3. The same quantities of 1 and **2a** and benzene were used as in the two previous cases; however, **2a** was washed with a 50% solution of K_2CO_3, and then dried ($MgSO_4$) and distilled under reduced pressure at 38 °C (1 torr). The reaction mixture was held at reflux for 84 h in a closed system with a reflux condenser in the absence of a Dean–Stark trap. The condenser was closed with an oil bubbler. After 84 h TLC did not show any appreciable amount of the cyclized product **5a**. Evaporation of benzene to dryness gave a quantitative recovery of **4a**.

4. The reaction sequence termed 3 above was repeated by employing a Dean–Stark trap but under a nitrogen (Ameri-Gas, 99%) atmosphere. After the reaction was held for 12 h in refluxing benzene, no trace of **5a** was observed (compare 50% in experiment 1), and after 48 h only 10% of **5a** had been formed.

5. The reaction sequence termed 1 above was carried out in the presence of 1.5 g (0.01 mol) of DBU (1,8-diazabicyclo-[5.4.0]undec-5-ene) although **2a** was pretreated as indicated under 3. After 70 h no **5a** was detected. Although DBU is a strong enough base[9] to act as a proton scavenger and also abstract the proton from the α position of the ester, the Schiff base was observed in this sequence by TLC. The same reaction was repeated (reagents the same as above) with the addition of 0.7 g (0.01 mol) of imidazole. After the mixture was held for 50 h in refluxing benzene, the amount of the cyclized product **5a** was estimated to be 10–15%.

Registry No. 1, 7303-49-3; **2a**, 100-52-7; **2b**, 2043-61-0; **3a**, 90414-29-2; **3b**, 90414-30-5; **4a**, 19779-75-0; **4b**, 90414-31-6; *cis*-**5a**, 50302-60-8; *trans*-**5a**, 50302-61-9; *cis*-**5b**, 75140-08-8; *trans*-**5b**, 73327-06-7.

Supplementary Material Available: Experimental details for the work with 1 and cyclohexanecarboxaldehyde (**2b**) and additional experiments with **2a** (2 pages). Ordering information is given on any current masthead page.

Mercury in Organic Chemistry. 28. Synthesis of (π-Allyl)palladium Compounds by Remote Palladium Migration

Richard C. Larock* and Kentaro Takagi[1]

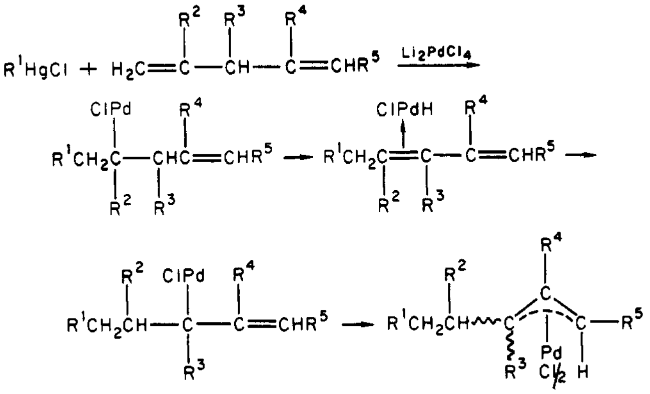
Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received November 28, 1983

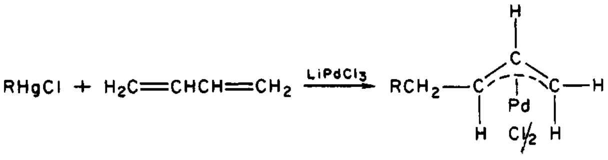
A variety of organomercurials react regioselectively with 1,4-, 1,5-, 1,6-, and 1,7-dienes and Li_2PdCl_4 to form good yields of (π-allyl)palladium compounds. These reactions apparently proceed by organopalladium addition to one of the diene double bonds and subsequent palladium migration.

(π-Allyl)palladium compounds were first prepared 25 years ago.[2] In the meantime, a number of procedures have been reported for their preparation,[3-6] the most important of which are the insertion of palladium(0) reagents into the carbon–halogen bond of allylic halides[7-11] and the direct allylic hydrogen substitution of alkenes by palladium salts.[12-17] The former method requires substrates difficult to prepare and handle, while the latter suffers from an inability to predict or control the regioselectivity of palladation.

Scheme I



The palladium-promoted addition of organomercurials to 1,3-dienes and alkenes has recently provided new routes to (π-allyl)palladium compounds. Thus, certain organomercurials react with $LiPdCl_3$ and 1,3-dienes to afford (π-allyl)palladium compounds (eq 1).[18,19] We have found



$$RHgCl + H_2C{=}CHCH{=}CH_2 \xrightarrow{LiPdCl_3} RCH_2CH\overset{\textstyle CH}{\cdots}CH_2\ (\mathrm{PdCl}_{1/2}) \quad (1)$$

R = CH_3, aryl, benzylic

that vinylmercurials readily react with Li_2PdCl_4 and simple

---

[1] Present address: College of Liberal Arts and Science, Okayama University, Tsushima, Okayama 700, Japan.

