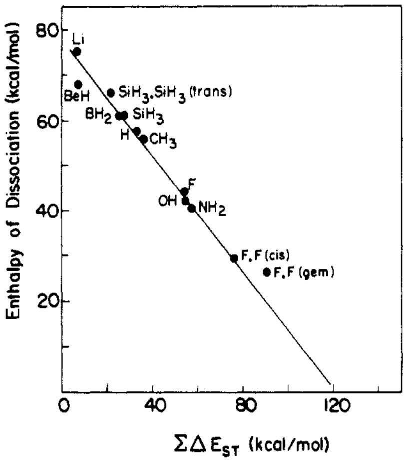

Figure 2. Plot of the dissociation energies of substituted disilenes to two singlet silylenes (MP3/6-31G*//6-31G* + ZPE at 6-31G*) vs $\Sigma\Delta E_{ST}$ of the corresponding silylenes (MP4SDTQ/6-31G*//3-21G$^{(*)}$).

stitution elongates the Si=Si bond by 0.079 Å, compared to only 0.028 Å in $H_2Si{=}CH_2$[8] and 0.001 Å in ethylene).

The degree of pyramidalization (θ) and the Si=Si bond distance in substituted disilenes correlate (Figure 1, parts a and b, respectively) with $\Sigma\Delta E_{ST}$, the sum of the singlet–triplet energy differences in the silylenes that formally compose the disilene (i.e., R_1R_2Si: and R_3R_4Si: for $R_1R_2Si{=}SiR_3R_4$).[10] A correlation between θ and $\Sigma\Delta E_{ST}$ was previously suggested by Malrieu and Trinquier using qualitative VB and MO analysis,[3] leading to the prediction that disilenes are trans-bent when $\Sigma\Delta E_{ST}$ > BDE (BDE = bond dissociation energy of a substituted disilene to the corresponding *singlet* silylenes).[11] This prediction is generally supported by our calculations, except for the region where the bending potential is flat: e.g., $H_2Si{=}SiH_2$ and $H_2Si{=}SiHCH_3$ are calculated to be trans-bent (Figure 1a) although $\Sigma\Delta E_{ST}$ < BDE [for $H_2Si{=}SiH_2$, $\Sigma\Delta E_{ST}$ = 32.8 kcal mol^{-1}) < (BDE = 57.2 kcal mol^{-1})].[12]

Most recently Liang and Allen suggested that the geometries of disilenes are dictated by the substituents' electronegativities: the more electronegative substituents induce larger distortions.[4a] We find that in addition to electronegativity the π-donation ability of the substituent is also important. Thus, r(Si=Si) and θ_H *decrease* (θ_R increases slightly) along the series **1b**, R = $NH_2 \rightarrow OH \rightarrow F$ (Figure 1, parts a and b), while the electronegativity of R *increases*. Changes in the geometries of disilenes are better predicted by $\Sigma\Delta E_{ST}$ of the corresponding silylenes, which are influenced by both the electronegativity and the π-donation ability of the substituents, than by the substituents' electronegativities.

The BDEs of substituted disilenes also correlate linearly with $\Sigma\Delta E_{ST}$ (Figure 2).[13] The changes in the BDEs of disilenes upon substitution are dramatic. Thus, the calculated BDE of *cis*-FHSi=SiHF of 29.5 kcal mol^{-1} is only half of the BDE of $H_2Si{=}SiH_2$ (57.2 kcal mol^{-1}).[14]

The correlation between $\Sigma\Delta E_{ST}$ and the BDE of disilenes can be used to predict the thermodynamic stabilities toward dissociation of unknown disilenes and for deciding which disilenes are reasonable targets for synthesis. For example, according to Figure 2 the BDE of (HO)HSi=SiH(OH) is as low as ca. 30 kcal mol^{-1}. As entropy favors dissociation, the $\Delta G°$ for the reaction (HO)HSi=SiH(OH) → 2(HO)HSi: is even lower, only ca. 20 kcal mol^{-1} at 298 K.[15] The isolation of dialkoxydisilenes is expected therefore to be extremely difficult, even at low temperatures.[16] Note that as the DBE decreases, other possible Si_2R_4 isomers [e.g., bridged RSi(μ-R_2)SiR] may compete with the classical disilene geometry (e.g., FHSi=SiHF for which BDE = 27.6 kcal mol^{-1}).[3c,17] Figure 2 also predicts that a substituted disilene for which $\Sigma\Delta E_{ST} \geq$ 120 kcal mol^{-1} will dissociate spontaneously to two silylenes even at 0 K. An example is $F_2Si{=}SiF_2$ ($\Sigma\Delta E_{ST}$ = 147.6 kcal mol^{-1}), which was found not to be a minimum on the Si_2F_4 potential energy surface.[3a,4b]

