Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Ligand-protected Au_4Ru_2 and Au_5Ru_2 nanoclusters: distinct structures and implications for site-cooperation catalysis

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Experimental Section

Synthesis of nanoclusters

Synthesis of $Au_4Ru_2(PPh_3)_2(SC_2H_4Ph)_8$: 0.14 mmol $AuPPh_3Cl$ and 0.055 mmol $Ru(PPh)_3Cl_2$ were dissolved in 6 mL ethanol and stirred vigorously for 15 min. 6 mL of 14 mg $NaBH_4$ ethanol solution was added to the above solution for 2 h. Then, the mixture was evaporated. The product was extracted with 15 mL CH_2Cl_2, and then 140 uL 2-phenethylmercaptan was added. The above mixture was stirred at 50°C for 2 h. The crude was washed three to five times with hexane and separated from the reaction mixture with CH_2Cl_2. The crude product dissolved in CH_2Cl_2 was pipetted on PTLC plate (10 cm × 20 cm), and the separation was conducted in developing tank (developing solvent: CH_2Cl_2) for 20 min. The bands on the PTLC plate were cut with a knife, and the green product was extracted with CH_2Cl_2. Green needle-like crystals of $Au_4Ru_2(PPh_3)_2(SC_2H_4Ph)_8$ were obtained from CH_2Cl_2/menthol for 3 to 5 days.

Synthesis of $Au_5Ru_2(PPh_3)_3(PMeC_5)_2Cl_2$ ($PMeC_5$=1,2,3,4,5-pentamethycyclopentane): 0.14 mmol $AuPPh_3Cl$ and 0.049 mmol dichloro(pentamethylcyclopentadienyl) ruthenium(III) polymer were dissolved in 6 mL ethanol. After vigorously stirring for 15 min, 6 mL ethanol solution of 14 mg $NaBH_4$ was added to the above solution. After 2 h, the mixture was evaporated. The reaction product was dissolving using ~15 mL CH_2Cl_2 and kept at 50 ^{o}C for 10 h. Then the clusters were separated from the reaction mixture by washing with n-hexane and extraction with CH_2Cl_2. The crude product dissolved in CH_2Cl_2 was pipetted on PTLC plate (10 cm × 20 cm), and the separation was conducted in developing tank (developing solvent: CH_2Cl_2/methanol=10:1) for 20 min. The bands on the PTLC plate were cut with a knife, and the pink product was extracted with methanol. The pink needle-like crystals of $Au_5Ru_2(PPh_3)_3(PMeC_5)_2Cl_2$ were obtained from CH_2Cl_2/n-hexane for 3 to 5 days.

Catalytic reaction

3 mg Au_xRu_2 (x = 4 or 5) clusters, the substrates (0.5 mmol), toluene (5.0 mL), 0.03 mmol tpy, and PhSiH (5 equiv) and a magnetic stir bar were loaded into a Teflon-lined autoclave reactor, respectively. The reactor was sealed, and then CO_2 (> 99.9%) was charged into the reactor to a certain pressure. The reactor placed in a preheated mantle at the desired temperature. After reaction, the products were collected and analyzed by gas chromatography-mass spectrometry (GC-MS) using Nanjing Hope Analysis Company 9860C instrument equipped with an HP-5 MS column (30 m in length, 0.25 mm in diameter).

Characterization

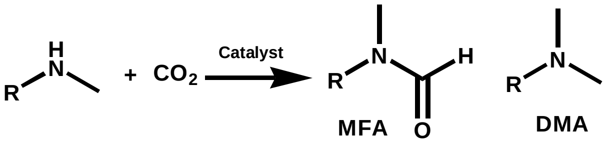
The X-ray crystallography was performed on a Bruker D8 VENTURE with Mo Kα radiation ($\lambda = 0.71073$ Å). The crystal structures were resolved by direct methods and refined by full-matrix least-squares methods with SHELXL-2013 (Sheldrick, 2013). UV/vis/NIR spectra with a range of 300-1400 nm were recorded on a UV3700 spectrophotometer (SHIMADZU). Diffuse reflectance UV-vis spectra were recorded on a UV-vis spectrometer using SHIMADZU UV-3600. Electrospray ionization (ESI) mass spectra were collected on a Waters Q-TOF mass spectrometer using a Z-spray source. The sample was first dissolved in toluene (0.5 mg/mL) and then diluted (2:1 v/v) with a methanol solution containing 50 mmol/L CsOAc. The X-ray Photoelectron Spectroscopy (XPS) of the samples were determined on the RBD upgraded PHI-5000C ESCA System in a high-vacuum chamber with the base pressure below 1×10^{-8} Torr. Correction of the charge effect was made with the C1s peak at 284.8 eV. The Ru K-edge and Au L_3-edge XAFS measurements were performed at BL14W1 station in

