)·$^1/_2$CH$_3$OH^a

Bond Distances			
Au–Cl	2.280(2)	Au–N(1)	1.972(6)
Au–N(2)	2.216(6)	Au–C(1)	2.017(7)

Bond Angles			
Cl–Au–N(1)	173.2(2)	Cl–Au–N(2)	104.6(1)
Cl–Au–C(1)	96.2(2)	N(1)–Au–N(2)	78.6(2)
N(1)–Au–C(1)	80.5(3)	N(2)–Au–C(1)	159.1(3)

^{a} Numbers in parentheses are estimated standard deviations in the least significant digits.

leading to the generation of a highly reactive gold(III) reagent.[24] However, auration on 2,9-diphenyl-1,10-phenanthroline requires prolong heating at high temperature, probably due to the steric bulkiness of the aromatic ligand. The cyclometalated [Au-(C$^{\wedge}$N$^{\wedge}$N-dpp)Cl]$^+$ product has been found to be unstable in solution under refluxing conditions. Formation of a significant amount of metallic gold was observed during the synthesis.

Use of perchlorate as a counteranion has been found to complicate the product composition. A satisfactory elemental analysis has not been obtained for **1b**, although its ^{1}H NMR and

UV–vis spectra are consistent with its formulation. The characterization of [Au(C$^{\wedge}$N$^{\wedge}$N-dpp)Cl]$^+$ is facilitated by the use of p-toluene sulfonate as counteranion because the ratio of integration values for protons on the cation and on the anion provides information on the product composition.

^{1}H NMR of 1a. The composition of **1a** is confirmed by ^{1}H NMR spectroscopy. Protons on the cyclometalated ligand are assigned with ^{1}H–^{1}H COSY (Figure 1). The chemical shifts of the protons on 4-CH$_3$C$_6$H$_4$SO$_3^-$ are recognized as a singlet at 2.28 ppm and a A$_2$X$_2$ multiplet at 7.10 and 7.47 ppm. The chemical shifts of the phenanthroline protons are correlated (H8-9, H10-11, and H12-13) and spread from 9.2 to 8.3 ppm. The pairs H8 and H13, H9 and H12, and H10 and H11 are not equivalent when one of the pendent phenyl rings of dpp is metalated. Chemical shift differences for H8 and H13 and for H9 and H12 are greater than that for H10 and H11 because the former two pairs are closer to the metal center. Chemical shifts for protons on both phenyl rings are clustered at 8.2–7.3 ppm. The Au–C–N–N plane approximates mirror symmetry for the pendent phenyl, which contains two sets of correlated protons with relative intensity 2:3 at 7.89 and 7.64 ppm, respectively. The less upfield signals are assigned to H16 and H20 because they are closer to the metal center than H17, H18, and H19. The four protons (H2-5) on the metallated phenyl are chemically non-equivalent. Proton H2 is more upfield (7.40 ppm) since it is close to the shielding region of the ring current from the pendent phenyl. Proton H5 is more down-field because of deshielding effect from the van der Waals interaction with H8. Chemical shifts of protons H3 and H4 are close to those of H17, H18, and H19 on the pendent phenyl. This is not surprising because they are the most furthest from the metal center.

Crystal and Molecular Structure of 1a. The crystal lattice of **1a** (Figure 2) consists of pairs of [Au(C$^{\wedge}$N$^{\wedge}$N-dpp)Cl]$^+$ cations with their molecular planes stacking on each other and without significant Au···Au interaction. The distance between the Au^{III} center and one of the oxygen atoms (O$_1$) on the tosylate anion is about 3.03 Å, which is close to the non-bonding Au···O distances (2.985–2.997 Å) observed in gold(III) dipeptide hydrates.[25] The tendency of gold(III) to extend its coordination sphere beyond four has been noted before.[26] A perspective view illustrating the dimeric structural motif [1a]$_2$ is shown in Figure 3. The plane defined by atoms C(1), N(1), N(2), and Cl deviates slightly from a regular square where the angles C(1)–Au–N(2) and N(1)–Au–Cl are 159.1(3) and 173.2(2)°, respectively. The dihedral angle between the pendent phenyl ring and the mean plane of the rest of the ligand (C$^{\wedge}$N$^{\wedge}$N-dpp) is 55.09 ± 0.17°, which is close to that observed in [Cu(dpp)$_2$]$^{2+}$ (~53°).[27]

