

gave the expected *trans* THF product **17** in 84% yield; the right-hand part of the molecule was intact. On the other hand, when **17** was treated with a stoichiometric amount of the oxochromium(vi) complex pyridinium chlorochromate (PCC),^[17] in CH₂Cl₂ at room temperature for 30 min,^[5] the bishomoallylic vicinal diol moiety was oxidatively cyclized, probably via a chelated dialkoxochromium intermediate,^[5a, 18] with complete *cis* diastereoselectivity to produce (+)-14-deacetylerylene (**2**).^[19] The spectral characteristics (¹H and ¹³C NMR, IR, MS, and HRMS) of synthetic **2** were identical to those reported for the natural product.^[1b] Finally, selective acetylation of the 14-hydroxy group in **2** afforded another objective, (+)-eurylene (**1**),^[19] whose spectral data were also consistent with the ¹H NMR spectrum of an authentic sample^[3a] and with the data reported for the natural product.^[1]

In conclusion, we have accomplished the first total synthesis of (+)-14-deacetylerylene (**2**), featuring chemoselective THF ring formations stereocontrolled by *syn*-oxidative cyclizations of the bishomoallylic monool and diol induced by oxorhenium(vii) and -chromium(vi) species, respectively. The reason for the intriguing relationship^[2] between the conformations and cytotoxicities of **1** and **2** is under investigation.

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- [19] **1**: M.p. 145–147 °C, [α]_D²⁵ = +4.86 (*c* = 0.275 in CHCl₃); ref. [1] m.p. 146–148 °C, [α]_D = +4.32 (*c* = 0.14 in CHCl₃). **2**: M.p. 64.3–67.4 °C, [α]_D²⁵ = +6.02 (*c* = 0.600 in CHCl₃); ref. [1b] m.p. 63–65 °C, [α]_D = +6 (*c* = 1.03 in CHCl₃).

Cuprophilicity: Spectroscopic and Structural Evidence for Cu–Cu Bonding Interactions in Luminescent Dinuclear Copper(II) Complexes with Bridging Diphosphane Ligands*

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Copper(I)–copper(I) bonding interactions have widely been invoked to be a driving force for the self-assembly of copper(I) aggregates and to play an important role with regard to the photoluminescence of polynuclear copper(I) complexes con-

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taining phosphane or pyridine ligands.^[1–6] Weak but real $d^{10} - d^{10}$ metal–metal bonding is well established for 2nd and 3rd transition-series metal complexes,^[7–10] but the important case of Cu^I centers has remained unresolved. A recent electron diffraction study on Cu_2O found evidence for Cu–Cu bonding,^[11] and this result is of possible relevance to copper oxide superconductors. There is also biological relevance with regard to the binuclear “ Cu_A ” site of cytochrome oxidases and the corresponding model compounds.^[12] However, several studies on binuclear Cu^I complexes have denied the existence of Cu–Cu bonding,^[13] so the existence of “cuprophilicity”, analogous to “aurophilicity” has remained unsubstantiated. While $\text{Cu}^I \cdots \text{Cu}^I$ separations as short as 2.412(1) Å are known,^[14] spectroscopic evidence for $\text{Cu} \cdots \text{Cu}$ interaction has been notably lacking, which can be principally attributed to the ubiquity of ligands incorporating organic unsaturated units that greatly complicate interpretation.