Shanghai Synchrotron Radiation Facility (SSRF). In situ FT-IR spectra were collected using TENSOR 27 spectrometer (Bruker, German) with a designed reaction cell. Au_5Ru_2 cluster and KBr (with a weight ratio of 5:100) were ground and compressed into a tablet. The sample tablet was lying at the center of the reaction cell. The reaction solution was pumped into the reaction cell by bubbling method, fully contacted with the sample tablet, and then filled with 1 MPa of CO_2. Then, the cell was heated to 50 °C, and the in situ FT-IR spectra were collected using a MCT detector along with the reaction.

Table S1. Binding energy values of Ru species and their relative quantities in the Au_4Ru_2 and Au_5Ru_2 clusters.

Sample	Binding energy of Ru species (eV)						Relative amount of Ru species		
	Ru 3p3/2			Ru 3p1/2			Ru^0	$Ru^{\delta+}$	Ru^{4+}
	Ru^0	$Ru^{\delta+}$	Ru^{4+}	Ru^0	$Ru^{\delta+}$	Ru^{4+}			
Au_4Ru_2	461.2	462.4	464.5	483.2	484.4	486.5	41.0%	34.1%	24.9%
Au_5Ru_2	461.1	462.4	464.5	483.1	484.4	486.5	38.2%	31.0%	30.8%

Table S2. Catalytic results of N-methylation of MA with CO_2 and PhSiH over various catalysts.



Entry	Catalyst	Conversion (%)	Selectivity (%)	
			MFA	DMA
1	$AuPPh_3Cl$	< 1%	--	--
2	$Ru(PPh_3)_3Cl_2$	< 1%	--	--
3	$Ru(PMeC_5)_2Cl_2$	< 1%	--	--
4	$AuPPh_3Cl+Ru(PMeC_5)_2Cl_2$	< 1%	--	--

Reaction conditions: 0.5 mmol substrate, 3 mg catalyst, 0.03 mmol tpy, PhSiH (5 equiv), toluene (5 mL), CO_2 (15 bar), 50 ^{o}C, 10 h. Determined by GC using M-xylene as an internal standard.

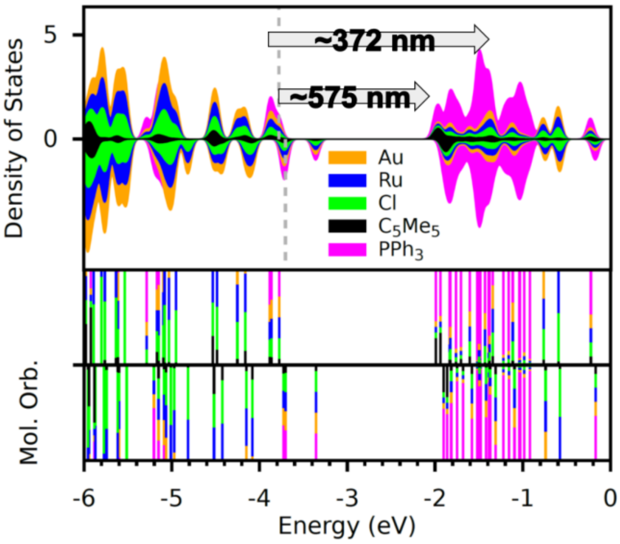


Fig. S1 Partial density of states (PDOS) of Au_5Ru_2 predicted at the PBE/LANL2DZ level.