The two Au–Cl bonds in the dimeric stack [1a]$_2$ are pointing in opposite directions. In addition, the Au–Au vector in [1a]$_2$ is inclined with respect to the two parallel planes defined by atoms C(1), N(1), and N(2).[28] The measured Au···Au separation of 3.6 Å in the dimeric stack is about 0.2 Å longer than the analogous Pt^{II}···Pt^{II} distance found in the related crystal structure of [Pt-(C$^{\wedge}$N$^{\wedge}$N-dpp)(NCCH$_3$)](ClO$_4$).[29] The longer metal–metal distance observed in [1a]$_2$ may partly be explained by the repulsive interaction between the pendent phenyl ring on one molecule of **1a** and the cyclometalated phenyl ring on the other. Comparison of the interplanar separation in the free ligand (3.373(9) Å)[27]

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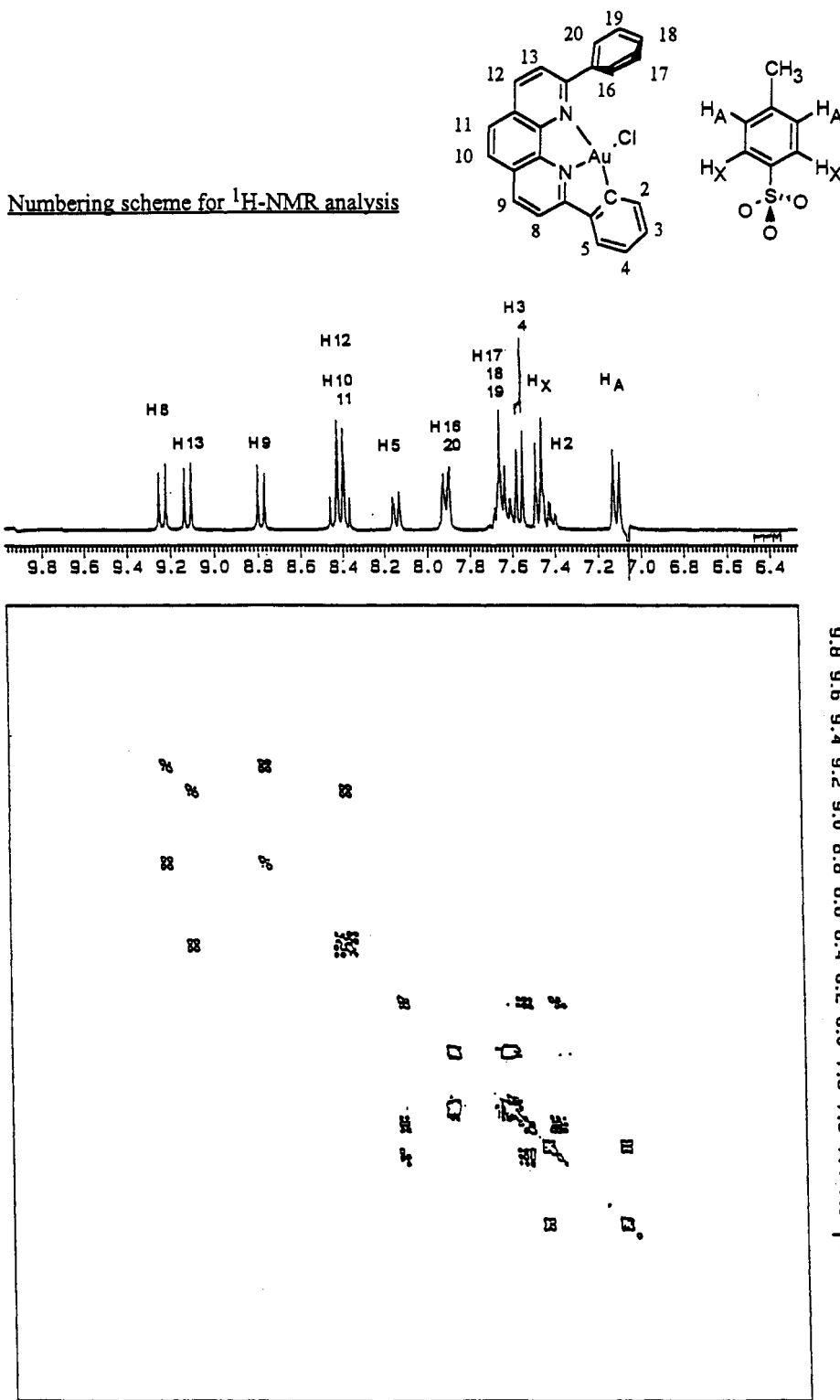
Figure 1. ^{1}H-^{1}H COSY spectrum of [Au(C$^\wedge$N$^\wedge$N-dpp)Cl]$^+$ recorded in DMSO-d_6 at room temperature.

