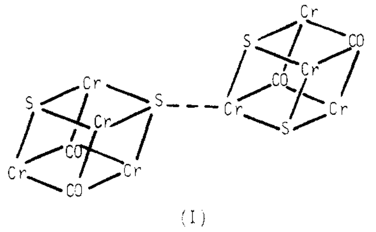
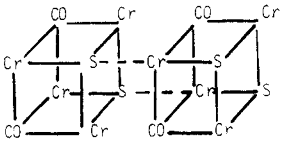
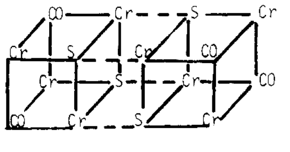


(I)



(IIA)



(IIB)

capable of initiating condensation via the formation of donor–acceptor S→M bonds. It is also observed that like other reported reactions involving CpCr entities and S ligands,[25,26] the thermolysis reactions studied also gave the cubane $Cp_4Cr_4S_4$ as the end product, indicating a great driving force toward its formation.

Acknowledgment. Financial support from the University of Malaya (L.Y.G and C.W.) and the Ming Yu Foundation (Grant 636011000 to T.C.W.M., administered by the Chinese University of Hong Kong) is gratefully acknowledged. We also thank Dr. J. K. MacLeod of the Research School of Chemistry, The Australian National University, Canberra, for the high-resolution mass spectrum of $Cp_4Cr_4S_4$.

Registry No. 1, 71549-26-3; 2, 89401-43-4; 3, 103835-71-8; 4, 79469-27-5; $[CpCr(CO)_3]_2$, 12194-12-6.

Supplementary Material Available: Tables of hydrogen atom coordinates and anisotropic thermal parameters (2 pages); a table of observed and calculated structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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[25] Fischer, E. O.; Ulm, K.; Kuzel, P. *Z. Anorg. Allg. Chem.* **1962**, *319*, 253.

[26] Pasynskii, A. A.; Eremenko, I. L.; Orazsakhatov, B.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1981**, *216*, 211.

Reactions of η^1-Allyl Complexes of Palladium(II) with Electrophiles. Molecular Structure of a [2 + 3] Cycloadduct of (η^1-Allyl)palladium with Maleic Anhydride

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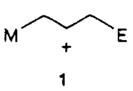
(η^1-Allyl)arylpalladium complexes react with some electrophiles (HCl, Br_2, NBS; NBS = *N*-bromosuccinimide) to give selective Pd–allyl bond cleavage (allylic substitution) with 1,3-transposition, while the corresponding (η^3-allyl)arylpalladium analogues react with these electrophiles via selective Pd–Ar bond cleavage. The η^1-allyl complexes also react with CCl_4 and $CHCl_3$ under very mild conditions to give good yields of $CH_2{=}CHCHR(CR'Cl_2)$ (R = H, Me; R′ = Cl, H). Reactions of maleic anhydride with some of the above (η^1-allyl)palladium complexes afford 1:1 adducts arising from formal [2 + 3] cycloaddition. The molecular structure of an adduct, $PdCHCH_2CHC(O)OC(O)CHCH_2](C_6F_5)((Z)\text{-}Ph_2PCH{=}CHPPh_2)$, has been determined by X-ray crystallography. Crystal data: triclinic, space group $P\bar{1}$, a = 9.526 (3) Å, b = 14.218 (5) Å, c = 14.122 (5) Å, α = 70.47 (3)°, β = 96.48 (3)°, γ = 92.64 (3)°, and Z = 2. The palladium and the carbonyl substituents are located trans to each other with respect to the five-membered ring. Possible pathways to the cycloadduct are discussed in terms of this stereoselectivity.

The chemistry of (η^1-allyl)metal compounds is receiving increasing attention from both synthetic and physicochemical points of view. The main-group metal derivatives are especially versatile reagents for the introduction of an allylic unit at electrophilic centers. Even though synthetic application of the transition-metal analogues is somewhat less developed, the η^1-allyl complexes of certain elements, e.g., Fe, are known to exhibit unique reactivities toward unsaturated electrophiles which appear to be difficult to realize in the main-group metal counterparts (e.g., [2 + 3] cycloaddition).[1,2]

The high reactivity of the η^1-allyl complexes toward electrophiles has been discussed in terms of electronic factors which contribute toward activation of the ground-state electronic structure, e.g., σ–π conjugation,[4] or to stabilization of the transition-state (or intermediate) structure, e.g., β-metallocarbonium ion **1**[5] or cationic olefin–metal complex **2**.[1] In this regard it seems of particular



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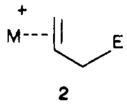

2

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[1] (a) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122. (b) Wojicki, A. *Ann. N. Y. Acad. Sci.* **1974**, *239*, 100.