The finding that *silyl substitution increases the DBE of disilenes* [Figure 2, e.g., the BDE of $(H_3Si)HSi{=}SiH(SiH_3)$ is calculated to be *8.7 kcal mol^{-1} higher* than that of $H_2Si{=}SiH_2$] is of special significance, because it suggests that disilenes such as $(R_3Si)_2Si{=}Si(SiR_3)_2$ should have a relatively high thermodynamic stability, making them interesting goals for synthesis.

In conclusion, both the geometries and the bond dissociation energies of substituted disilenes correlate with $\Sigma\Delta E_{ST}$ of the corresponding silylenes. This correlation can be used to predict the structures and the BDEs of yet unknown disilenes and to find which disilenes are capable of existence.

Acknowledgment. We thank Professor Robert West for many stimulating discussions and for sharing with us his unpublished results and Professors J.-P. Malrieu and G. Trinquier for helpful comments. This study was partially supported by the Venezuela Technion Society Research Fund and the Fund for the Promotion of Research at the Technion.

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(9) Heinrich, N.; Koch, W.; Frenking, G.; Schwarz, H. *J. Am. Chem. Soc.* **1986**, *108*, 593.

(10) Of the silylenes studied, HSiLi and HSiBeH are the only ground-state triplets, and they were therefore not included in Figure 1. $H_2Si{=}SiHLi$ and $H_2Si{=}SiHBeH$ are both planar, with Si=Si bond lengths of 2.159 and 2.145 Å, respectively.

(11) According to Malrieu and Trinquier, doubly bonded species are trans-bent when $\Sigma\Delta E_{ST} > 0.5E_{\sigma+\pi}$,[3a,b] where $E_{\sigma+\pi}$ is the binding energy of the disilene relative to the corresponding two divalent *triplet* silylenes. When the divalent fragments are singlets (i.e., $\Sigma\Delta E_{ST} > 0$), as for most silylenes, $E_{\sigma+\pi}$ = BDE + $\Sigma\Delta E_{ST}$ and the $\Sigma\Delta E_{ST} > 0.5E_{\sigma+\pi}$ condition suggested by MT becomes $\Sigma\Delta E_{ST}$ > BDE.

(12) MT also predict, using somewhat different values ($\Sigma\Delta E_{ST}$ = 38 kcal mol^{-1}) > ($0.5E_{\sigma+\pi}$ = 37 kcal mol^{-1}), that $H_2Si{=}SiH_2$ is trans-bent.[3b]

(13) A similar correlation was suggested for substituted olefins: Carter, E. A.; Goddard, W. A., III. *J. Phys. Chem.* **1986**, *90*, 998. Carter, E. A.; Goddard, W. A., III. *J. Chem. Phys.* **1988**, *88*, 1752.

(14) Note that while the Carter–Goddard equation suggests a slope of −1,[13] we obtain in Figure 2 a slope of −0.62.

(15) The calculated (6-31G*) $\Delta S°$ for the dissociation of $H_2Si{=}SiH_2$ is (2 × 49.5) − 64.6 = 34.4 cal K^{-1} mol^{-1}.

(16) In agreement, attempts to synthesize such disilenes were indeed so far unsuccessful (R. West, personal communication).

(17) Maxka, J.; Apeloig, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 737.

One-Step Construction of Fused Tricyclic and Tetracyclic Structures from Acyclic Precursors via Cyclic Carbopalladation[†,1]

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Ei-ichi Negishi*

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Construction of two or more rings in one synthetic operation is an attractive synthetic strategy. Among the most noteworthy examples is W. S. Johnson's cationic polyene cyclization reaction[2] (an example of "crochet"-mode cyclization), which has been applied to bi- through tetracyclization. Although a conceptually distinct "zipper"-mode cyclization strategy schematically shown in Scheme I is also potentially applicable to construction of a number of rings in one step, its application beyond bicyclization[3] has been very limited.[4]