and that observed in this example (3.55 Å) indicates considerable columbic repulsion between the two [Au(C$^\wedge$N$^\wedge$N-dpp)Cl]$^+$ units.

Structurally characterized gold(III) α-diimine complexes have been reported.[30] The Au–N(1) distance is close to the related Au–N distance observed in [Au(terpy)(Cl)]$^{2+}$ (1.931(7) Å) (where terpy = 2,2':6',2''-terpyridine).[30a] The Au–Cl distance falls within the range (2.26–2.42 Å) found in other Au^{III}–Cl complexes.[31] The Au–N distances within the [Au(C$^\wedge$N$^\wedge$N-dpp)-

Cl]$^+$ cation are significantly different, with the one trans to carbon σ-donor being 0.24 Å longer than that trans to chloride. Similar Au–N distances have also been found in [Au(phen)(CH$_2$Si-(CH$_3$)$_3$)$_2$]$^+$ and [Au(bipy)(mes)$_2$]$^+$ (where phen = 1,10-phenanthroline, bipy = 2,2'-dipyridine, and mes = mesityl).[30b] The longer Au–N(2) distance is not unexpected given the large σ-trans effect of the cyclometalated carbon donor. The measured Au–C(2) distance of 2.017(7) Å is comparable to those Au–C distances found for [Au(phen)(CH$_2$Si(CH$_3$)$_3$)$_2$]$^+$ (2.031–2.039 Å), [Au-