[2] Recent works revealed that more reactive allenylsilanes undergo similar [2 + 3] cycloaddition.[3]

[3] Danheiser, R. L.; Kwasigroch, C. A.; Tsai, Y. M. *J. Am. Chem. Soc.* **1985**, *107*, 7233 and references therein.

[4] (a) Brown, R. S.; Eaton, D. F.; Hosomi, A.; Traylor, T. G.; Wright, J. M. *J. Organomet. Chem.* **1974**, *66*, 249 and references therein. (b) Schweig, A.; Weidner, U.; Manuel, G. *Ibid.* **1974**, *67*, C4.

[5] Negishi, E. *Organometallics in Organic Synthesis*; Wiley: New York, 1980; Vol. 1, p 416.

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Table I. ^{1}H NMR Data[a] of (η^1-Allyl)palladium Complexes

		olefin protons[b]				
	$PdCH_2$	H^1	H^2	H^3	Me	isomer
3a	2.88 (q, $J_H = J_P = 9$)	6.27 (m)	4.07 (br d, $J_H = 16$)	4.47 (br d, $J_H = 11$)		
3b	2.91 (q, $J_H = J_P = 8$)	5.88 (m)	4.65 (br m)		1.51 (br)	*E*
				5.1 (v br)	1.32 (t, $J_H = J_P = 6$)	*Z*
3d	2.93 (q, $J_H = J_P = 8$)	5.97 (br m)	4.9 (v br)		1.55 (t, $J_H = J_P = 6$)	*E*
					1.42 (t, $J_H = J_P = 6$)	*Z*
3e	2.98 (q, $J_H = J_P = 8$)	6.15 (br m)	4.28 (br d, $J_H = 17$)	4.44 (br d, $J_H = 10$)		

[a] In toluene-d_8 at −20 °C (**3a**, **3e**) or in benzene-d_6 at 25 °C (**3b**, **3d**). Chemical shifts in ppm; *J* in Hz. The resonances due to the phosphine ligands are not shown. [b] Proton numbering scheme:

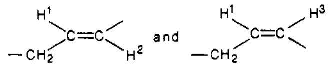


Table II. Reactions of (η^1-Allyl)- and (η^3-Allyl)palladium Complexes with Electrophiles[a]

complex	E–X[b]	product (% yield)[c]
3a	H–Cl	$CH_2{=}CHCH_3$ (90)
	Br–Br	$CH_2{=}CHCH_2Br$ (60)
	Br–suc	$CH_2{=}CHCH_2Br$ (67)
3b	H–Cl	$CH_2{=}CHCH_2CH_3$ (80)
	Br–suc	$CH_2{=}CHCH(CH_3)Br$ (90)
3d[d]	Br–suc	$CH_2{=}CHCH(CH_3)Br$ (84)
4a	H–Cl	C_6F_5H (87)
	Br–Br	C_6F_5Br (73)
	Br–suc	C_6F_5Br (70)
4b	Br–suc	C_6F_5Br (84)

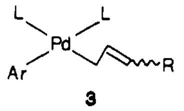
[a] In chloroform at room temperature except as noted. [b] suc = $\overline{NC(O)CH_2CH_2C}(O)$. [c] By GLC and ^{1}H NMR spectra. [d] In dichloromethane.

interest to know the reactivity pattern of (η^1-allyl)palladium(II) complexes, for the η^3-allyl group bound to Pd(II) is well-known to undergo facile attack of *nucleophiles*. This is the primary basis for extensive applications of (η^3-allyl)palladium chemistry in synthesis.[6] Very little is known, however, about the chemistry of the (η^1-allyl)palladium complexes. It appears that the reason for the paucity of such knowledge comes in part from the very limited number of well-characterized, structurally rigid η^1-allyl complexes of Pd(II) available.