We prepared $[\text{Cu}_2(\text{dcpm})_2]\text{X}_2$ (dcpm = bis(dicyclohexylphosphanyl)methane, $\text{X} = \text{ClO}_4^-$ (**1**), PF_6^- (**2**), and I^- (**3**)) and $[\text{Cu}_2(\text{dcpm})_2(\text{CH}_3\text{CN})_2]\text{X}_2$ ($\text{X} = \text{ClO}_4^-$ (**4**), PF_6^- (**5**)) complexes by reacting the appropriate Cu^I salts, $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{X}$ or CuI , with dcpm in acetone solutions. The absence of CH_3CN in (**1**) and (**2**) requires recrystallization from dichloromethane. Their crystal structures have been determined.^[15] Complexes **4** and **5** recrystallized from CH_3CN and have CH_3CN ligands coordinated to each copper atom, resulting in Y-shaped trigonal P_2CuN configurations. In $[\text{Cu}_2(\text{dcpm})_2]\text{X}_2$ (**1–3**), counteranions weakly interact with the Cu atoms in a similar trigonal fashion ($\text{X} = \text{ClO}_4$, $\text{Cu} \cdots \text{O}$, av. 2.687; $\text{X} = \text{PF}_6$, $\text{Cu} \cdots \text{F}$ 2.79(1); $\text{X} = \text{I}$, $\text{Cu} \cdots \text{I}$, av. 2.622 Å). The intramolecular $\text{Cu} \cdots \text{Cu}$ separations fall in the range 2.639(2)–2.938(2) Å, which are shorter than or close to the sum of the Van der Waals radii of Cu^I centers and increase in the order: **1**(average separations 2.685), **2**(2.790(5)) < **4**(2.8096(9)), **5**(2.810(2)) < **3**(av. 2.905 Å). This is consistent with the idea that a stronger Cu^I -anion/solvent interaction such as that in **3** would lead to weaker intramolecular metal–metal interaction. These $\text{Cu} \cdots \text{Cu}$ separations are all substantially shorter than that of the previously reported complex $[\text{Cu}_2(\text{dppm})_2(\text{CH}_3\text{CN})_4](\text{ClO}_4)_2$ ($\text{Cu} \cdots \text{Cu} = 3.426(3)$ Å; dppm = bis(diphenylphosphanyl)methane) in which the Cu atoms adopt pseudo-tetrahedral geometry with four donor ligands^[16a] and of $[(\text{Cu}_2)(i\text{Pr})_2\text{PCH}_2\text{P}(i\text{Pr})\text{H}_2](\text{CH}_3\text{CN})_2]$ ($\text{Cu} \cdots \text{Cu} = 2.973(1)$ Å) in which the Cu atoms are three coordinate.^[16b] The mononuclear compound $[\text{Cu}(\text{PCy}_3)_2]\text{ClO}_4$ (**6**; PCy_3 = tricyclohexylphosphine) has also been prepared by reacting $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ with PCy_3 ; its crystal structure reveals a trigonal $\text{P}_2\text{CuO}-\text{ClO}_3$ geometry with no intermolecular Cu–Cu contacts in the crystal lattice.^[15]

In the compounds of the present study there is a clear propensity for the coordination of ligands, in addition to the bridging diphosphanes, which exceeds that of the analogous binuclear Au^I dcpm complexes.^[17] However, the steric hindrance of dcpm appears to limit the number of additional ligands to a single one per Cu^I center, so a close metal–metal contact can be maintained, albeit with trigonally coordinated geometry at each Cu^I center (Figure 1). Indeed, the ^{31}P NMR spectroscopy data in CD_2Cl_2 solution clearly indicate a Cu^I -anion interaction in that the chemical shifts depend on the