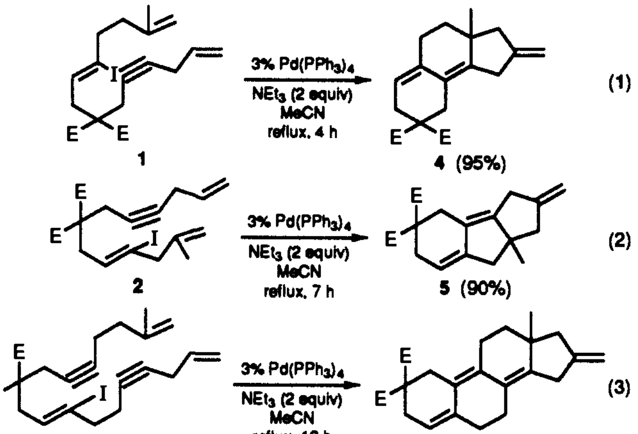
[†] This paper is dedicated to the memory of Professor J. K. Stille.

(1) The critical results described in this paper were orally presented. (a) Zhang, Y.; Negishi, E. Presented at the 5th IUPAC Symposium on Organometallic Chemistry Directed towards Organic Synthesis, Florence, Italy, Oct 1–6, 1989; OP-B07. (b) Negishi, E. Presented at the 1989 International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Dec 17–22, 1989; ORGN 711.

(2) For tetracyclization of polyenes, see: Johnson, W. S.; Wiedhaup, K.; Brady, S. F.; Olson, G. L. *J. Am. Chem. Soc.* **1974**, *96*, 3979.

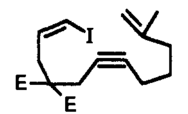
(3) In addition to numerous organometallic bicyclization reactions, we have recently reported some examples of bicyclization reactions producing fused bicycles via cyclic carbopalladation: Zhang, Y.; Negishi, E. *J. Am. Chem. Soc.* **1989**, *111*, 3454.

We now report novel and rare examples of a "zipper"-mode one-step tricyclization and tetracyclization reaction involving cyclic carbopalladation. Specifically, treatment of **1–3** with 3 mol % of $Pd(PPh_3)_4$ and 2 equiv of NEt_3 in MeCN under reflux cleanly provided **4–6**[5] in 95, 90, and 76% isolated yields, respectively.[6]



E = COOEt

The results herein reported are in significant contrast with a previously reported tricyclization reaction of **7** to produce **8** via cyclopropanation.[3] Specifically, no cyclopropanation was observed in the reaction of **1–3**, even though the penultimate cyclization step presumably produces a neopentyl-like alkylpalladium species represented by **9** that can undergo cyclopropanation to give an allylpalladium derivative **10**. The remarkably high yielding and clean results herein reported suggest that the "zipper"-mode cyclic carbopalladation of alkynes most likely is applicable to one-step generation of even a greater number of rings and that 1,1-dialkyl-substituted and monoalkyl-substituted alkenes can serve as penultimate and terminal functional groups, respectively.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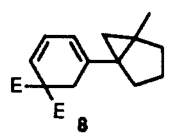
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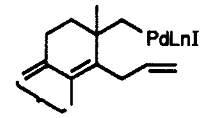
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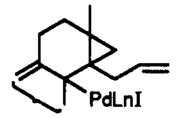
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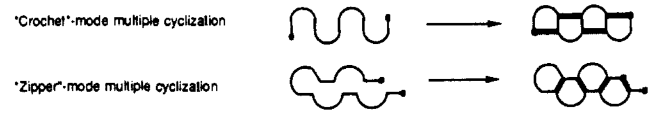
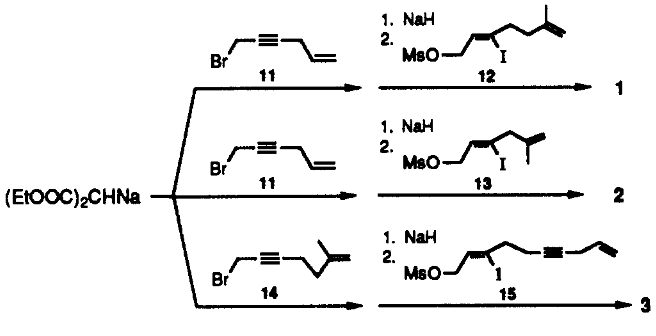
Scheme I