The (η^1-allyl)palladium species have long been known to be formed upon treatment of η^3-allyl complexes with donor ligands, mostly as only a transient intermediate in dynamic NMR spectral aspects.[7] Some years ago we isolated unusually rigid η^1-allyl complexes of type **3**.[8] We report here that the allyl moiety of **3** reacts with some electrophiles with much greater ease than the η^3-bound allyl group of analogous complexes of type **4**.[9] During the course of the present study other workers reported some reactivities of another type of (η^1-allyl)palladium complexes **5** toward electrophiles.[12] However, it seems ambiguous in principle to determine whether it is the η^1- or the η^3-allyl part of **5** that has actually undergone the reaction with the electrophile. The different type of (η^1-allyl)platinum(II) complexes has previously been reported to undergo [2 + 3] cycloaddition with tetracyanoethylene.[13]

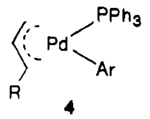
Results and Discussion

Synthesis and NMR Spectra of (η^1-Allyl)palladium Complexes. Complexes **3b**, **3d**, and **3e** were synthesized by the reaction of **4a**, **4b**, and **4d** with bis(diphenylphosphino)ethane (dppe) and -ethylene (dppen) in a manner similar to that used for **3a** and **3c**.[8] ^{1}H NMR spectral data of **3** are shown in Table I. Unambiguous ^{1}H NMR spectral assignments for **3c** have already been described.[8]



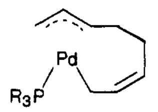
3

	L_2	Ar	R
a	dppe	C_6F_5	H
b	dppe	C_6F_5	Me
c	dppe	C_6HCl_4-2,3,5,6	H
d	dppe	C_6HCl_4-2,3,5,6	Me
e	dppen	C_6F_5	H



4

	Ar	R
a	C_6F_5	H
b	C_6F_5	Me
c	C_6HCl_4-2,3,5,6	H
d	C_6HCl_4-2,3,5,6	Me



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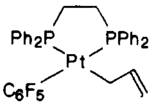

6

The resonances due to the Pd—CH_2 and C=CH_2 protons of **3e** (see Table I) became very broad at room temperature, and these coalesced to a broad doublet (δ 3.63 (J_H = 11 Hz)) at 70 °C. The chemical shift of the -C*H*=C proton resonance remained at ca. 6.1 ppm from −20 up to 70 °C, and this resonance appeared as a quintet at 70 °C. The variable-temperature (−20 to +70 °C) spectra of **3a** showed a similar feature. The IR spectrum of **3e** in solution clearly showed a band attributable to the terminal C=C bond, as in the spectra of **3a** and **3c** described previously.[8] These observations may be explained by rapid interconversion of the Pd—CH_2 and C=CH_2 protons of **3a** and **3e** on the NMR time scale at the higher temperatures, probably via an (η^3-allyl)palladium intermediate. The spectra of another η^1-allyl complex **3c** did not change up to 70 °C except that the coupling of Pd–CH_2 protons with ^{31}P had disappeared.

The spectra of the crotyl complexes **3b** and **3d** also showed no significant change up to 70 °C except for the

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(6) (a) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: New York, 1980. (b) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385.

(7) Vrieze, K. *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 441.

(8) Numata, S.; Okawara, R.; Kurosawa, H. *Inorg. Chem.* **1977**, *16*, 1737.

(9) Part of the present work was reported in a communication.[10] The X-ray work was also a portion of another communication.[11]

(10) Kurosawa, H.; Urabe, A. *Chem. Lett.* **1985**, 1839.

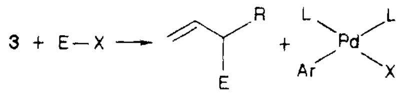
(11) Kurosawa, H.; Emoto, M.; Urabe, A.; Miki, K.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 8253.

(12) (a) Benn, R.; Jolly, P. W.; Mynott, R.; Raspel, B.; Schenker, G.; Schick, K. P.; Schroth, G. *Organometallics* **1985**, *4*, 1945. (b) Benn, R.; Gabor, G.; Jolly, P. W.; Mynott, R.; Raspel, B. *J. Organomet. Chem.* **1985**, *296*, 443.

(13) Calligaris, M.; Carturan, G.; Nardin, G.; Scrivanti, A.; Wojicki, A. *Organometallics* **1983**, *2*, 865.

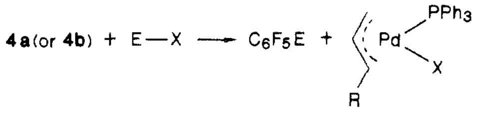
occurrence of gradual decomposition of the complexes and disappearance of the couplings with ^{31}P nuclei. Notable here is that **3b** and **3d** exist as only a 2-butenyl isomer (E/Z = ca. 2/1 and 3/1),[14] but not as a 1-methyl-2-propenyl isomer.