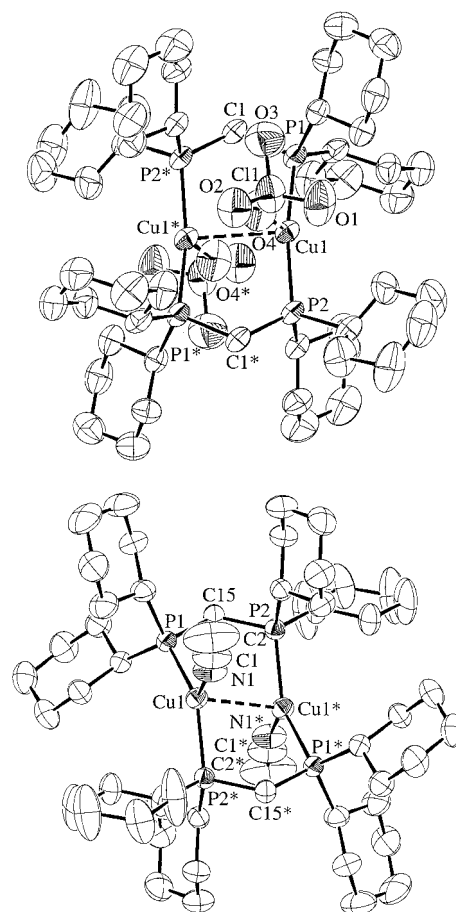


Figure 1. ORTEP plots of a) **1** and b) **4**; thermal ellipsoids set at the 40% probability level. Selected distances [Å] and angles [°] for one independent molecule of **1**: $\text{Cu1} \cdots \text{Cu1}^*$ 2.731(2), $\text{Cu1} \cdots \text{O4}$ 2.558(6), $\text{Cu1}-\text{P1}$ 2.228(2), $\text{Cu1}-\text{P2}$ 2.229(2); $\text{P1}-\text{Cu1}-\text{P2}$ 162.48(8), $\text{P1}-\text{Cu1}-\text{P2}^*$ 113.5(3); for **4**: $\text{Cu1} \cdots \text{Cu1}^*$ 2.8096(9), $\text{Cu1}-\text{N1}$ 2.029(4), $\text{Cu1}-\text{P1}$ 2.248(1), $\text{Cu1}-\text{P2}^*$ 2.249(1); $\text{P1}-\text{Cu1}-\text{P2}^*$ 143.86(4), $\text{P1}-\text{Cu1}-\text{N1}$ 108.8(1), $\text{P2}^*-\text{Cu1}-\text{N1}$ 105.7(1), $\text{N1}-\text{C1}-\text{C2}$ 176.4(9), $\text{P1}-\text{C15}-\text{P2}$ 111.5(2).

anion: $\delta = 15.9$ for **1** and **4**; $\delta = 18.4$ for **2** and **5**; $\delta = 4.5$ for **3**. In contrast, **1**, **2**, **4**, and **5** have identical ^{31}P chemical shifts in CD_3CN , ($\delta = 9.8$ – 9.9), which indicate anion displacement by the solvent.

Spectroscopic and photophysical data are summarized in Table 1. In dichloromethane solution, the UV/Vis spectra of complexes **1** and **2** show intense absorption at 311 and 307 nm respectively, with extinction coefficients greater than $10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ similar to the assigned $^1(d_{\sigma}^* \rightarrow p_{\sigma})$ transitions of $[\text{Au}_2(\text{dcpm})_2]^{2+}$ ^[17] and $[\text{Au}_2(\text{dmpm})_3]^{2+}$ ^[18] (dmpm = bis(dimethylphosphanyl)methane). As mononuclear Cu^I phosphane complexes such as **6** do not have any significant absorption at wavelengths greater than 280 nm, we assign this absorption at 311 or 307 nm to a metal–metal $3d \rightarrow 4p$ transition. This is strongly supported by resonance Raman spectroscopy. Figure 2 shows the resonance Raman spectrum obtained with 299.1 nm excitation and the absorption spectrum of complex **1** in dichloromethane. As with $[\text{Au}_2(\text{dcpm})_2]^{2+}$, Raman intensity appears only in a single low-frequency mode and its overtone, which we assign to the Cu^I-Cu^I stretch; this reveals that the excited-state distortion is concentrated in the Cu–Cu bond. The assigned $\tilde{\nu}(\text{Cu}_2)$ of

Table 1. Spectroscopic and photophysical properties of complexes **1**–**6**.

