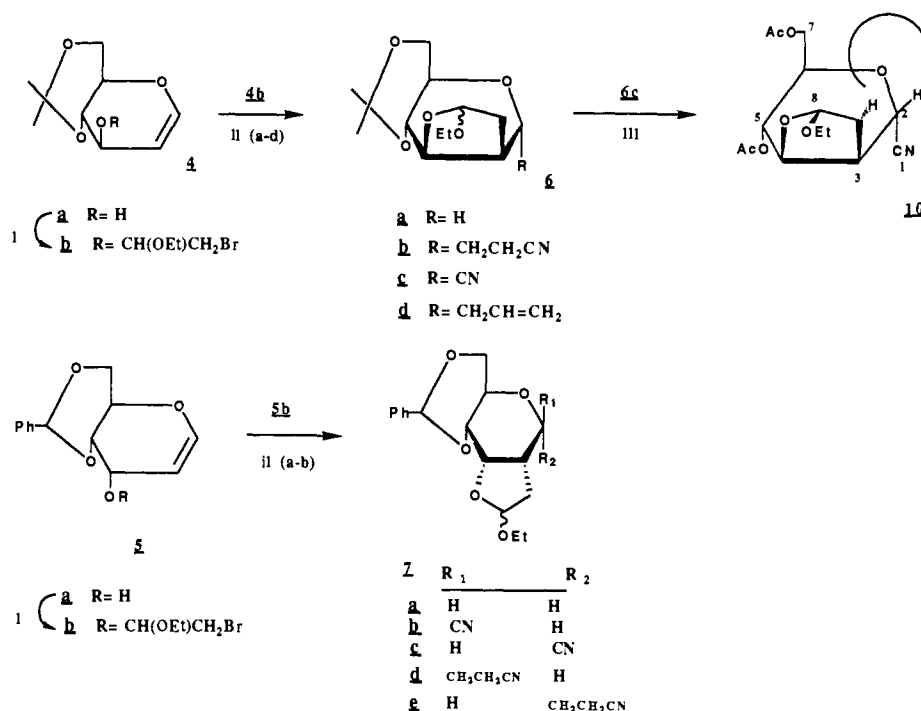
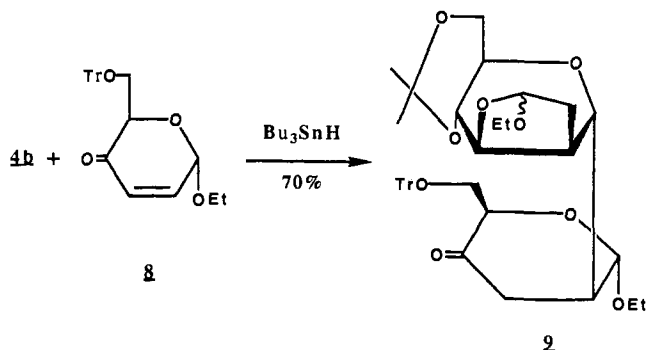


Scheme II^a

^a (i) Ethyl vinyl ether (9 equiv), bromine (6 equiv), methylene chloride, -78 °C 30 min → room temperature 1 h; then **4** in NEt₃ 0 °C room temperature 3 h; [(ii) (a-c) Bu₃SnH (1.1 equiv), AIBN (catalyst), syringe pump addition 4 h over **4b** (0.01–0.005 M), benzene, 80 °C; (b) acrylonitrile (10 equiv); (c) *t*-BuNC (20 equiv); (d) allyltri-*n*-butyltin (2 equiv), AIBN (0.2 equiv), benzene (0.5 M), 80 °C]; (iii) AcOH/H₂O (8:2), room temperature 4 h; Ac₂O, pyridine room temperature overnight.

Scheme III



The configurations at the anomeric center in compounds **6b–d** and **9** were expected to be α , and this was supported by the range of values for $J_{1,2} = 1.5\text{--}3.9$ Hz for these compounds. This assignment was further verified, as indicated in Scheme II. Although the C8 epimers of **6c** could not be separated chromatographically, hydrolysis and acetylation afforded **10**, which was isolated as a pure diastereomer. An NOE effect between H2 and H9 endo confirmed the α orientation at anomeric center.