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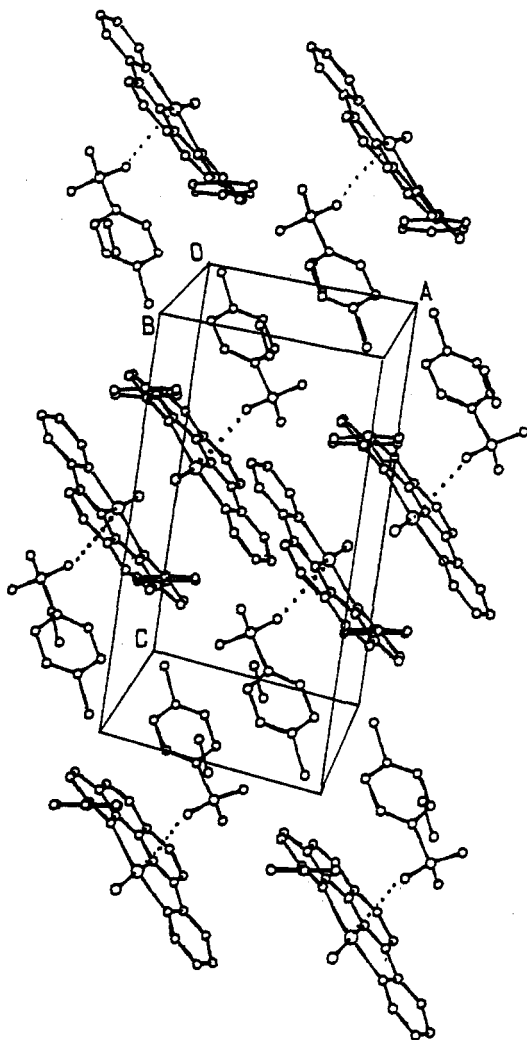
Figure 2. Crystal lattice diagram of [Au(C^N^N-dpp)Cl](CH₃C₆H₄-SO₃). The interaction between the O(1) atom of tosylate and Au^III is indicated by the dotted line (⋯).
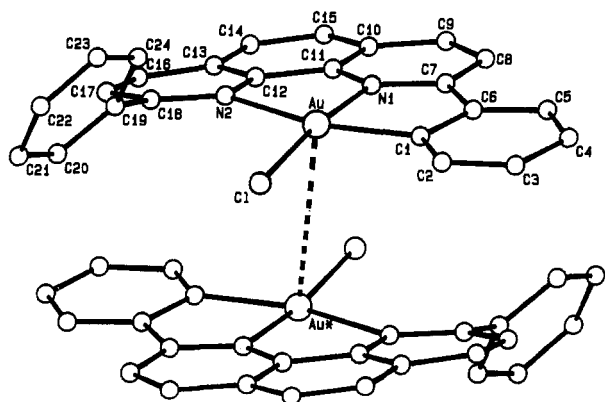
Figure 3. Perspective view of the dimeric structure of {[Au(C^N^N-dpp)Cl]₂}²⁺.

(bipy)(mes)₂]⁺ (2.020–2.029 Å),³⁰ᵇ [Au(CH₃)₂{HB(pz)₃}] (2.04–2.05 Å),³² and [Au(CH₃)₂(dpk·H₂O)]⁺ (2.02–2.04 Å)³³ (where pz = pyrazol-1-yl, dpk = di-2-pyridyl ketone).

Electronic Absorption and Emission Spectra. The electronic absorption spectrum of **1a** shown in Figure 4 is similar to that of **1b**, and this is in agreement with the ¹H NMR results where

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(33) Byers, P. K.; Canty, A. J.; Engelhardt, L. M.; Patrick, J. M.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 981.
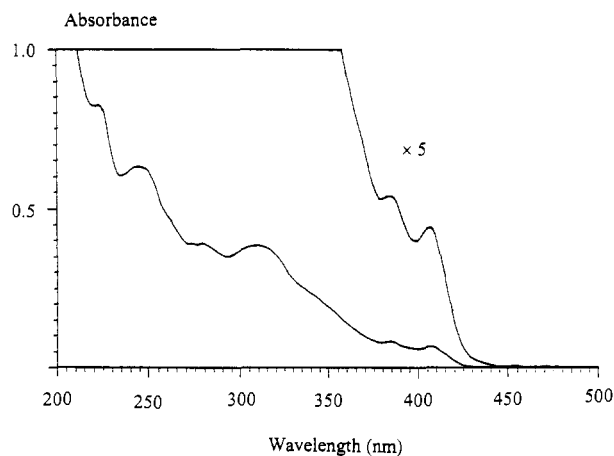
Figure 4. UV–vis absorption spectrum of [Au(C^N^N-dpp)Cl]⁺ (≈10⁻⁵ M) in acetonitrile.
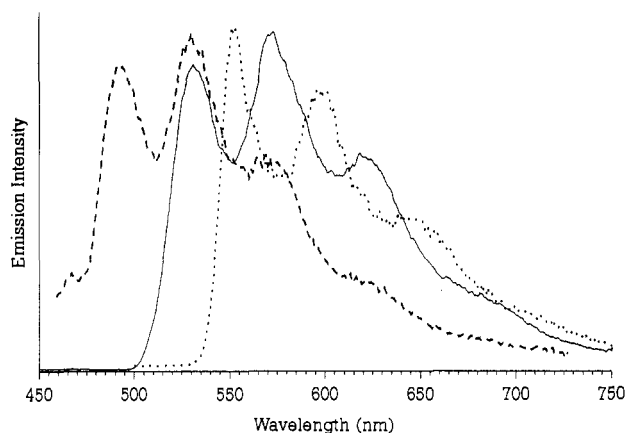
Figure 5. Emission spectra of dpp (---), [Pt(C^N^N-dpp)(NCCH₃)]⁺ (⋯) and [Au(C^N^N-dpp)Cl]⁺ (—) (λₑₓcᵢₜ = 355 nm) in 77 K methanol glasses.