Comparison of (η^1-Allyl)- and (η^3-Allyl)palladium Complexes in Reactions with Electrophiles. The η^1-allyl complexes of type **3** reacted rapidly at room temperature with an equimolar amount of HCl, Br_2, and N-bromosuccinimide (NBS) to give good yields of products from electrophilic allylic substitution (eq 1; E = H, Br)


(1)

(Table II). Importantly, the products from **3b** and **3d** were almost exclusively the isomers of the formula $CH_2{=}CHCH(E)Me$ (E = H, Br), demonstrating the direct attack of the electrophile at the C=C bond of the η^1-allyl group. The previous work also assumed similar electrophilic substitution of (η^1-allyl)palladium species.[12] However, the position of the attack of the electrophile was not established definitely.

Quite in contrast to eq. 1 is the selective Pd–C_6F_5 bond cleavage in reactions of **4a** and **4b** with HCl, Br_2, or NBS (1:1 ratio) under the similar conditions, giving rise to good yields of C_6F_5E (E = H, Br) (eq 2) (Table II). In the


(2)

reaction of eq 2 the electrophile may have attacked either at the Pd atom first or directly at the C_6F_5–Pd bond. The former path may have induced a considerable decrease of the electron density on the Pd atom. If this happens to be the actual path, then the subsequent step to afford C_6F_5E is contrasted to a different reactivity pattern exhibited by an apparently analogous type of intermediate; that is, the facile and selective reductive elimination affords $CH_2{=}CHCH_2C_6F_5$ from an intermediate having a similarly electron-deficient Pd atom which is formed by complexation of **4a** with olefinic electrophiles such as maleic anhydride (MA).[11,15] The position of the attack of MA seems also different in the reactions with **4a** (Pd atom) and with **3a** (allylic C=C terminal; see later).

Cleavage of the Pd–allyl bond of **4a** occurred when **4a** was treated with Br_2 or NBS in the presence of more than 5 molar quantities of $[Ph_4P]Br$; $CH_2{=}CHCH_2Br$ (60%) and C_6F_5Br (12%) were obtained with Br_2/Br^- and $CH_2{=}CHCH_2Br$ (94 %) and C_6F_5Br (trace) with NBS/Br^-. The reaction of **4b** with NBS/Br^- gave not only $CH_2{=}CHCHMeBr$ (41 %) but also $MeCH{=}CHCH_2Br$ (17%),[16] this pattern being different from the selective formation of the former product in the reaction of eq 1. It is possible that the bromide ion has attacked at the η^3-allyl ligand bound to the electron-deficient Pd atom which has been generated by the action of the electrophile; similar oxidant-promoted nucleophilic attack at the η^3-allyl group has been confirmed kinetically in the paraquinone-mediated nucleophilic substitution of (η^3-allyl)palladium complexes.[17]

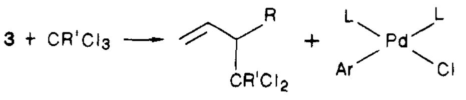
Table III. Reactions of (η^1-Allyl)palladium Complexes with $CR'Cl_3$[a]

complex	R′	time, h	product (% yield)[b]
3a	Cl	5	$CH_2{=}CHCH_2CCl_3$ (75)
3b	Cl	5	$CH_2{=}CHCH(CH_3)CCl_3$ (70)
3c	H	24	$CH_2{=}CHCH_2CHCl_2$ (73)
	Cl	1	$CH_2{=}CHCH_2CCl_3$ (90)
3d	H	24	$CH_2{=}CHCH(CH_3)CHCl_2$ (70)
	Cl	5	$CH_2{=}CHCH(CH_3)CCl_3$ (85)

[a] In dichloromethane at room temperature. Condition: [**3**] = 0.1 mol/L, $[CCl_4]$ = 1.5 mol/L, or $[CHCl_3]$ = 4.0 mol/L. [b] By ^{1}H NMR spectra.

However, more work, including stereochemical examination, is necessary before any definitive explanation for the behavior of **4** in its reactions with electrophiles is presented.