[2] Slade, P. E., Jr.; Jonassen, H. B. *J. Am. Chem. Soc.* **1957**, *79*, 1277.

[3] Volger, H. C. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 225 and literature cited therein.

[4] Hartley, F. R. *Chem. Rev.* **1969**, *69*, 799.

[5] Hüttel, R. *Synthesis* **1970**, 225.

[6] Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol. 1, Chapter 5.

[7] Dent, W. T.; Long, R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585.

[8] Sakakibara, M.; Takahashi, Y.; Sakai, S.; Ishii, Y. *J. Chem. Soc. D* **1969**, 396.

[9] Tsuji, J.; Iwamoto, N. *Chem. Commun.* **1966**, 828.

[10] Dent, W. T.; Long, R. British Patent 1082248, 1967; *Chem. Abstr.* **1968**, *68*, 114748.

[11] Larock, R. C.; Burkhart, J. P. *Synth. Commun.* **1979**, *9*, 659.

[12] Tsuji, J.; Imamura, S.; Kiji, J. *J. Am. Chem. Soc.* **1964**, *86*, 4491.

[13] Trost, B. M.; Strege, P. E. *Tetrahedron Lett.* **1974**, 2603.

[14] Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 630.

[15] Trost, B. M.; Strege, P. E. *J. Am. Chem. Soc.* **1975**, *97*, 2534.

[16] Trost, B. M.; Weber, L. *J. Am. Chem. Soc.* **1975**, *97*, 1611.

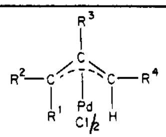
[17] Trost, B. M.; Metzner, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 3572.

[18] Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5542.

[19] Stakem, F. G.; Heck, R. F. *J. Org. Chem.* **1980**, *45*, 3584.

0022-3263/84/1949-2701$01.50/0

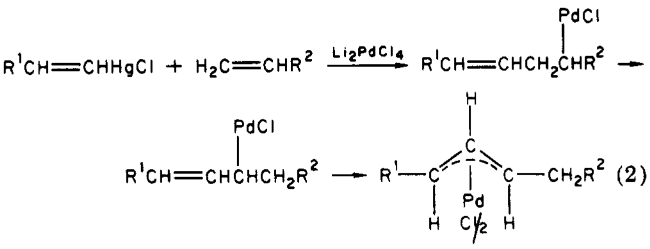
Table I. Synthesis of (π-Allyl)palladium Compounds



entry	organo-mercurial	diene	temp, °C	R^1	R^2	R^3	R^4	compd no.	% yield[a]
1	C_6H_5HgCl	$H_2C{=}CHCH_2CH{=}CH_2$	0 → 25	H	$C_6H_5(CH_2)_2$	H	H	**1**	100 (61)
2	CH_3O_2CHgCl		-10 → +25		$CH_3O_2C(CH_2)_2$			**2**	53 (30)
3	CH_3HgCl		0 → 40 (4 h)		$CH_3(CH_2)_2$			**3**	87 (44)
4	C_6H_5HgCl	*trans*-$H_2C{=}CHCH_2CH{=}CHCH_3$	0 → 25		$C_6H_5(CH_2)_2$		CH_3	**4**	91 (48)
5		$H_2C{=}CHCH_2C(CH_3){=}CH_2$				CH_3	H	**5**	100 (51)
6		$H_2C{=}CHCH(CH_3)CH{=}CH_2$		CH_3		H		**6**	~93[b]
7	CH_3CH_2HgCl	$H_2C{=}C(CH_3)CH_2C(CH_3){=}CH_2$		H	$(CH_3)_2CH$	CH_3		**7**	25 (17)[b]
8	CH_3O_2CHgCl	$H_2C{=}CH(CH_2)_2CH{=}CH_2$	-10 → +25		$CH_3O_2C(CH_2)_2$	H		**8**	43 (24)[c]
					$CH_3(CH_2)_2$			**3**	3[b]
9	C_6H_5HgCl		0 → 25		$C_6H_5(CH_2)_3$			**9**	~60 [~40][d]
					$CH_3(CH_2)_2$			**3**	~25 [~50][d]
10	CH_3CH_2HgCl		-78 → +25					**3**	55 (50)
11		$H_2C{=}CH(CH_2)_3CH{=}CH_2$	0 → 25		$CH_3(CH_2)_3$			**10**	61 (55)
12		$H_2C{=}CH(CH_2)_4CH{=}CH_2$					CH_3	**11**	69
					$CH_3(CH_2)_4$		H	**12**	23

[a] Isolated yield (recrystallized yield). [b] Syn/anti mixture (R^1 and R^2 reversed). [c] Plus 16% of compound **14**. [d] Reaction run with 10 equiv of diene; 42% *trans*-1-phenyl-1,5-hexadiene and isomers observed.

acyclic[20] or cyclic[21] alkenes to afford good to excellent yields of (π-allyl)palladium compounds apparently through a palladium hydride rearrangement (eq 2). With the great current interest in applications of (π-allyl)palladium compounds in organic synthesis,[22,23] we were interested in exploring whether this latter type of remote palladium migration could be extended to other systems, especially those in which the palladium was even further removed from the carbon–carbon double bond. During the course of our work, Heck has reported that the palladium-catalyzed arylation and vinylation of 1,4-dienes apparently proceeds by just such reactions to generate (π-allyl)palladium intermediates that under his conditions afford allylic amines and 1,3-dienes.[24] At this time we wish to report that organomercurials do indeed react with Li_2PdCl_4 and 1,4-, 1,5-, 1,6-, and 1,7-dienes to give good yields of (π-allyl)palladium compounds by remote palladium migration.