Complex	Medium (<i>T</i> [K])	λ_{abs} [nm] (ϵ [dm ³ mol ⁻¹ cm ⁻¹])	λ_{em} [nm]/ τ [μ s] ^[a]	ϕ_{em}
[Cu ₂ (μ -dcpm) ₂](ClO ₄) ₂ (1)	CH ₃ CN (298)	269 (4830), 319 (4820)	480/4.2	0.048
	CH ₂ Cl ₂ (298) ^[c]	278 (5840), 311 (14090)	~480 (w, br)	< 10 ⁻⁴
	glass (77) ^[b]		420	
	solid (298)		475/44	
[Cu ₂ (μ -dcpm) ₂](PF ₆) ₂ (2)	CH ₃ CN (298)	269 (4850), 319 (4830)	480/4.2	0.045
	CH ₂ Cl ₂ (298) ^[c]	307 (16660)	~440 (w, br)	< 10 ⁻⁴
	glass (77) ^[b]		417/29	
	solid (298)		475/63 ^[d]	
[Cu ₂ (μ -dcpm) ₂]I ₂ (3)	CH ₂ Cl ₂ (298)	280 (7410), 323 (3450)	485/2.4	5.7 × 10 ⁻⁴
	glass (77) ^[b]		456/17	
	solid (298)		460/8.3	
			480/4.4	
[Cu ₂ (μ -dcpm) ₂ (CH ₃ CN) ₂](ClO ₄) ₂ (4)	CH ₃ CN (298)	269 (4880), 319 (4850)	480/4.4	0.046
	CH ₂ Cl ₂ (298) ^[c]	278 (5590), 311 (13510)	~480 (w, br)	< 10 ⁻⁴
	glass (77) ^[b]		420/43	
	solid (298)		418/1.9	
[Cu ₂ (μ -dcpm) ₂ (CH ₃ CN) ₂](PF ₆) ₂ (5)	CH ₃ CN (298)	269 (4890), 319 (4850)	480/4.4	0.044
	CH ₂ Cl ₂ (298) ^[c]	307 (16550)	~440 (w, br)	< 10 ⁻⁴
	glass (77) ^[b]		420	
	solid (298)		411/8.2	
[Cu(PCy ₃) ₂]ClO ₄ (6) ^[e]	CH ₃ CN (298)	210 (23400), 230 (sh) (12500), 272 (900)	nonemissive	
	CH ₂ Cl ₂ (298) ^[c]	238 (11500), 248 (9700), 275 (sh) (270)	nonemissive	
	glass (77) ^[b]		416/182	
	solid (298)		491 ^[f]	

[a] For emission spectra measurements excitation wavelength: 330 nm; for luminescence lifetime measurements excitation wavelength: 355 nm. [b] Solvent: EtOH/MeOH (1/4). [c] In dilute CH₂Cl₂ solution slow decomposition occurred. [d] A weak emission maxima at 380 nm was also observed. [e] For emission spectra measurements excitation wavelength: 280 nm; for luminescence lifetime measurements excitation wavelength: 266 nm. [f] Biexponential decay, τ_1 : 3.2 μ s; τ_2 : 14.3 μ s.