Scheme II



The preparation of **1–3**[7] was achieved in good yields via NaH-promoted double alkylation of diethyl malonate (Scheme II[8]). The following procedure for converting **4** into **6** is representative of the cascade cyclic carbopalladation reaction. A mixture of 0.262 g (0.5 mmol) of **3**, $Pd(PPh_3)_4$ (0.017 g, 0.015 mmol), and NEt_3 (0.101 g, 1 mmol) in 3 mL of MeCN was heated to reflux for 12 h. The reaction mixture was quenched with 3 N HCl, extracted with Et_2O, washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated. Flash column chromatography (silica gel, 1:20 ether–pentane) provided 0.15 g (76%) of **6**: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.96 (s, 3 H), 1.21 (t, J = 7 Hz, 6 H), 1.4–2.0 (m, 2 H), 2.0–3.2 (m, 14 H), 4.0–4.3 (m, 4 H), 4.92 (br s, 1 H), 4.96 (br s, 1 H), 5.35 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.08, 23.28, 23.54, 26.59, 30.08, 31.23, 31.64, 35.21, 35.63, 41.82, 50.35, 54.55, 61.44, 107.13, 112.64, 117.53, 123.83, 135.51, 130.58, 135.17, 143.67, 149.76, 171.85; UV (95% EtOH) λ_{max} = 288.5 nm, ϵ = 13800. Anal. Calcd for $C_{25}H_{32}O_4$: C, 75.75; H, 8.08. Found: C, 75.51; H, 8.17.

In all three cases the desired cyclization must have proceeded nearly quantitatively with little or no sign of side reactions, as judged by NMR and HPLC analyses. For example, the ^{13}C NMR spectra of **4–6**, isolated as viscous oils by mere concentration and short-path chromatography primarily to remove inorganic and organometallic compounds, show only one set of signals. The total absence of alkyne signals indicates complete consumption of the acyclic precursors. All carbon atoms except those of the two COOEt groups show discrete ^{13}C NMR signals associated with the expected chemical shifts and the expected numbers of directly attached hydrogens. Although neither the two CO carbons nor the two Et carbons in **6** show discrete signals, the two CO carbons

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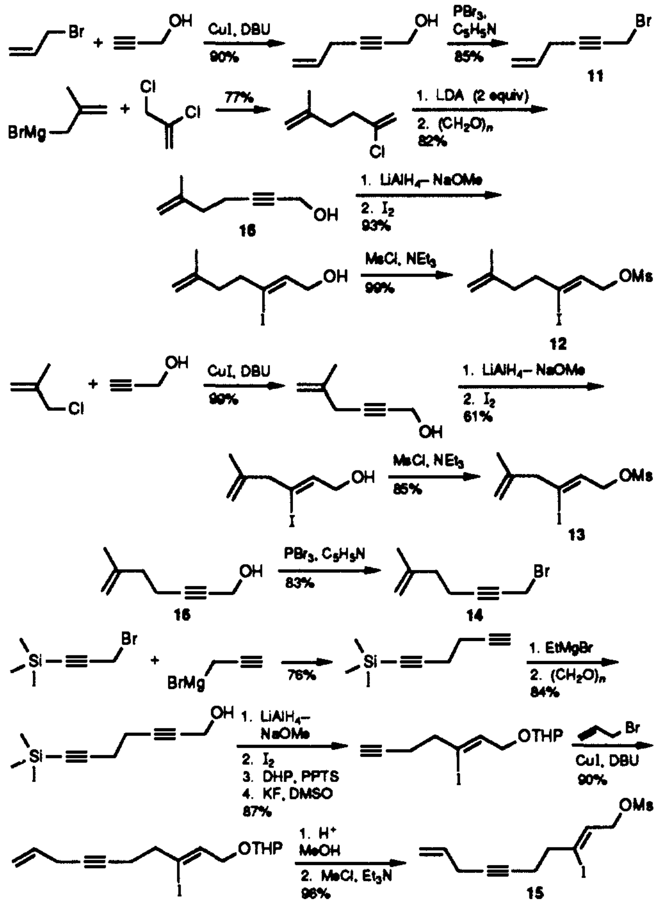
(4) For a review of biogenetic polyketide cyclization reactions, see: Harris, T. M.; Harris, C. M. *Tetrahedron* **1977**, *33*, 2159.

(5) Satisfactory spectral and analytical data have been obtained from these compounds.