Results and Discussion

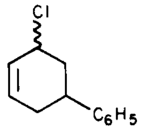
While our earlier work with vinylmercurials, Li_2PdCl_4, and simple olefins[20,21] (eq 2) clearly indicated that homoallylic palladium compounds could cleanly rearrange via palladium hydride elimination–readdition to afford (π-allyl)palladium compounds, we chose to prepare these same intermediates by a different pathway, namely, organopalladium additions to 1,4-,dienes, to see if (π-allyl)palladium compounds could also be generated in this manner (Scheme I). The results of these experiments are summarized in entries 1–7 in Table I. Good to excellent yields can indeed be obtained in this fashion.

Organopalladium additions to 1,4-dienes appear to be highly regioselective (entries 4 and 5), attack occurring on the least substituted double bond exclusively. In contrast to the recent results of Heck,[24] we do not see any products derived from the organic moiety adding to the internal carbon of the double bond. We are not certain if this is due to the lower temperatures involved in our work, the absence of phosphine or amine ligands, or the difference in the organopalladium precursors (organomercurials vs. organic halides).

The reaction of 3-methyl-1,4-pentadiene and phenylmercuric chloride (entry 6) was examined to establish if palladium is able to migrate to a branched carbon. Indeed, one obtains a high yield of an approximately 1:1 mixture of the expected syn and anti isomers **6**. Unfortunately, unknown impurities prevented these compounds from being obtained in pure form.

To determine if palladium can migrate past a branched carbon, the reaction of 2,4-dimethyl-1,4-pentadiene and ethylmercuric chloride was studied (entry 7). This reaction apparently proceeds by elimination of palladium hydride from the initially formed ethylpalladium species and subsequent addition to the diene. This approach to the generation of a palladium hydride has been used previously by Heck in his work on additions to 1,3-dienes.[19] The anticipated product is obtained in 25% yield as an approximately 3:2 mixture of the syn and anti isomers **7**, respectively. We attribute the low yield to the increased substitution about the double bonds of the diene.

The reaction of Li_2PdCl_4, phenylmercuric chloride, and 1,4-cyclohexadiene gave unexpected results. Rather than isolating the anticipated (π-allyl)palladium compound, the corresponding allylic chloride **13** (stereochemistry undetermined) was obtained instead. It is not clear why the intermediate organopalladium compound in this case is not stable.



13

---

(20) Larock, R. C.; Mitchell, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 180.

(21) Larock, R. C.; Takagi, K.; Hershberger, S. S.; Mitchell, M. A. *Tetrahedron Lett.* **1981**, 5231.

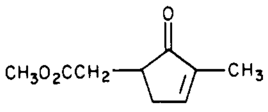
(22) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615.

(23) Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer-Verlag: New York, 1980.

(24) Bender, D. D.; Stakem, F. G.; Heck, R. F. *J. Org. Chem.* **1982**, *47*, 1278.

In conclusion, homoallylic palladium compounds generated by either vinylpalladium addition to alkenes[20,21] or by organopalladium addition to 1,4-dienes readily undergo palladium migration to form (π-allyl)palladium compounds.

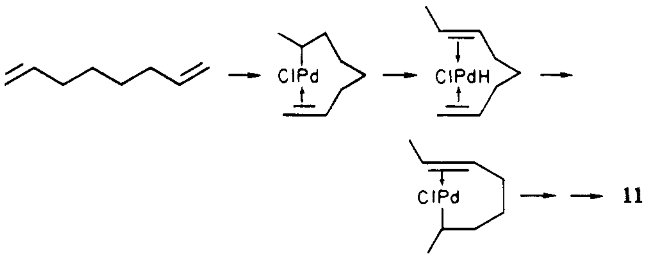
A greater challenge lies in the reaction of 1,5-dienes with organopalladium compounds, since the palladium moiety in this situation is required to migrate two carbon atoms prior to (π-allyl)palladium formation. Nevertheless, reasonably good yields of (π-allyl)palladium compounds are obtained from 1,5-hexadiene as illustrated by entries 8–10 in Table I. This unique approach to (π-allyl)palladium compound 8 is particularly interesting, since this compound[11] has recently proved useful in the synthesis of highly biologically active prostaglandin endoperoxide analogues.[25] This particular reaction also gives rise to an interesting cyclopentenone product 14. A similar cyclization product has been observed in the palladium-catalyzed carbonylation of 1,5-hexadiene.[26] With 1,5-dienes, however, a complication is encountered that is not observed with 1,4-dienes. Palladium hydride elimination becomes a significant side reaction as evidenced by the formation of *trans*-1-phenyl-1,5-hexadiene and other isomers in entry 9. Rather than decompose, however, the palladium hydride apparently adds to the starting 1,5-diene generating a second (π-allyl)palladium complex 3. With phenylmercuric chloride (entry 9) and a 10-fold excess of 1,5-hexadiene, one can very efficiently trap the palladium. A combined yield of the two (π-allyl)palladium compounds 9 and 3 of ~90% can be obtained. To generate the hydride-derived (π-allyl)palladium product cleanly, all one needs to do is to employ ethylmercuric chloride. In entries 8–10 it is not obvious if the palladium hydride derived product is arising from hydride addition to the terminal carbon or the internal carbon of the diene. The palladium-catalyzed hydro- or deuteriocyanation of terminal alkenes results in hydrogen or deuterium adding to the internal carbon of the alkene.[27] If this is happening in our case, that means that the palladium moiety is now migrating three carbons to form the (π-allyl)palladium product.