Reaction of (η^1-Allyl)palladium Complexes with Halomethanes. Complexes **3c** and **3d** underwent formal electrophilic substitution of the allylic unit with CCl_4 and $CHCl_3$ in dichloromethane solution under very mild conditions (eq 3) (Table III). **3a** and **3b** also reacted with CCl_4


(3)

in similar fashion. However, the reaction of these complexes with $CHCl_3$ was slower and afforded no significant amounts of coupling products after longer reaction periods. In this reaction a low yield of propene or 1-butene was formed, but the major portion of products remains to be identified. Propene and 1-butene were also formed as byproducts in the reaction of **3c** and **3d** with $CHCl_3$.

The η^3-allyl complexes **4** did not react with CCl_4 and $CHCl_3$ under conditions identical with those used in eq 3. Nor did the platinum analogue **6** react at all with CCl_4 under similar conditions. Only after very long periods (more than a week) did a small amount of propene begin to appear.

Some (η^1-allyl)tin compounds have previously been found to undergo S_H2' reaction with haloalkanes in the presence of radical initiators (≥80 °C) or under photoirradiation (at room temperature).[18] The present reaction required no such initiator or irradiation even at room temperature, but the course of the reaction with CCl_4, which was followed by ^{1}H NMR spectroscopy, clearly involved short induction periods. Unfortunately, the duration of the latter was found to depend on which batch of crystals of **3** was used in the reactions. **3b** and **3d** afforded only the isomer of formula $CH_2{=}CHCH(Me)CR'Cl_2$. Thus, the presently available results suggest that the reaction of eq 3 also proceeds via a radical chain, S_H2' pathway, similar to that proposed in the tin case.

[2 + 3] Cycloaddition of (η^1-Allyl)palladium Complexes with Maleic Anhydride. The fact[15,19] that reductive elimination of **4** to afford the coupling products is accelerated by the action of maleic anhydride (MA) prompted us to examine the reaction of **3** with this olefin. All of **3** examined reacted with MA very rapdily, but in no cases was the reductive elimination observed to occur. Instead, the reaction of **3a** and **3e** gave rise to 1:1 adducts in ca. 60 and 30% yield (by NMR) which may be formulated as **7** (see later). Other products included propene

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[14] These ratios are similar to that of $Pd(CH_2CH{=}CHMe)(C_6H_3Cl_2\text{-}2,5)(dppe)$ (E/Z = ca.2/1) which affords, via reductive elimination, $MeCH{=}CHCH_2C_6H_3Cl_2\text{-}2,5$ having the almost identical E/Z ratio.[15]

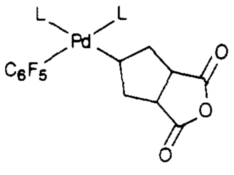
[15] Kurosawa, H.; Emoto, M., unpublished results.

[16] It was confirmed separately that isomerization of $CH_2{=}CHCHMeBr$ to $MeCH{=}CHCH_2Br$ is much slower under the conditions employed.

[17] Bäckvall, J. E.; Nystrom, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 3676 and references therein.

[18] (a) Grignon, J.; Servens, C.; Pereyre, M. *J. Organomet. Chem.* **1975**, *96*, 225. (b) Kosugi, M.; Kurino, K.; Takayama, K.; Migita, T. *Ibid.* **1973**, *56*, C11.

[19] Numata, S.; Kurosawa, H. *J. Organomet. Chem.* **1977**, *131*, 301.



7a, L_2 = dppe
b, L_2 = dppen

which amounted to ca. 50% in the case of **3e**. **3c** and MA also gave propene in a high yield, formation of a small amount of the cycloadduct of the type **7** having been confirmed only by ^1H NMR spectroscopy. Similarly, 1-butene was the major product in the reaction of **3b** with MA from which no characterizable metal-containing products could be separated. **3a** and **3e** did not react with dimethyl fumarate and maleate under similar conditions.

The reaction of the platinum analogue **6** and $Pt(\eta^1\text{-}C_3H_5)(C_6F_5)(PPh_3)_2$[8] with MA gave propene predominantly. Interestingly, MA also induced the generation of methane from the methylplatinum(II) analogue $PtMe(C_6F_5)(dppe)$, even though the reaction rate was much slower than that of **6**.

Molecular Structure of 7b. A perspective view of the molecular structure is depicted in Figure 1 (ORTEP-II drawing).[20] Bond lengths and angles are listed in Tables IV and V, respectively.