the proton chemical shifts are the same irrespective of counteranions. Strong absorption bands in the 222–310 nm region (ε > 10⁴) can be assigned to the intraligand transitions. Absorption bands near the visible region 384–427 nm (ε > 10³) may have metal character since the free and protonated forms of dpp do not absorb strongly in this region.³⁴

The [Au(C^N^N-dpp)Cl]⁺ complex is emissive in solid, fluid solution, and glass matrices. Figure 5 shows the emission spectrum (λₑₓcᵢₜ = 355 nm) of **1a** measured in 77 K methanol glass. For comparison purpose, the emission spectra of dpp and [Pt(C^N^N-dpp)(NCCH₃)]⁺ recorded under similar conditions are also given. The excitation (monitored at λₑₘᵢₛₛᵢₒₙ = 520 nm) and absorption spectra of **1a** recorded in acetonitrile at 298 K are essentially identical as should be the case for all emissions from thermally equilibrated excited states. The emission profile of **1a** shows strong vibronic structure with vibrational progression of ~1400 cm⁻¹ which is close to the value of skeleton vibration frequency of aromatic rings.

The room temperature emission spectra of **1a** measured in methanol, dichloromethane, and acetonitrile are almost identical. The emission lifetimes in the methanol and acetonitrile solutions (10⁻⁵ M) are 0.42 and 0.55 μs respectively and the corresponding quantum yields are 3 × 10⁻⁴ and 4 × 10⁻⁴. The emission quantum yield and lifetime of **1a** in halocarbons are difficult to measure because of its low solubility.

Luminescent gold(III) complexes are scarce. The assignment of the excited state of [Au(C^N^N-dpp)Cl]⁺ may partly be

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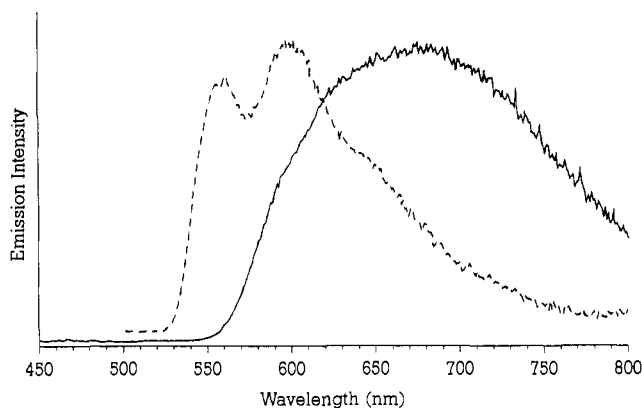
Figure 6. Solid state emission spectra of [Au(C^N^N-dpp)Cl](CH33C6H4SO3) (---) and [Pt(C^N^N-dpp)(NCCH3)]-(ClO4) (—) at 77 K (λ_{excit} = 355 nm).

resolved by comparing its emission spectrum with that of the free ligand (dpp). The emission spectra of dpp, [Au(C^N^N-dpp)-Cl]+ and the related [Pt(C^N^N-dpp)(NCCH3)]+ [29] are depicted in Figure 5. The emission maximum is red-shifted from 20.3 × 10³ cm⁻¹ in the free ligand to 18.9 × 10³ cm⁻¹ in [Au(C^N^N-dpp)Cl]+ and 18.1 × 10³ cm⁻¹ in [Pt(C^N^N-dpp)(NCCH3)]+. The spectral shift of 2200 cm⁻¹ suggests a stronger MLCT character in the excited state of [Pt(C^N^N-dpp)(NCCH3)]+ than in that of [Au(C^N^N-dpp)Cl]+ where a spectral shift of only 1400 cm⁻¹ from dpp is observed.[35] We tentatively assign the emission of [Au(C^N^N-dpp)Cl]+ to come from a metal-perturbed ³ππ* state.[36]