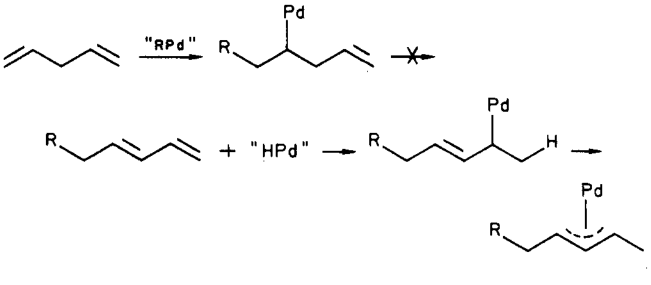
14

To test this possibility, we have looked at the reactions of 1,6-heptadiene and 1,7-octadiene. Ethylmercuric chloride reacts cleanly with 1,6-heptadiene and Li_2PdCl_4 to give a 61% yield of the expected (π-allyl)palladium compound 10 (entry 11). No isomeric (π-allyl)palladium compounds are observed. On the other hand, the analogous reaction with 1,7-octadiene gives approximately a 3:1 mixture of two (π-allyl)palladium compounds 11 and 12 in 92% isolated yield (64% recrystallized yield) (entry 12). Note that the major isomer is not 12, the compound expected from simple palladium hydride addition and migration. It would appear that the major product 11 arises by palladium hydride transfer from one double bond to another as shown in Scheme II. Increasing the amount of 1,7-octadiene from 3 to 30 equiv failed to change the ratio of 11 to 12. This perhaps suggests that the intermediate palladium hydride remains strongly coordinated throughout the reaction to the molecule to which addition originally occurred and is not easily transferred to another diene. Presumably intramolecular coordination of the other double bond promotes intramolecular palladium hydride transfer that results in preferential formation of compound 11. It is not obvious why similar rearrangements are not encountered with 1,6-heptadiene, although the stereochemistry of intermediate (diene)HPdCl complexes may be responsible.

Scheme II



Scheme III



A couple of other general comments are in order here. In this work it appears that the relative reactivity of the organomercurials is $CH_3O_2CHgCl > C_6H_5HgCl \geq CH_3CH_2HgCl > CH_3HgCl$ as judged by the disappearance of the rust red color of Li_2PdCl_4. These changes are observed at about −10 °C with CH_3O_2CHgCl, ~0 °C for C_6H_5HgCl and CH_3CH_2HgCl, and ~40 °C for CH_3HgCl.

Regarding the mechanism of these reactions, the majority of results are most easily explained by initial organopalladium or hydridopalladium addition to the less hindered double bond of the diene, followed by a series of palladium hydride elimination–readdition reactions until an allylpalladium compound is formed. The intermediate palladium hydride species formed in these elimination reactions apparently remains strongly coordinated to the newly generated double bond. Were it to completely eliminate from the diene, we might expect to see additional (π-allyl)palladium compounds derived from palladium hydride addition to this new diene (Scheme III). Only in the reaction of 1,7-octadiene is such a product observed.

In conclusion, organopalladium additions to 1,4-, 1,5-, 1,6-, and 1,7-dienes provide a novel new method for the preparation of (π-allyl)palladium compounds. These reactions are regioselective and allow for the incorporation of functional groups as well.

Experimental Section

Reagents and Equipment. 1,4-Pentadiene (99%), 1,4-cyclohexadiene (97%), 1,5-hexadiene (98%), and phenylmercuric chloride were purchased from Aldrich Chemical Co. in the purity indicated and used without further purification. 2-Methyl-1,4-pentadiene (99%), 3-methyl-1,4-pentadiene (99%), 2,4-dimethyl-1,4-pentadiene (99%), *trans*-1,4-hexadiene (98%), and 1,6-heptadiene (99%) were purchased from Chemical Samples Co. (now Wiley Organics). 1,7-Octadiene (>95%), ethylmercuric chloride, and methylmercuric chloride were purchased from Tokyo Kasei. Carbomethoxymercuric chloride was prepared according

---

(25) Larock, R. C.; Burkhart, J. P.; Oertle, K. *Tetrahedron Lett.* **1982**, 1071.

(26) Brewis, S.; Hughes, P. R. *Chem. Commun.* **1965**, 489.

(27) Jackson, W. R.; Lovel, C. G. *Tetrahedron Lett.* **1982**, 1621.

to a literature procedure.[28] Palladium chloride was generously provided by Johnson Matthey and Engelhard Industries on their academic loan programs.