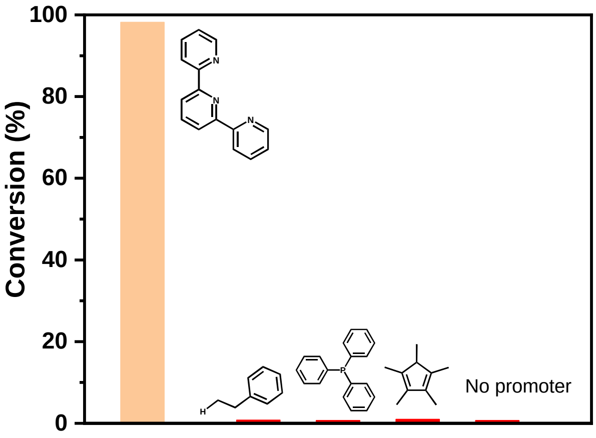


Fig. S2 Catalytic results of N-Methylation of MA with CO_2 and PhSiH on the Au_5Ru_2 clusters by different promoters. Reaction conditions: 0.5 mmol substrate, 3 mg catalyst, 0.03 mmol promoters, silane (5 equiv), toluene (5 mL), CO_2 (15 bar), 50 ^{o}C, 10 h.

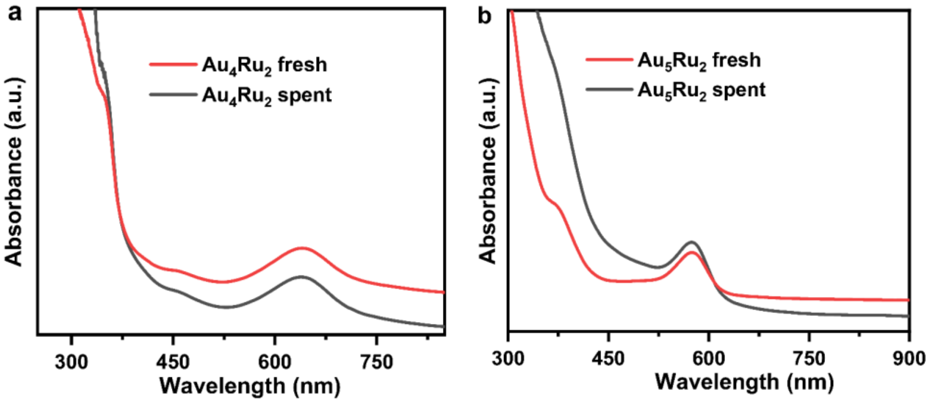


Fig. S3 UV-vis spectra of (a) the fresh and spent Au_4Ru_2 clusters. (b) UV-vis spectra of the fresh and spent Au_5Ru_2 clusters.

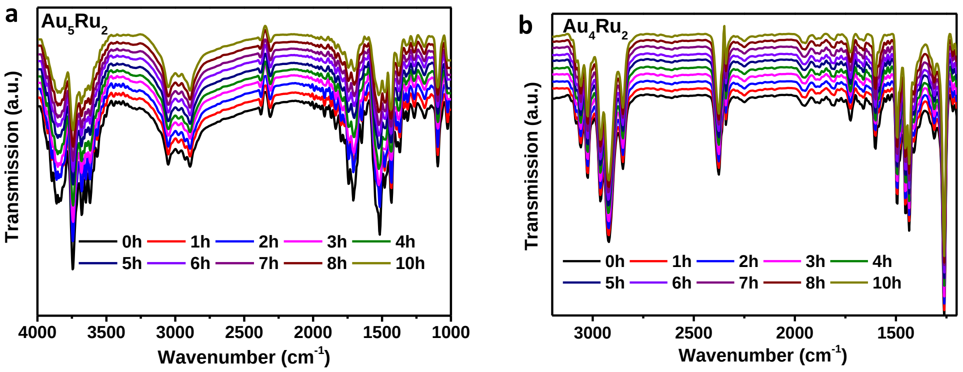


Fig. S4 Time-resolved in situ FT-IR spectra of the (a) Au$_4$Ru$_2$ and (b) Au$_5$Ru$_2$ samples treated at 50 ^{o}C in Ar atmosphere for different time.