The solid-state emission spectra of [Au(C^N^N-dpp)Cl](CH3C6H4SO3) and [Pt(C^N^N-dpp)(NCCH3)](ClO4) recorded at 77 K are compared in Figure 6. The two emission bands are different in that vibronic progression can only be recorded in the gold complex. In addition, the spectral red-shift from their corresponding glass state emission bands are smaller for the gold (1340 cm⁻¹) than for the platinum (~4000 cm⁻¹) complex. This can be attributed to the excimeric interaction in the dimeric stack of [Pt(C^N^N-dpp)(NCCH3)]2²+, which has a much shorter intermolecular metal–metal distance than that in [1a]2.[37]

Excited-State Reactions of [Au(C^N^N-dpp)Cl]+ (1a). In dimethylformamide, the cyclic voltammogram of complex 1a displays an irreversible reduction wave at –0.84 V (vs Fc•+/Fc), and this is tentatively assigned to Au^III + e → Au^II. The first emission maximum of [Au(C^N^N-dpp)Cl]+ in acetonitrile is at 521 nm, suggesting that E_{0-0} corresponds to 2.38 V (vs NHE). E_{red}* for the process *Au^III + e → Au^II could then be estimated by the equation *E_{red} = E_{red} + E_{0-0}. The estimation of *E_{red} of ~2.2 V (vs NHE) indicates that the excited state of [Au(C^N^N-dpp)Cl]+ is an powerful oxidant when compared with other reported systems.[38]

The photoinduced oxidation of 1,4-dimethoxybenzene (DMB) by [Au(C^N^N-dpp)Cl]+ in acetonitrile (1a:DMB = 1:100) has also been investigated. The transient absorption spectrum measured 12 μs after the solution was excited with a laser pulse at 355 nm is depicted in Figure 7a. The spectrum shows intense absorption peaks at 460 and 440 nm and a shoulder at 420 nm
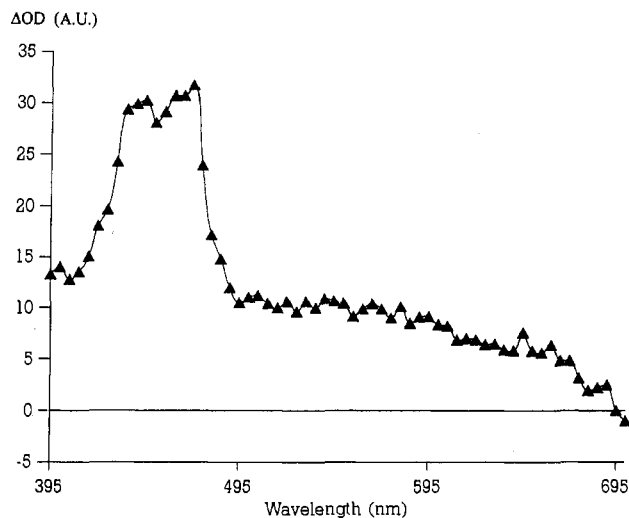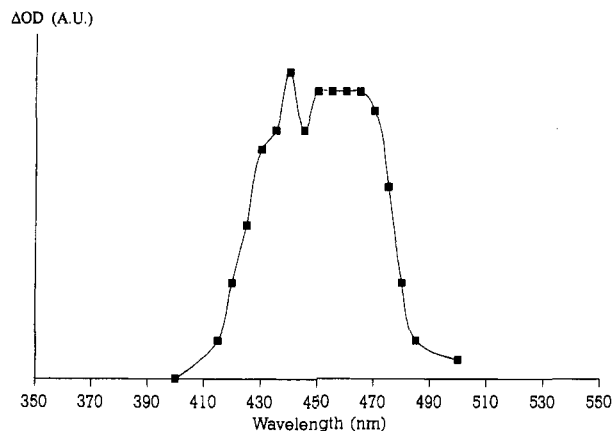