Reactions of **5b** were expected to be less stereocontrolled because steric effects favor the trans product with β anomeric orientation, whereas the radical anomeric effect favors α orientation. Indeed, products from the trapping experiments gave the anomeric mixtures of **7b/7c** and **7d/7e** in 5:1 and 3:1 ratios, respectively. In the case of the former pair, the reduced material **7a** was obtained in equal amounts as the nitriles **7b/7c**. The assignment of the β anomers as the major products was made readily on the basis of their ¹H NMR spectra.

Note Added in Proof. Since submission of this manuscript, three radical cyclizations involving carbohydrates have appeared:

(29) For the first example of intramolecular radical addition to an enol ether see: Ladlow, M.; Pattenden, G. *Tetrahedron Lett.* **1984**, 25, 4317.

DeMesmaeker, A.; Hoffmann, P.; Ernst, B. *Tetrahedron Lett.* **1988**, 29, 6585. DeMesmaeker, A.; Hoffmann, P.; Ernst, B. *Tetrahedron Lett.* **1989**, 30, 57. Chapleur, Y.; Moufid, N. *J. Chem. Soc., Chem. Commun.* **1989**, 39.

Supplementary Material Available: Preparation and spectral data (¹H NMR and ¹³C NMR) for **4b,d**, **6a–d**, **12**, **9**, **5b**, and **7a–e** (12 pages). Ordering information is given on any current masthead page.

The First d–d Fluorescence of a Six-Coordinate Copper(II) Ion

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The structural diversity and relatively simple electronic structure have made copper(II) complexes a spectroscopic favorite.¹ However, metal-centered (d–d) emission of copper(II) complexes has only been observed in tetrahedral sites (in ZnS and CdS type semiconductors²). The improbability of observable emission in six-coordinate copper(II) complexes can be rationalized by the existence of a low-lying excited state, arising from the Jahn–Teller split component of the (octahedral) ²T_g(E_g) state which will be strongly coupled with the ground state, providing an efficient pathway for radiationless relaxation. Notwithstanding this argument, we report the unambiguous structured fluorescence for copper(II)-doped KZnF₃ and K₂ZnF₄ crystals.

(1) Lever, A. B. P. *Inorganic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.

(2) Maier, H.; Scherz, U. *Phys. Stat. Solidi B* **1974**, 62, 153–164.

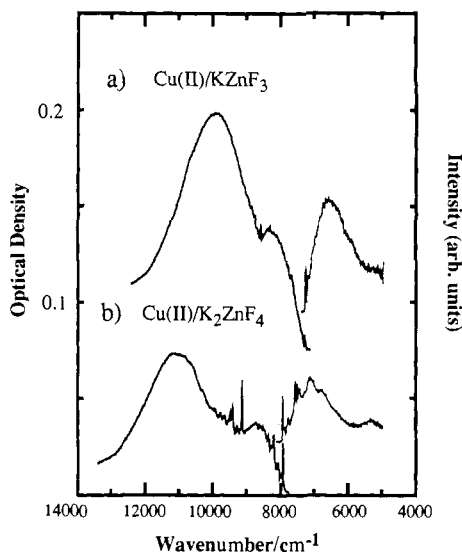


Figure 1. The absorption and fluorescence spectra of (a) $\text{Cu}^{\text{II}}/\text{KZnF}_3$ and (b) $\text{Cu}^{\text{II}}/\text{K}_2\text{ZnF}_4$. The absorption spectrum in b is in α polarization. The left- and right-hand y -axes refer to the absorption and fluorescence, respectively.