Infrared spectra were recorded on Beckman 4250 or Hitachi 260-10 infrared spectrometers, and proton NMR spectra were obtained in $DCCl_3$ solvent by using either a JEOL PMX 60 or Hitachi Perkin-Elmer R20B NMR spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., and the Office of Elemental Analysis, Institute for Chemical Research, Kyoto University.

Synthesis of (π-Allyl)palladium Compounds. The following preparation of bis-(μ-chloro)bis[(1-3-η)-5-phenyl-2-pentenyl]dipalladium (compound 1, entry 1, Table I) is representative of the procedure used for the preparation of all (π-allyl)palladium compounds. To 75 mL of tetrahydrofuran (THF) containing 510 mg (12 mmol) of LiCl, 887 mg (5 mmol) of $PdCl_2$, and 0.80 mL (7.5 mmol) of 1,4-pentadiene, 1.57 g (5 mmol) of phenylmercuric chloride was added under nitrogen while the flask was maintained at 0 °C. The solution was allowed to slowly warm to room temperature and stirred overnight. Ether and activated carbon were added to the reaction mixture that was then filtered, washed several times with aqueous ammonium chloride and aqueous sodium chloride, and dried over anhydrous sodium sulfate. After removal of the solvent, the resulting oil was chromatographed on a silica gel column using 4:1 hexane/ethyl acetate as the eluant. Evaporation of the solvent afforded 1.44 g (100% yield) of a yellow oil that was crystallized from methylene chloride giving 0.88 g (61%) of pure (π-allyl)palladium complex: mp 124–125 °C; R_f 0.32 (silica gel, 3:1 hexane/ethyl acetate); ^1H NMR ($DCCl_3$) δ 7.28 (s, 5 H, phenyl), 5.25 (td, J = 12 and 7 Hz, 1 H, C_2H), 3.92 (d, J = 7 Hz, 1 H, syn C_1H), 3.63–4.13 (m, 1 H, C_3H), 2.92 (t, J = 7 Hz, 2 H, C_5H), 2.85 (d, J = 12 Hz, 1 H, anti C_1H), 1.83–2.23 (m, 2 H, C_4H). Anal. Calcd for $C_{22}H_{26}Cl_2Pd_2$: C, 46.02; H, 4.56. Found: C, 45.77; H, 4.62.

All other (π-allyl)palladium compounds were prepared in a similar fashion. Table I gives the experimental details. In most cases, the crude product tends to be pretty pure and losses upon purification appear to be due more to inefficient recrystallization than impurities. The spectroscopic and elemental analysis data follow.

Bis(μ-chloro)bis[(1-3-η)-5-carbomethoxy-2-pentenyl]dipalladium (2): mp 100–101 °C; R_f 0.26 (silica gel, 3:2 hexane/ethyl acetate); IR ($DCCl_3$) 1735 cm^{-1} (C=O); ^1H NMR ($DCCl_3$) δ 5.38 (td, J = 12 and 7 Hz, 1 H, C_2H), 3.95 (d, J = 7 Hz, 1 H, syn C_1H), 3.63–4.07 (m, 1 H, C_3H), 3.72 (s, 3 H, OCH_3), 2.87 (d, J = 12 Hz, 1 H, anti C_1H), 2.62 (t, J = 7 Hz, 2 H, C_4H). Anal. Calcd for $C_{14}H_{22}Cl_2O_4Pd_2$: C, 31.25; H, 4.12. Found: C, 31.14; H, 4.23.

Bis(μ-chloro)bis[(1-3-η)-2-hexenyl]dipalladium (3): mp 98–99 °C (lit.[29] mp 98–99 °C); R_f 0.41 (silica gel, 3:1 hexane/ethyl acetate); ^1H NMR ($DCCl_3$) δ 5.35 (td, J = 12 and 7 Hz, 1 H, C_2H), 3.92 (d, J = 7 Hz, 1 H, syn C_1H), 3.70–4.18 (m, 1 H, C_3H), 2.87 (d, J = 12 Hz, 1 H, anti C_1H), 1.47–1.93 (m, 4 H, $C_{4,5}H$), 0.83–1.16 (m, 3 H, CH_3). Anal. Calcd for $C_{12}H_{22}Cl_2Pd_2$: C, 32.03; H, 4.93. Found (product from CH_3HgCl, entry 3): C, 31.71; H, 4.95. Found: (product from CH_3CH_2HgCl, entry 10); C, 32.00; H, 5.01.

Bis(μ-chloro)bis[(2-4-η)-6-phenyl-3-hexenyl]dipalladium (4): mp 153–154 °C; R_f 0.38 (silica gel, 3:1 hexane/ethyl acetate); ^1H NMR ($DCCl_3$) δ 7.30 (s, 5 H, phenyl), 5.17 (t, J = 11 Hz, 1 H, C_3H), 3.47–3.93 (m, 2 H, $C_{2,4}H$), 2.90 (t, J = 7 Hz, 2 H, C_6H), 1.80–2.13 (m, 2 H, C_5H), 1.28 (d, J = 7 Hz, 3 H, CH_3). Anal. Calcd for $C_{24}H_{30}Cl_2Pd_2$: C, 47.86; H, 5.02. Found: C, 47.67; H, 4.93.