(6) For other examples of tandem bicyclization via carbopalladation, see, for example: (a) Abelman, M. M.; Overman, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 2328. (b) Trost, B. M.; Lee, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 7255. (c) Wu, G.; Lamaty, F.; Negishi, E. *J. Org. Chem.* **1989**, *54*, 2507. (d) Carpenter, N. E.; Kucera, D. J.; Overman, L. E. *J. Org. Chem.* **1989**, *54*, 5846. (e) Grigg, R.; Dorrity, M. J.; Malone, J. F. *Tetrahedron Lett.* **1990**, *31*, 1343.

(7) Satisfactory spectral data have been obtained for these compounds.

(8) The preparations of **11–15** were performed as follows:



of **4** and **5**, as well as the two Me carbons of the COOEt groups in **5**, are distinguished by the lone asymmetric center. The ^{1}H NMR spectra of **4–6** show the presence of a trisubstituted alkene (5.2–5.35 ppm) and a 1,1-disubstituted alkene (two broad singlets in the 4.88–4.96 ppm region). In addition to the signals for the two Et groups, a Me group is clearly seen. The UV spectra of **4–6** indicate the presence of either a conjugated diene or triene. These spectral data, together with the correct elemental analyses and the consistent ^{1}H 2D NOESY and COSY NMR spectra, as well as ^{1}H–^{13}C HETCOR spectra for **6**, firmly identify **4–6**.[9]

Acknowledgment. We thank the National Institutes of Health (GM 36792) for support. We also thank Johnson Mathey for a loan of PdCl$_2$.

Supplementary Material Available: ^{1}H and ^{13}C NMR and IR data for **1–5** (1 page). Ordering information is given on any current masthead page.

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[9] Several attempts to convert **6** into crystalline derivatives for X-ray analysis have failed. Further attempts to obtain X-ray data are in progress.

Triply Bridging Trifluorophosphine. Formation of $[(\mu_3\text{-}F_3P)Pd_3(\mu\text{-}Ph_2PCH_2PPh_2)_3(\mu\text{-}Cl)]^+$ by Disproportionation of $Pd_2(\mu\text{-}Ph_2PCH_2PPh_2)_2Cl_2$

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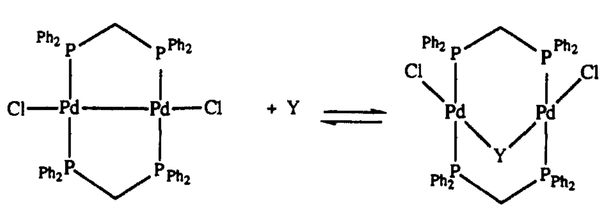
The analogy between trifluorophosphine and carbon monoxide as ligands was first made by Chatt in 1950,[1] and since then a variety of complexes have been obtained in which the fluorophosphine acts as a terminal ligand.[2] Pursuing this analogy, we considered the possibility that trifluorophosphine might also be capable of acting as a bridging ligand. Bridging monophosphine ligands have not previously been observed,[3] but numerous forms of bridging carbon monoxide are known.[4]

To this end we examined the reaction of trifluorophosphine with Pd$_2$(μ-dpm)$_2$Cl$_2$ (dpm is bis(diphenylphosphino)methane) (**1**), which is known to undergo ready, and frequently reversible, insertion of a variety of ligands, Y, including inter alia carbon monoxide via eq 1.[5] However, the reaction does not follow eq 1. Rather, the novel disproportionation reaction shown in eq 2 occurs.



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(1)

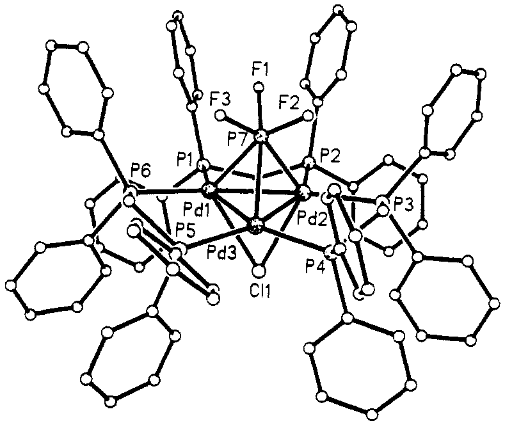
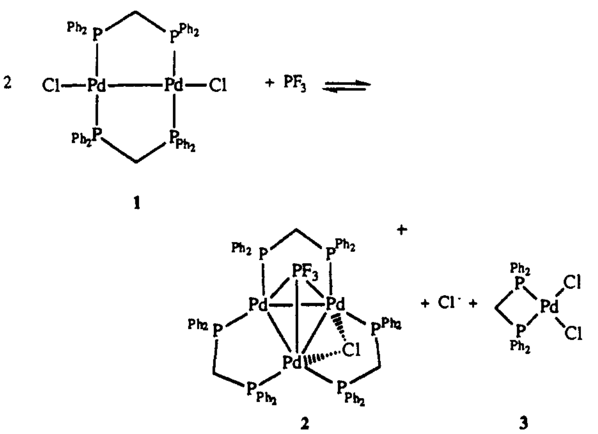