The host lattices have been well characterized.³ KZnF_3 has corner-sharing ZnF_6^{4-} octahedra, while K_2ZnF_4 has layers of corner-sharing octahedra with axial coordination by nonbridging fluoride ions. The metal site symmetry is O_h and D_{4h} , respectively. At low doping concentrations, it is known from EPR studies^{4,5} that the guest copper ions occupy these sites. In a cubic site, a copper(II) complex with six identical ligands will undergo a Jahn-Teller distortion removing the electronic degeneracy of the ground state. At low temperatures (~ 5 K) the EPR spectrum of $\text{Cu}^{\text{II}}/\text{KZnF}_3$ is characteristic of the electronic hole of the copper(II) d^9 configuration in a $d_{x^2-y^2}$ orbital, implying an elongated geometry.⁴ This is due to the trapping of the complex is one of the three equivalent minima in the Q_θ - Q_ϵ space of the Jahn-Teller active e_g vibrational coordinate that correspond to the three possible orientations of the elongated axis. The trapping is caused by random crystal strains. At slightly higher temperature (~ 20 K) we have observed that the EPR spectrum becomes isotropic, indicating rapid exchange between the vibronic levels based in each of the minima and implying a rather low energy barrier for interconversion. In the K_2ZnF_4 host, however, EPR studies⁵ reveal a copper(II) complex with a ground electronic state characteristic of an electron hole in the d_{z^2} orbital, indicating a tetragonally compressed geometry. Since the axial and equatorial Zn-F bond lengths are equal within experimental error³ it has been inferred⁵ that the nonbridging axial fluorides are stronger bonding ligands causing the copper ion to adopt an octahedrally *compressed* rather than the (preferred) elongated geometry.

The low-temperature single-crystal absorption and fluorescence spectra of the two doped systems are shown in Figure 1. The absorption spectra were recorded on a Cary 17 spectrometer with the samples cooled to 5 K in a helium flowtube. The fluorescence spectra were obtained with pulsed 1060-nm excitation from a Nd/YAG laser with the samples immersed in liquid helium. A double monochromator and cooled InSb diode was used for detection. The emission spectra were corrected for system response.

Figure 1 gives a rare example in the electronic spectroscopy of copper(II) complexes of sharp electronic origins as well as considerable vibrational structure. The lowest (zero phonon) lines observed are coincident in absorption and emission and thus are magnetic dipole in nature. Assignments of these spectra as transitions between the ligand field states of the CuF_6^{4-} complex are given in Table I. These assignments arise from a detailed

Table I. Electronic Assignments of $\text{Cu}^{\text{II}}/\text{KZnF}_3$ and $\text{Cu}^{\text{II}}/\text{K}_2\text{ZnF}_4$

absorption ^a	energy ^b /cm ⁻¹	emission	energy/cm ⁻¹
KZnF₃			
$\Gamma_8(E_g) \rightarrow \Gamma_7(T_{2g})$	6829 (7600)	$\Gamma_7(T_{2g}) \rightarrow \Gamma_8(E_g)$	6830 (6150)
$\rightarrow \Gamma_8(T_{2g})$	8129 (9500)		
K₂ZnF₄			
$\Gamma_6(A_{1g}) \rightarrow \Gamma_7(E_g)$	7497 (8250)	$\Gamma_7(E_g) \rightarrow \Gamma_6(A_{1g})$	7498 (6680)
$\rightarrow \Gamma_6(E_g)$	8704 (9300)	$\rightarrow \Gamma_7(B_{1g})$	(<5000)
$\rightarrow \Gamma_7(B_{2g})$	(10700)		

^a The spin-orbit electronic states are all Kramers doublets labeled by their irreducible representations in the O_h (for KZnF_3) and D_{4h} (for K_2ZnF_4) double point groups in Bethe's notation. The corresponding orbital bases are given in parentheses. ^b The energies given are those of the magnetic dipole origins, with the Franck-Condon maxima in brackets. The uncertainty of the peak positions is ± 2 cm⁻¹ for the origins and ± 50 cm⁻¹ for the Franck-Condon maxima.