Bis(μ-chloro)bis[(1-3-η)-2-methyl-5-phenyl-2-pentenyl]dipalladium (5): mp 173–174 °C (lit.[18] mp 169.5–170.5 °C); R_f 0.34 (silica gel, 3:1 hexane/ethyl acetate); ^1H NMR ($DCCl_3$) δ 7.28 (s, 5 H, phenyl), 3.73 (s, 1 H, syn C_1H), 3.58 (t, J = 7 Hz, 1 H, C_3H), 2.73–3.10 (m, 2 H, C_5H), 2.68 (s, 1 H, anti C_1H), 1.98 (s, 3 H, CH_3), 1.80–2.18 (m, 2 H, C_4H). Anal. Calcd for $C_{24}H_{30}Cl_2Pd_2$: C, 47.86; H, 5.02. Found: C, 46.90; H, 5.12.

The two isomers of bis(μ-chloro)bis[(1-3-η)-3-methyl-5-phenyl-2-pentenyl]dipalladium (6) could not be isolated in pure form (silica gel, 3:1 hexane/ethyl acetate R_f 0.38 and 0.42) but could be recognized by the presence of the syn methyl at δ 1.47 and the anti methyl at δ 1.25 in the proton NMR spectrum. The spectrum was too complicated to make further assignments.

The syn and anti isomers of bis(μ-chloro)bis[(1-3-η)-2,4-dimethyl-2-pentenyl]dipalladium (7) were inseparable by chromatography (silica gel, 3:1 hexane/ethyl acetate, R_f 0.43), but the relative ratio of syn/anti (3:2) could be determined by integration of the appropriate NMR peaks assigned as follows, *syn*-7: ^1H NMR ($DCCl_3$) δ 3.72 (s, 1 H, syn C_1H), 3.46 (d, J = 9 Hz, 1 H, anti C_3H), 2.63 (s, 1 H, anti C_1H), 2.13 (s, 1 H, C_2CH_3), ~2.2 (m, 1 H, C_4H), 1.27 (d, J = 7 Hz, 6 H, C_4CH_3, C_5H). *Anti*-7: ^1H NMR ($DCCl_3$) δ 4.33 (d, J = 9 Hz, 1 H, C_3H), 3.87 (s, 1 H, syn C_1H), 3.20 (s, 1 H, anti C_1H), 2.05 (s, 3 H, C_2CH_3), ~1.3 (m, 1 H, C_4H), 1.08 (d, J = 7 Hz, 3 H, C_4CH_3), 0.92 (d, J = 7 Hz, 3 H, C_5H). Anal. Calcd for $C_{14}H_{26}Cl_2Pd_2$: C, 35.17; H, 5.48. Found: C, 35.29; H, 5.25. The melting point of the mixture was 156–161 °C.

Bis(μ-chloro)bis[(1-3-η)-6-carbomethoxy-2-hexenyl]dipalladium (8): mp 79–80 °C (lit.[11] mp 78.5–81.5 °C); R_f 0.19 (silica gel, 3:2 hexane/ethyl acetate); IR ($DCCl_3$) 1735 cm^{-1} (C=O); ^1H NMR ($DCCl_3$) δ 5.38 (td, J = 12 and 7 Hz, 1 H, C_2H), 3.95 (d, J = 7 Hz, 1 H, syn C_1H), 3.43–4.10 (m, 1 H, C_3H), 3.70 (s, 3 H, OCH_3), 2.92 (d, J = 12 Hz, 1 H, anti C_1H), 2.25–2.55 (m, 2 H, C_6H), 1.67–2.00 (m, 4 H, $C_{4,5}H$). Anal. Calcd for $C_{16}H_{26}Cl_2O_4Pd_2$: C, 33.95; H, 4.63. Found: C, 34.04; H, 4.72. This compound was identical with a previously prepared sample[11] in all respects.

Bis(μ-chloro)bis[(1-3-η)-2-heptenyl]dipalladium (10): mp 60–61 °C; R_f 0.48 (silica gel, 3:1 hexane/ethyl acetate); ^1H NMR ($DCCl_3$) δ 5.36 (td, J = 12 and 7 Hz, 1 H, C_2H), 3.9 (d, J = 7 Hz, 1 H, syn C_1H), 3.75–4.1 (m, 1 H, C_3H), 2.86 (d, J = 12 Hz, 1 H, anti C_1H), 1.22–2.0 (m, 6 H, $C_{4,5,6}H$), 0.81–1.1 (m, 3 H, CH_3). Anal. Calcd for $C_{14}H_{26}Cl_2Pd_2$: C, 35.17; H, 5.48. Found: C, 35.19; H, 5.66.