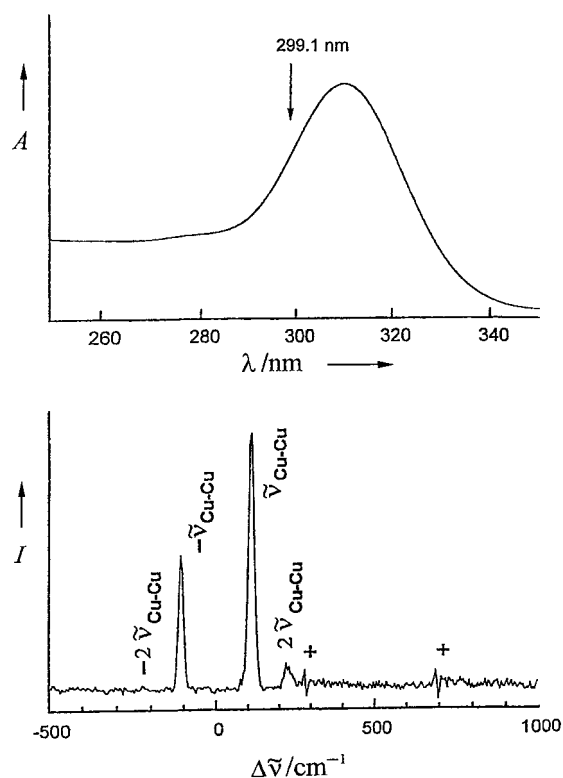


Figure 2. UV/Vis absorption spectrum of **1** (top) and resonance Raman spectrum (bottom) of **1** with excitation at 299.1 nm in dichloromethane (solvent subtraction artifacts marked by +).

104 cm⁻¹ can be compared to a $\tilde{\nu}(\text{Au}_2)$ of 88 cm⁻¹ for [Au₂(dcpm)₂]²⁺.^[7e] Clearly the [Cu^I]₂ bond must be much weaker than that of [Au^I]₂, since a simple mass calculation

predicts that the diatomic M₂ stretching frequency should be larger for Cu₂ than Au₂ by a factor of 1.76 for equivalent force constants. Using previously described calculation methods,^[7e] the excited state Cu–Cu stretching vibration is estimated to occur at 150 cm⁻¹, consistent with the electronic assignment of a transition to an excited state with increased metal–metal bonding. In acetonitrile, the binuclear Cu^I complexes show an absorption at 315–320 nm with a substantially lower extinction coefficient (Figure 3). We suggest that coordination of the acetonitrile solvent molecules to the Cu^I centers may greatly weaken the Cu^I...Cu^I interaction. The persistence of the weak absorption at 315–320 nm in CH₃CN solution may indicate equilibrium among complexes with differing numbers of bound acetonitrile molecules.

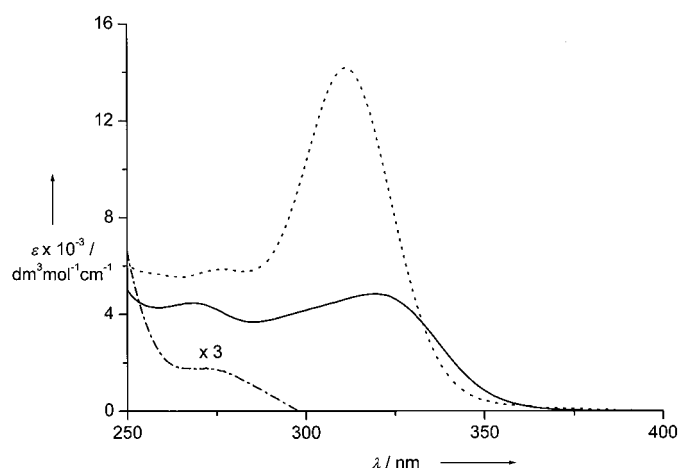


Figure 3. Electronic absorption spectra of **1** (---), **6** (-.-.-), and **4** (—) in acetonitrile at room temperature.

In the solid state, the binuclear Cu^I complexes show intense phosphorescence with emission maxima that are sensitive to the anion and solvent (Table 1). Remarkably, the change in the solid-state emission maxima is large, 411 to 475 nm (complexes **4** and **1** in Table 1), simply by coordination of CH_3CN to the $[\text{Cu}_2(\text{dcpm})_2]^{2+}$ core. Because the mononuclear Cu^I compound **6** shows an intense room-temperature solid-state emission at 491 nm, assignment of the lower-energy emission at 475–480 nm of the binuclear Cu^I complexes to a Cu–Cu bonded excited state is not favored. We suggest that increased interaction between neighboring solvent molecules or anions with Cu^I centers in the Cu–Cu bonded excited state in the crystal lattice may lower the energy of essentially single-center excited states and give rise to lower-energy photoluminescence. While the binuclear Cu^I complexes are weakly emissive in noncoordinating dichloromethane (quantum yield $< 10^{-4}$, broad emission at ~ 440 nm for compounds **2** and **5**, ~ 480 nm for **1** and **4**), they show an intense emission at around 480 nm in acetonitrile solution.