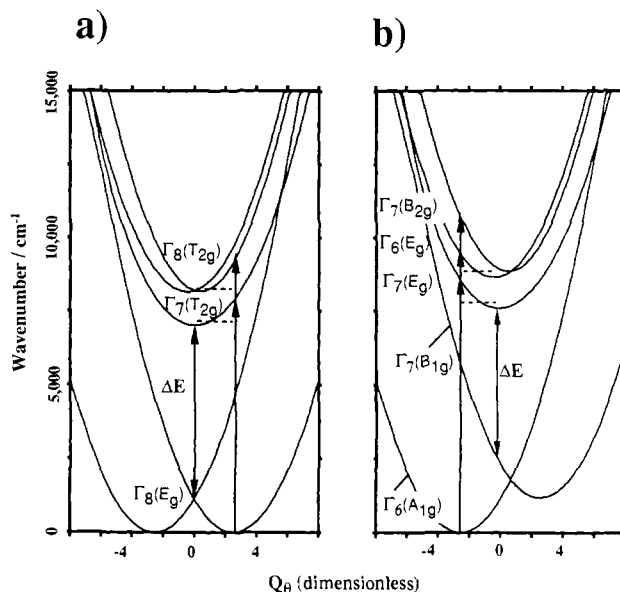


Figure 2. Schematic potential surfaces of six-coordinated copper(II) in (a) a cubic and (b) a tetragonally compressed octahedral environment as a function of the tetragonal component of the Jahn-Teller e_g vibration. The cubic symmetry labels in part a are only appropriate for $Q_\theta = 0$. The energy gap ΔE is thought to be an important quantity in determining the rate of radiationless relaxation from the emitting state. This gap becomes smaller for larger tetragonal fields imposed by the host lattice. The Franck-Condon maxima in absorption are indicated by upward arrows and the position of the origins by horizontal dashed lines.

study of the linear and magnetic circular dichroism.⁶

The d-d emission spectra shown in Figure 1 appear to be the first reported for six-coordinate copper(II) complexes and they immediately raise a number of intriguing questions. First, the lower energy d-d transition between the Jahn-Teller split e_g -($d_{x^2-y^2}, d_{z^2}$) orbitals has not been observed in either of these dilute systems. The fact that these compounds fluoresce would at first seem to imply that this state must lie to higher energy than the emitting state. However, simple ligand field calculations show that for all reasonable parameters appropriate to these systems, the spin-orbit coupling quenches the T_{2g} Jahn-Teller coupling in the T_{2g} manifold, so that the minima of the emitting state has approximate octahedral symmetry. As shown schematically in Figure 2, the absent electronic state (the upper branch of the $\Gamma_8(E_g)$ state in octahedral or the $\Gamma_7(B_{1g})$ state in tetragonal symmetry) must be at *lower* energy at the *relaxed* excited state geometry at which the emission occurs, regardless of where the transition occurs in absorption. Since the observed emission is then not from the lowest excited state, there must exist a significant energy gap, ΔE , shown in Figure 2.

The energy gap is expected to be *larger* in a cubic complex and to decrease with increasing "tetragonal strain" of a host. Ex-

(3) Herdtweck, E.; Babel, D. *Z. Kristallogr.* **1980**, *153*, 189-199.

(4) Friebel, C.; Reinen, D. *Z. Anorg. Allg. Chem.* **1974**, *407*, 193-200.

(5) (a) Reinen, D.; Krause, S. *Inorg. Chem.* **1981**, *20*, 2750-2759. (b) Riley, M. J.; Hitchman, M. A.; Reinen, D. *Chem. Phys.* **1986**, *102*, 11-28.

(6) Riley, M. J.; Dubicki, L.; Moran, G.; Krausz, E. R.; Yamada, I. In preparation.

perimentally, the $\text{Cu}^{\text{II}}/\text{K}_2\text{ZnF}_4$ system has a shorter lifetime (0.5 μs) and evidently less efficient emission than the cubic system (1.8 μs) while the related $\text{Cu}^{\text{II}}/\text{Ba}_2\text{ZnF}_6$ system, where the copper(II) is at a site of stronger tetragonal compression, showed no observable d-d emission. The ability of a six-coordinate copper(II) complex to fluoresce would seem to depend on a large (cubic) ligand field splitting at a site of near cubic symmetry as well as the absence of high energy accepting modes that act as a relaxation pathway.