Figure 7. Transient absorption spectra of a degassed acetonitrile solution of dimethoxybenzene (DMB) and [Au(C^N^N-dpp)Cl]+ (1a) with mole ratios of 1a:DMB being (a, top) 1:100 and (b, bottom) 1:50. (Absorption was taken 12 μs after 355 nm pulse-excitation.)

which are attributed to the absorption bands of the radical cation of dimethoxybenzene (DMB•+). Similar absorption bands have been detected in the photooxidation of DMB by s-trinitrobenzene in acetonitrile.[39]

When the concentration of DMB was scaled down (1a:DMB = 1:50), a broad hump of absorption from 500 to 700 nm, which was not significantly interfered by the presence of air, was also observed (Figure 7b). The origin of this absorption band is not clear at this stage. However, both gold colloid and gold sol supported on organic substrates are known to have visible absorption bands at about 500–600 nm.[40] The 500–700-nm absorption in Figure 7b may be due to gold colloid, which was produced through intramolecular redox reaction(s) of the gold-(III) excited state.

It was noticed that the absorption at 406 nm, characteristic of [Au(C^N^N-dpp)Cl]+, decreased by 2.3% after repetitive flash-photolysis. Steady-state photolyses of [Au(C^N^N-dpp)Cl]+ in the presence (0.03 M) and absence of DMB in degassed acetonitrile for the same time interval led to 8 and 40% losses of [Au(C^N^N-dpp)Cl]+, respectively. While [Au(C^N^N-dpp)-Cl]+ was converted into pinkish colloidal gold particles, the formation of Au⁰ in the absence of DMB could be taken as an indication of an intramolecular redox reaction. The excited state of [Au(C^N^N-dpp)Cl]+ is reactive, even in "inert" solvent such

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(36) The emission spectrum of cyclometalated mercury(II) complex of dpp [(Hg(C^N-dpp)Cl]2 was identical to that of the free ligand. The isolation and characterization of this complex will be published elsewhere.

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(40) (a) Olsen, A. W.; Kafafi, Z. H. *J. Am. Chem. Soc.* **1991**, *113*, 7758. (b) Au Yeung, S.; Hobson, R.; Biggs, S.; Grieser, F. *J. Chem. Soc., Chem. Commun* **1993**, 378.
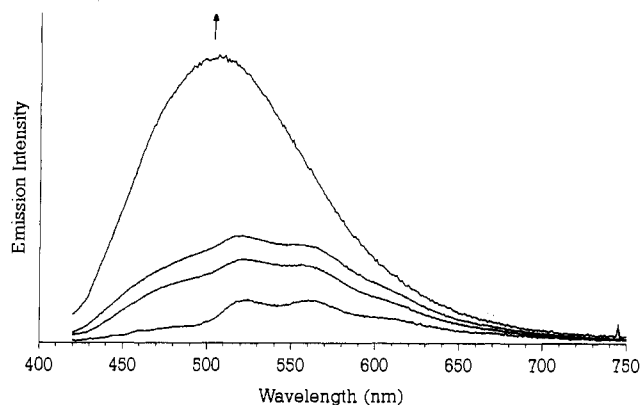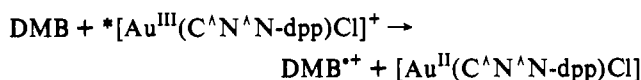
Figure 8. Spectral changes of emission from $[Au(C^\wedge N^\wedge N\text{-dpp})Cl]^+$ in a degassed acetonitrile solution with 0.05 M THF (complex concentration 3×10^{-4} M; irradiation time 1, 5, 10, and 20 min.).