Figure 1. A perspective view of the cation in $[(\mu\text{-}F_3P)Pd_3(\mu\text{-dpm})_3(\mu\text{-}Cl)][PF_6]\cdot 0.5CH_2Cl_2$.



1 **2** **3**

(2)

Exposure of an orange dichloromethane solution of **1** to 1 atm of phosphorus trifluoride results in a darkening to produce a rich red-brown solution after 1 h. Gradual addition of ethyl ether produces a light yellow precipitate of Pd(dpm)Cl$_2$ (**3**), which was identified by comparison with an authentic sample.[6] Further addition of ethyl ether yields a deep red-brown powder of $[(\mu_3\text{-}F_3P)Pd_3(\mu\text{-dpm})_3(\mu\text{-}Cl)]Cl$, which may be converted into the corresponding hexafluorophosphate salt by metathesis. The ^{31}P{^{1}H} NMR spectrum consists of a resonance centered at −12.3 ppm due to the dpm phosphorus that consists of a doublet due to coupling to a unique phosphorus (^2J(P,P) = 60 Hz) that is further split into a quartet due to coupling to three equivalent fluorines (^3J(P,F) = 8.6 Hz) and a resonance centered a 101.5 ppm due to the coordinated trifluorophosphine which consists of a quartet due to coupling to three fluorine atoms (^1J(P,F) = 1295 Hz) that is further split into a heptet because of coupling to six equivalent phosphorus atoms (^2J(P,P) = 60 Hz). Cooling the sample to −70 °C produces broadening of the resonance at −12.3. This may result from localization of the halide ligand (as seen in the crystallographic study, vide infra), which is otherwise free to move between the three palladium atoms. The electronic spectrum shows a broad peak in the visible range with λ_{max} = 458 nm. Reaction 2 is

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[1] Chatt, J. *Nature* **1950**, *165*, 637.

[2] Wilkinson, G. *J. Am. Chem. Soc.* **1951**, *73*, 5501. Chatt, J.; Williams, A. A. *J. Chem. Soc.* **1951**, 3061. Clark, R. J.; Busch, M. A. *Acc. Chem. Res.* **1973**, *6*, 246. Nixon, J. F. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 42.

[3] A μ-PF$_3$ structure has been considered for the PF$_3$ adduct of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dpm})_3]^{2+}$, but the available data did not allow differentiation between a bridged structure and a fluxional monodentate one. Bradford, A. M.; Douglas, G.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1990**, *9*, 409.

[4] Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1. Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219.

[5] Olmstead, M. M.; Hope, H.; Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1977**, *99*, 5502. Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 6099. Balch, A. L. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; p 167.

[6] Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 1641. Steffen, W. L.; Palenick, G. J. *Inorg. Chem.* **1976**, *15*, 2432.

[7] Deep red-brown crystals were obtained by diffusion of ethyl ether into a dichloromethane solution of the complex. $[(\mu\text{-}F_3P)Pd_3(\mu\text{-dpm})_3(\mu\text{-}Cl)]PF_6\cdot 0.5CH_2Cl_2$ crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions a = 26.725 (11) Å, b = 27.101 (12) Å, c = 21.304 (9) Å, and β = 110.70 (2)° at 130 K with Z = 8. Refinement of 6509 reflections with $F > 4.0\,\sigma(F)$ and 546 parameters yielded R = 0.109, R_w = 0.123. The asymmetric unit contains two independent cations, two hexafluorophosphate ions, and 1.5 dichloromethane molecules with disorder in one of the hexafluorophosphate ions and one of the dichloromethane molecules. The disordered dichloromethane site was refined with 50% occupancy. See the supplementary material for details.

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