The Cu...Cu distances of the dinuclear Cu^I complexes described herein are comparable with those of most of the reported polynuclear Cu^I aggregates that show visible photoluminescence at wavelengths greater than 500 nm.^[3, 4] The large Stokes shift in emission energies suggests that metal–ligand influenced states may dominate the Cu^I luminescence, as has been concluded from recent studies of $\text{Au}^{II[17]}$ and $\text{Ag}^{II[19]}$ systems.

Experimental Section

Details of solvent purification for the photophysical studies, and resonance Raman measurements have been described elsewhere.^[20, 21] $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{X}$ ($\text{X} = \text{ClO}_4^-$ or PF_6^-) were prepared according to the published procedures.^[22] All reactions and manipulations were carried out under an argon atmosphere unless otherwise indicated.

$[\text{Cu}_2(\mu\text{-dcpm})_2]\text{X}_2$ ($\text{X} = \text{ClO}_4^-$ **1** or PF_6^- **2**): A mixture of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{X}$ and dcpm (1:1 molar ratio) in acetone (20 mL) was stirred for 1 h at room temperature. Upon removal of solvent and subsequent addition of diethyl ether, a white solid was obtained, which was recrystallized from CH_2Cl_2 /diethyl ether. For **1**, yield 89%. $^{31}\text{P}\{^1\text{H}\}$ NMR $\delta = 9.9$ (in CD_3CN), 15.9 (in CD_2Cl_2); FT-IR (Nujol, NaCl): $\tilde{\nu} = 1110.9(\text{s})$, $1033.8(\text{s}, \text{ClO}_4^-)$ cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{52}\text{O}_8\text{P}_4\text{Cl}_2\text{Cu}_2$: C 52.53, H 8.11; found C 52.59, H 8.26. For **2**, yield 86%; $^{31}\text{P}\{^1\text{H}\}$ NMR $\delta = 9.8$ (in CD_3CN), 18.4 (in CD_2Cl_2); FT-IR (Nujol, NaCl): $\tilde{\nu} = 821.6(\text{s})$, $844.8(\text{s}, \text{PF}_6^-)$ cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{50}\text{P}_6\text{F}_{12}\text{Cu}_2$: C 48.66, H 7.51; found: C 48.56, H 7.65.

$[\text{Cu}_2(\mu\text{-dcpm})_2]\text{I}_2$ **3**: A mixture of CuI and dcpm (1:1 molar ratio) in acetone (15 mL) was stirred for 2 h at room temperature. The white suspension was filtered and the solid recrystallized from CH_2Cl_2 /diethyl ether, yield 95%; $^{31}\text{P}\{^1\text{H}\}$ NMR $\delta = 4.5$ (in CD_2Cl_2); elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{52}\text{P}_4\text{I}_2\text{Cu}_2$: C 50.13, H 7.74; found: C 49.86, H 7.92.

$[\text{Cu}_2(\mu\text{-dcpm})_2(\text{CH}_3\text{CN})_2]\text{X}_2$ ($\text{X} = \text{ClO}_4^-$ **4** or PF_6^- **5**): Recrystallization of compound **1** or **2** in CH_3CN /diethyl ether gave **4** or **5**. Their structures were determined by X-ray crystallography. The coordinated CH_3CN molecule is easily lost upon prolonged exposure to air and satisfactory elemental analyses have not been obtained. For **4**: $^{31}\text{P}\{^1\text{H}\}$ NMR $\delta = 9.8$ (in CD_3CN), 15.9 (in CD_2Cl_2), FT-IR (Nujol, NaCl): $\tilde{\nu} = 2304.8(\text{w})$, $2268.1(\text{m}, \text{C}\equiv\text{N})$, $1093.6(\text{vs})$, $1039.6(\text{s}, \text{ClO}_4^-)$ cm^{-1} . For **5**: $^{31}\text{P}\{^1\text{H}\}$ NMR $\delta = 9.9$ (in CD_3CN), 18.4 (in CD_2Cl_2); FT-IR (Nujol, NaCl): $\tilde{\nu} = 2310.6(\text{w})$, $2268.1(\text{m}, \text{C}\equiv\text{N})$, $837(\text{vs}, \text{PF}_6^-)$ cm^{-1} .