as acetonitrile. 1,4-Dimethoxybenzene would quench the excited state of $[Au(C^\wedge N^\wedge N\text{-dpp})Cl]^+$ by the formation of the cationic radical $(DMB^{\bullet+})$

$$DMB + {}^*[Au^{III}(C^\wedge N^\wedge N\text{-dpp})Cl]^+ \rightarrow$$
$$DMB^{\bullet+} + [Au^{II}(C^\wedge N^\wedge N\text{-dpp})Cl]$$

The excited-state oxidizing power of $[Au(C^\wedge N^\wedge N\text{-dpp})Cl]^+$ (1a) has also been demonstrated by its photoreaction with tetrahydrofuran (THF) in degassed acetonitrile. Figure 8 shows the emission spectral change of $[Au(C^\wedge N^\wedge N\text{-dpp})Cl]^+$ in the presence of THF (1a:THF = 1:170) upon excitation at 406 nm. The broad emission at 500 nm rapidly developed within 20 min, and metallic gold was deposited after 85% of $[Au(C^\wedge N^\wedge N\text{-dpp})Cl]^+$ was decomposed. In the absence of THF, the emission spectrum of $[Au(C^\wedge N^\wedge N\text{-dpp})Cl]^+$ recorded under similar conditions has little spectral change. Here, tetrahydrofuran may act as proton source because the emission band developed around 500 nm is characteristic of the protonated salt of 2,9-diphenyl-1,10-phenanthroline $(Hdpp^+)$ $(\lambda_{max} = 500\text{ nm})$.[34] The photoreaction may be due to a redox reaction between THF and $[Au(C^\wedge N^\wedge N\text{-dpp})Cl]^+$.

Oxidative ring cleavage of THF to form a carbonyl compound has been investigated before.[41] Here, the oxidation product of THF was detected by UV–vis spectrophotometry. About 2.3 μmol of a carbonyl compound was produced from 0.35 μmol of $[Au(C^\wedge N^\wedge N\text{-dpp})Cl]^+$.

Scheme 1
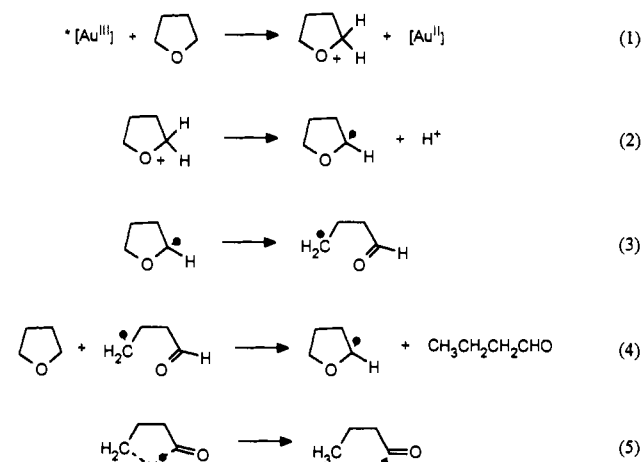
Trivalent metal ions such as cobalt(III) are known to induce alcohol oxidation through a charge-transfer mechanism. If a similar pathway is followed, electron abstraction from THF by the excited $[Au(C^\wedge N^\wedge N\text{-dpp})Cl]^+$ complex followed by a proton loss from α-carbon is expected. Possible reaction paths are outlined in Scheme 1. The resulting radical species would decompose in ways similar to those generated with organic peroxides.[41] The successful detection of a carbonyl product seems in agreement with this hypothesis. However, no adduct of THF and maleic anhydride was obtained in the radical-trap experiment in the presence of maleic anhydride.[42]

The course of photoinduced oxidation by $[Au(C^\wedge N^\wedge N\text{-dpp})\text{-}Cl]^+$ requires further study. The well-known electrophilic and coordinatively unsaturated properties of gold(III) have been demonstrated by the relatively short counteranion to metal distance. The very favorable interaction is vital for substrate binding, which is promising in either catalyst or inorganic drug design.[15]

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