The (π-allyl)palladium compounds **9** and **3** obtained as a mixture from experiments indicated in entry 9, Table I, were not easily separable, so yields and characterization were established by NMR spectroscopy. Several isomeric phenylhexadienes were observed by GC–MS and NMR spectroscopy, the major isomer (~70%) being *trans*-1-phenyl-1,5-hexadiene [^1H NMR ($DCCl_3$) δ 7.2 (s, 5 H, phenyl), 6.4 (d, J = 15 Hz, 1 H, C_1H), 6.2 (m, 1 H, C_2H), 5.4–6.0 (m, 1 H, C_5H), 5.0–5.2 (m, 1 H, cis C_6H), 4.9 (s, 1 H, trans C_6H), 2.25 (s, 4 H, $C_{3,4}H$)].

The mixture of (π-allyl)palladium compounds **11** and **12** was also inseparable by chromatography. Their relative ratio was determined by integration of appropriate NMR peaks which were assigned as follows. Bis(μ-chloro)bis[(2-4-η)-3-octenyl]dipalladium (11): ^1H NMR ($DCCl_3$) δ 5.25 (t, J = 11 Hz, 1 H, C_3H), 3.5–3.9 (m, 2 H, $C_{2,4}H$), 1.1–2.0 (m, 6 H, CH_2's), 1.3 (d, J = 8 Hz, 3 H, C_1CH_3), 0.7–1.1 (m, 3 H, C_8CH_3). Bis(μ-chloro)bis[(1-3-η)-2-octenyl]dipalladium (12): ^1H NMR ($DCCl_3$) δ 5.37 (td, J = 12 and 7 Hz, 1 H, C_2H), 3.95 (d, J = 7 Hz, 1 H, syn C_1H), 2.90 (d, J = 12 Hz, 1 H, anti C_1H). Since compound **12** is the minor product in the mixture, no further attempt to assign NMR peaks was made. There was no evidence for bis(μ-chloro)bis[(3-5-η)-4-octenyl]dipalladium by ^1H or ^{13}C NMR analysis. The elemental analysis of the mixture of **11** and **12** follows. Anal. Calcd for $C_{16}H_{30}Cl_2Pd_2$: C, 37.97; H, 5.97. Found: C, 38.10; H, 6.12. The melting point of the mixture was 87–95 °C. Compound **12** reportedly melts at 126 °C.[30]

The physical data for compounds **13** and **14** follow. 3-Chloro-5-phenylcyclohexene (13): ^1H NMR ($DCCl_3$) δ 7.05 (s, 5 H, phenyl), 5.7–5.8 (m, 2 H, vinyl), 4.55 (s, 1 H, CHCl), 3.15 (tt, J = 10 and 5 Hz, 1 H, CHPh), 2.0–2.3 (m, 4 H, CH_2's); IR (neat) 3040 cm^{-1} (C=CH); mass spectrum, m/z 192.07084 (calcd for $C_{12}H_{13}Cl$, 192.07058). 2-Methyl-5-(carbomethoxymethyl)-2-cyclopenten-1-one (14): ^1H NMR ($DCCl_3$) δ 7.25 (s, 1 H, vinyl), 3.2 (s, 3 H, CH_3O), 1.9–2.9 (m, 5 H), 1.75 (s, 3 H, CH_3); IR (neat) 1700, 1735 (C=O), 820 (=CH) cm^{-1}; mass spectrum, m/z 168.07850 (calcd for $C_9H_{12}O_3$, 168.07865).

Acknowledgment. We gratefully acknowledge the National Institutes of Health (AM-21795) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research. We also wish to express our appreciation

---

[28] Schoeller, W.; Schrauth, W.; Essers, W. *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 2864.

[29] Takahashi, Y.; Tsukiyama, K.; Sakai, S.; Ishii, Y. *Tetrahedron Lett.* **1970**, 1913.

[30] Donati, M.; Conti, F. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 343.

to Johnson Matthey, Inc., and Engelhard Industries for generous loans of palladium chloride.

Registry No. 1, 87993-70-2; 2, 90414-23-6; 3, 31666-74-7; 4, 90414-24-7; 5, 33111-55-6; 6 (isomer I), 90414-25-8; 6 (isomer II), 90527-94-9; 7 (isomer I), 41529-00-4; 7 (isomer II), 41529-00-4; 9, 90414-26-9; 10, 31886-52-9; 11, 87993-71-3; 12, 12112-73-1; 13, 90414-27-0; 14, 90414-28-1; C_6H_5HgCl, 100-56-1; CH_3O_2CHgCl, 17261-26-6; CH_3HgCl, 115-09-3; CH_3CH_2HgCl, 107-27-7; $H_2C{=}CHCH_2CH{=}CH_2$, 591-93-5; *trans*-$H_2C{=}CHCH_2CH{=}CHCH_3$, 7319-00-8; $H_2C{=}CHCH_2C(CH_3){=}CH_2$, 763-30-4; $H_2C{=}CHCH(CH_3)CH{=}CH_2$, 1115-08-8; $H_2C{=}C(CH_3)CH_2C(CH_3){=}CH_2$, 4161-65-3; $H_2C{=}CH(CH_2)_2CH{=}CH_2$, 592-42-7; $H_2C{=}CH(CH_2)_3CH{=}CH_2$, 3070-53-9; $H_2C{=}CH(CH_2)_4CH{=}CH_2$, 3710-30-3; Li_2PdCl_4, 15525-45-8; *trans*-1-phenyl-1,5-hexadiene, 56644-04-3; 1,4-cyclohexadiene, 628-41-1.