$[\text{Cu}(\text{PCy}_3)_2]\text{ClO}_4$ **6**: A mixture of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ and PCy_3 (1:2 molar ratio) in acetone (15 mL) was stirred for 2 h at room temperature. The solvent was removed and the white solid was recrystallized from CH_2Cl_2 /diethyl ether, yield 43%; FAB-MS (+ve, m/z): $624[M^+ - \text{ClO}_4]$; $^{31}\text{P}\{^1\text{H}\}$

NMR $\delta = 18.2$ (in CDCl_3); elemental analysis calcd (%) for $\text{C}_{36}\text{H}_{66}\text{P}_2\text{ClO}_4$ –Cu: C 59.74, H 9.19; found: C 60.12, H 9.28.

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- Crystal data for **1**: $\text{C}_{30}\text{H}_{52}\text{P}_4\text{Cl}_2\text{Cu}_2 \cdot 2\text{ClO}_4$, formula weight = 1143.17, monoclinic, space group $P2_1/a$ (No. 14), $a = 17.591(5)$, $b = 14.553(3)$, $c = 23.174(6)$ Å, $\beta = 106.69(2)^\circ$, $V = 5682(2)$ Å³, $Z = 4$, $D_c = 1.336$ g cm^{−3}, $F(000) = 2432$, $T = 301$ K, 595 parameters; $R_1 = 0.062$, $R_w = 0.089$, GOF = 2.78 for 5115 data ($I > 3\sigma(I)$), max./min. residual electron density $1.10/-1.15$ e Å^{−3}. Diffractometer: Rigaku AFC7R; $\mu(\text{MoK}\alpha) = 10.03$ cm^{−1}; one crystallographic asymmetric unit comprises two independent halves of the complex cation and two perchlorate anions; Crystal data for **4**: $\text{C}_{36}\text{H}_{66}\text{N}_2\text{P}_4\text{Cu}_2 \cdot 2\text{ClO}_4$, formula weight = 1225.27, orthorhombic, space group $Pbca$ (No. 61), $a = 15.295(3)$, $b = 20.000(3)$, $c = 20.419(3)$ Å, $V = 6246(1)$ Å³, $Z = 4$, $D_c = 1.303$ g cm^{−3}, $F(000) = 2608$, $T = 301$ K, 317 parameters; $R_1 = 0.067$, $R_w = 0.095$, GOF = 2.98 for 4855 data ($I > 3\sigma(I)$), max./min. residual electron density $1.09/-1.01$ e Å^{−3}. MAR diffractometer; $\mu(\text{MoK}\alpha) = 9.18$ cm^{−1}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142369 **1**, -142370 **2**, -142371 **3**, -142609 **4**, -142372 **5**, -142373 **6**. Copies of the data can be obtained free of charge on

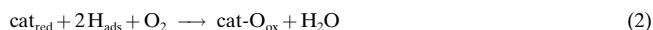
application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Low-Temperature Activation of Dioxygen and Hydrocarbon Oxidation Catalyzed by a Phosphovanadomolybdate: Evidence for a Mars–van Krevelen Type Mechanism in a Homogeneous Liquid Phase**

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Aerobic heterogeneous catalytic oxygenation of hydrocarbons with transition metal oxides often proceeds by a Mars–van Krevelen (M-vK) type mechanism [Eqs. (1) and (2)].^[1]