Acknowledgment. We thank Dr. Hans Riesen for his assistance with some of the experiments.

Palladium-Catalyzed Cascade Carbometalation of Alkynes and Alkenes as an Efficient Route to Cyclic and Polycyclic Structures¹

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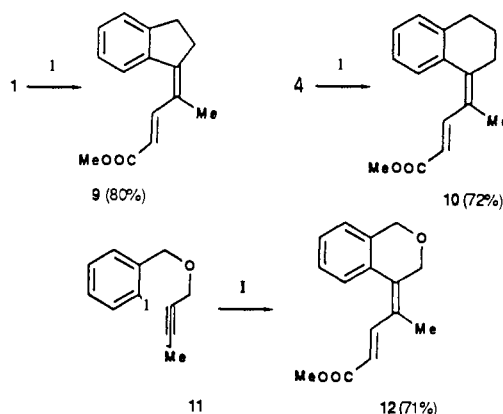
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The Pd-catalyzed arylation and alkenylation of alkenes (the Heck reaction) have been widely used intermolecularly,² and their intramolecular versions are rapidly growing into a major new tool for the synthesis of heterocycles^{2,3} and carbocycles.⁴ On the other hand, the corresponding reaction of alkynes have not been extensively investigated.⁵⁻⁸ Whereas alkene carbopalladation can be readily followed by dehydropalladation for recycling Pd complexes as catalysts, alkyne carbopalladation generally produces thermally stable alkenylpalladium species in a stoichiometric manner, requiring further transformations for recycling Pd complexes.

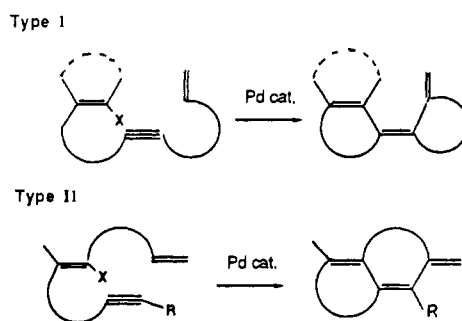
Our efforts to trap the alkenylpalladium species by carbonylation were only partially successful due to competitive carbonylation before carbopalladation. Thus, treatment of **1** with CO (600 psi), NEt_3 (1.5 equiv), MeOH (4 equiv), and 3 mol % of

Scheme I^a

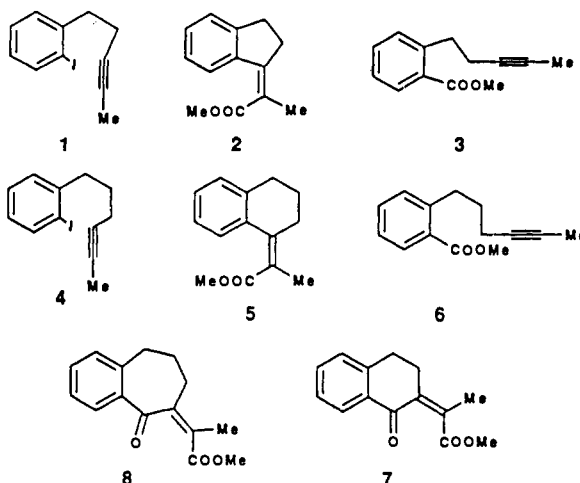


^a **1** = $\text{CH}_2=\text{CHCOOMe}$ (1 equiv), NEt_3 (2 equiv), 3 mol % Pd(PPh_3)₄, MeCN reflux, 12 h.

Scheme II



Pd(PPh_3)₄ in MeCN at 100 °C⁹ gave a 60:40 mixture of **2** and **3** in 70% combined yield, while the reaction of **4** produced a 30:70 mixture of **5** and **6** in 60% combined yield. In neither case was the third expected product **7** or **8**⁹ obtained. The formation of **2** and **5** was >95% stereoselective.