Electron Donor-Acceptor Quenching and Photoinduced Electron Transfer for Coumarin Dyes

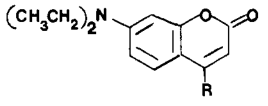
Guilford Jones, II,* Susan F. Griffin, Chol-yoo Choi, and William R. Bergmark[1]

Department of Chemistry, Boston University, Boston, Massachusetts 02215

Received March 9, 1984

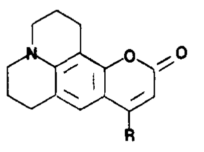
The fluorescence of 7-aminocoumarins is quenched by a variety of organic electron donors or acceptors in acetonitrile. In general, donors with half-wave oxidation potentials less positive than 1.0 V vs. SCE and acceptors with reduction potentials less negative than −1.5 V vs. SCE are candidates for diffusion limited quenching of coumarin singlet states. Profiles of quenching rates are consistent with calculated free energies for electron transfer between excited coumarins and donors or acceptors. In flash photolysis experiments electron transfer for several dyes and quenchers (e.g., methyl viologen) is demonstrated. Relatively low yields of net electron transfer are consistently obtained due to inefficient ionic photodissociation via singlet quenching or a low yield of more photoactive coumarin triplets. Electrochemical properties of the coumarins have been investigated by cyclic voltammetry with the indications of reversible oxidation and irreversible reduction as important processes.

The 7-aminocoumarins (e.g., 1–5) constitute an important class of organic dyes which lase[2] and which in some circumstances may act as photosensitizers.[3,4] These structures are also related to the furocoumarins which have received much attention due to their photobiological properties.[5] In previous papers in this series, photophysical and photochemical properties for coumarin dyes have been reported with particular attention given to the pronounced medium dependences of spectral properties and emission yields associated with the highly polar coumarin excited states (nominally depicted by 6).[6] Other recent investigations have been directed to the mechanism of coumarin photodegradation,[7] the behavior of coumarin dyes in water and in aqueous detergent media,[8] and the effects of medium and additives on photostability and emission yield under lasing conditions.[9–11]



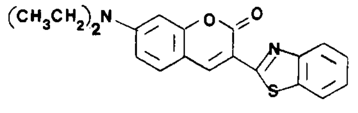
1, R = CH_3

2, R = CF_3

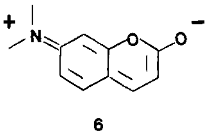


3, R = CH_3

4, R = CF_3



5



6

Table I. Absorption and Emission Properties of Coumarin Dyes in Acetonitrile

	λ_a[a]	λ_f[a]	τ_f,[b] ns
1	367	434	2.8
2	396	501	0.60
3	380	451	2.8
4	418	521	4.6
5	454	501	(3.1)[c]

[a] Absorption (λ_a) and emission (λ_f) maxima in nm. [b] Fluorescence lifetimes reported for N_2- or Ar-purged solutions (ref 6) corrected for fluorescence quenching by O_2 in air-saturated solutions (ref 6c). [c] Obtained from dimethylaniline quenching results (see text).

The coumarin dyes give rise to strong, broad absorption bands extending into the visible accompanied by solvent dependent red shifts in emission indicative of an emissive state having a large dipole moment (i.e., 6). The interaction of such excited species with added quenchers has not been studied in detail although coumarin singlet[6c,12]

---

[1] On sabbatical leave from Ithaca College, Ithaca, NY.

[2] Drexhage, K. D. "Dye Lasers"; Schafer, F. P., Ed.; Springer-Verlag: New York, 1977; Vol. 1.

[3] Specht, D. P.; Martic, P. A.; Farid, S. *Tetrahedron* **1982**, *38*, 1203.

[4] Jones, G., II; Xuan, P. T.; Schwarz, W. *Tetrahedron Lett.* **1982**, *23*, 5505.

[5] Melo, M. T.; Averbeck, D.; Bensasson, R. V.; Land, E. J.; Salet, C. *Photochem. Photobiol.* **1979**, *30*, 645 and references cited therein.

[6] (a) Jones, G., II; Jackson, W. R.; Halpern, A. M. *Chem. Phys. Lett.* **1980**, *72*, 391. (b) Jones, G., II; Jackson, W. R.; Kanoktanaporn, S.; Halpern, A. M. *Opt. Commun.* **1980**, *23*, 315. (c) Jones, G., II; Jackson, W. R.; Choi, C.; Bergmark, W. R., submitted for publication.

[7] Jones, G., II; Bergmark, W. R. *J. Photochem.*, in press.

[8] Jones, G., II; Jackson, W. R.; Kanoktanaporn, S.; Bergmark, W. R., submitted for publication.

[9] von Trebra, R. J.; Koch, T. H. *Appl. Phys. Lett.*, in press.

[10] von Trebra, R. J.; Koch, T. H. *Chem. Phys. Lett.* **1982**, *93*, 315.

[11] Fletcher, A. N.; Knipe, R. H.; Pietrak, M. E. *Appl. Phys.* **1982**, *B27*, 93 and references cited therein.