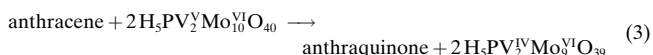
This mechanism involves activation of the C–H bond and transfer of lattice oxygen from the oxide to yield the product and the reduced catalyst. Re-oxidation of the catalyst by dioxygen and formation of water then follows. Heterogenization of homogeneous catalysis seeks to combine the selectivity and mild conditions typical of homogeneous catalysis with the handling advantages inherent in heterogeneous catalysis.^[2] Here, we consider the application of the inverse concept, that is, homogenization of heterogeneous catalysis, to M-vK type oxygenations. Since archetypal M-vK oxygenation reactions can both activate C–H bonds in hydrocarbons and utilize dioxygen as a terminal oxidant, such catalysis in

homogeneous media could lead to viable, selective low-temperature aerobic oxidation of hydrocarbons.

Polyoxometalates (POMs)^[3] are discrete, anionic and soluble (mixed) metal oxides. They have the potential to activate dioxygen^[4] and to function as oxidation catalysts.^[5] Oxygen transfer in the liquid phase has been demonstrated using chromium(v)-oxo-containing POMs^[6] and activation of a C–H bond has been observed using phosphovanadomolybdates.^[7] Thus, hydrocarbons such as cyclic dienes are oxydehydrogenated but to our knowledge there are no reports of combined hydrocarbon activation, oxygen transfer, and dioxygen activation through a M-vK type mechanism in homogeneous media.^[8]

We now report that the phosphovanadomolybdate $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ can activate both aromatic and benzylic C–H bonds in hydrocarbons, for example, anthracene and xanthene, in homogeneous liquid phases by electron transfer. Subsequent oxygen transfer from the POM leads to the formation of the quinone/ketone. The reaction occurs by a M-vK type mechanism.

Hydrocarbons (60 mM) and $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40} \cdot 34\text{H}_2\text{O}$ ^[9] (1 mM) were treated with one atmosphere of O_2 in CH_3CN at 60 °C for 18 h. Analysis of the reaction mixtures showed that selective oxidation (> 99 %) of anthracene to anthraquinone, xanthene to xanthone, fluorene to fluorenone, and diphenylmethane to benzophenone occurred with turnover numbers of 24, 30, 13, and 1, respectively. Initial strong support for a M-vK type mechanism, namely, that the source of the oxygen in the product was from the POM lattice and not from atmospheric O_2 , was obtained by a classic $^{18}\text{O}_2$ -labeling experiment. In the oxidation of anthracene or xanthene (20 mM) catalyzed by $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40} \cdot 34\text{H}_2\text{O}$ (1 mM) in CH_3CN under $^{18}\text{O}_2$ (1 atm, 96.1 % purity) at 60 °C, the amount of ^{18}O found in the product by GC-MS increased as the reaction progressed. Incorporation of ^{18}O was 0, 14.8, and 22.5 mol % after 1, 5.4, and 10.2 turnovers for anthraquinone and 0, 12.3, and 19.6 mol % after 1, 4.9, and 11.4 turnovers for xanthone. Full incorporation of ^{18}O is expected from the outset for autooxidation since the initial radical formed will always react with $^{18}\text{O}_2$. Second, a reaction (60 °C, 24 h) of equimolar amounts of anthracene or xanthene and $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ under Ar in an NMR tube also yielded 48 % of anthraquinone and 71 % of xanthone, as evidenced by ^1H NMR spectroscopy. Since each POM molecule can be formally considered as a three-electron oxidant [Eqs. (3) and (4)], the maximum conversions into anthraquinone and xanthone are 50 and 75 %, respectively.



Third, similar anaerobic reactions of equimolar amounts of anthracene and $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ enriched with ^{17}O or ^{18}O yielded labeled anthraquinone as measured by ^{17}O NMR spectroscopy ($\delta = 515$) and GC-MS (^{18}O), respectively. An approximately 75 % ^{18}O -enriched $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ yielded

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