In view of the above results, we were pleased to find that treatment of **1** and **4** with methyl acrylate (1 equiv) in refluxing MeCN for 12 h in the presence of 3 mol % Pd(PPh_3)₄ and NEt_3 (2 equiv) afforded **9** and **10** in 80 and 72% yields, respectively, without contamination by the noncyclized cinnamate esters. The stereoisomeric purities of **9** and **10** were >98 and >95%, respectively. Similarly **11** gave >98% pure **12** in 71% yield. Prolonged reaction times must be avoided, since they led to lower stereoselectivity figures. Throughout this investigation, the ste-

(1) Metal-Promoted Cyclization. 25. Part 24: Negishi, E.; Iyer, S.; Rousset, C. *J. Tetrahedron Lett.* **1989**, *30*, 291. The results herein described were presented at the 196th American Chemical Society Meeting, Los Angeles, CA, September 25-30, 1988; ORGN 264.

(2) (a) Heck, R. F. *Org. React.* **1982**, *27*, 345. (b) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: New York, 1985.

(3) For recent papers not cited in ref 2b, see: (a) Kasahara, A.; Izumi, T.; Murakami, S.; Yanai, H.; Takatori, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 927. (b) Grigg, R.; Sridharan, V.; Stevenson, P.; Worakun, J. *J. Chem. Soc., Chem. Commun.* **1986**, 1697. (c) Abelman, M. M.; Oh, T.; Overman, L. E. *J. Org. Chem.* **1987**, *52*, 4133. (d) Larock, R. C.; Babu, S. *Tetrahedron Lett.* **1987**, *28*, 5291. (e) Burns, B.; Grigg, R.; Ratananukul, P.; Sridharan, V.; Stevenson, P.; Worakun, T. *Tetrahedron Lett.* **1988**, *29*, 4329. (f) Negishi, E.; Nguyen, T.; O'Connor, B.; Evans, J. M.; Silveira, A., Jr. *Heterocycles* **1989**, 0000.

(4) (a) Narula, C. K.; Mak, K. T.; Heck, R. F. *J. Org. Chem.* **1983**, *48*, 2792. (b) Grigg, R.; Stevenson, P.; Worakun, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1073; *Tetrahedron* **1988**, *44*, 2033. (c) Tour, J. M.; Negishi, E. *J. Am. Chem. Soc.* **1985**, *107*, 8289. (d) Negishi, E.; Zhang, Y.; O'Connor, B. *Tetrahedron Lett.* **1988**, *29*, 2915. (e) Larock, R. C.; Song, H.; Baker, B. E.; Gong, W. H. *Tetrahedron Lett.* **1988**, *29*, 2919. (f) O'Connor, B.; Zhang, Y.; Negishi, E.; Luo, F. T.; Chen, J. W. *Tetrahedron Lett.* **1988**, *29*, 3903. (g) Zhang, Y.; O'Connor, B.; Negishi, E. *J. Org. Chem.* **1988**, *53*, 5588. (5) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971; Vol. II.

(6) For arene-forming reactions similar to those described in ref 5 that are mostly stoichiometric in Pd, see: Wu, G.; Geib, S. J.; Rheingold, A. L.; Heck, R. F. *J. Org. Chem.* **1988**, *53*, 3238 and earlier references cited therein.

(7) For catalytic carbopalladation of alkynes followed by hydrogenolysis, see: (a) Arcadi, A.; Cacchi, S.; Marinelli, F. *Tetrahedron* **1985**, *41*, 5121. (b) Burns, B.; Grigg, R.; Sridharan, V.; Worakun, T. *Tetrahedron Lett.* **1988**, *29*, 4325.

(8) After completion of this study, a paper describing a cascade carbopalladation involving enynes in a different context was published [Trost, B. M.; Lee, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 7255].

(9) Tour, J. M.; Negishi, E. *J. Am. Chem. Soc.* **1985**, *107*, 8289.