In the bicyclic $C_7H_7O_3$ group, the orientation of the metal and the two carbonyl substituents is mutually trans with regard to the C_5 ring. Three planes defined by C(1), C(2), C(5) (plane A), C(2), C(3), C(4), C(5) (plane B), and C(3), C(4), C(6), C(7), O(1) (plane C) are almost perpendicular to the coordination plane of the Pd atom (82.2°, 80.7°, and 88.6°, respectively). The dihedral angles between plane B and planes A and C are 137.5° and 116.5°, respectively. The C(1)–hydrogen atom is not directed toward the C_6F_5 side but toward the side of the phosphine ligand, which may be due to steric hindrance between the *P*-phenyl group and the C(2)– and C(5)–hydrogen atoms cis to Pd.

The geometry around the Pd atom is square-planar; maximum atomic deviation from the least-squares plane of the Pd, P(1), P(2), C(1), and C(51) atoms is 0.055 Å. The Pd–C(1) bond length falls in the range of the usual Pd(II)–C(sp^3) bonds. The geometry of dppen ligand is very similar to that found in $PdI_2(dppen)$.[21] The C(8) and C(9) atoms almost lie on the coordination plane, deviations from this plane being 0.04 and 0.08 Å, respectively. The Pd–P(1) bond is 0.052 Å longer than the Pd–P(2) bond, which may be caused by the trans influence difference of the $C_7H_7O_3$ and C_6F_5 groups. The C_6F_5 group is also perpendicular to the coordination plane (84.5°). The Pd–C(51) bond length, which is comparable to the Pd–C length in $[Pd(C_6F_5)(PEt_3)_2(S_2CPEt_3)]ClO_4$ (2.057 (12) Å),[22] is slightly shorter than the Pd–C(1) length. This can be interpreted by the difference of the covalent radii of sp^2 and sp^3 carbons.

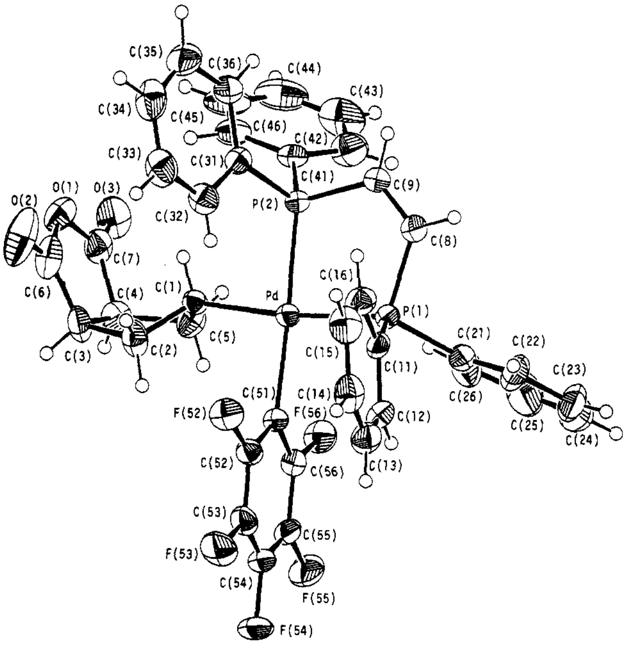
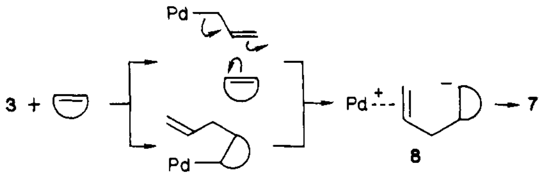


Figure 1. A perspective view of the molecular structure of **7b** with the atomic numbering system. Non-hydrogen atoms are represented by thermal ellipsoids with 30% probability levels, whereas hydrogen atoms are drawn by a sphere with B = 1.0 Å^2.

Table IV. Bond Lengths (Å) and Their Estimated Standard Deviations in Parentheses for Non-Hydrogen Atoms

Pd–C(1)	2.100 (6)	Pd–P(1)	2.3113 (16)
Pd–P(2)	2.2591 (15)	Pd–C(51)	2.077 (6)
C(1)–C(2)	1.511 (9)	C(1)–C(5)	1.526 (9)
C(2)–C(3)	1.559 (11)	C(3)–C(4)	1.519 (11)
C(3)–C(6)	1.471 (12)	C(4)–C(5)	1.549 (10)
C(4)–C(7)	1.502 (11)	C(6)–O(1)	1.374 (11)
C(6)–O(2)	1.180 (13)	C(7)–O(1)	1.377 (10)
C(7)–O(3)	1.165 (10)		
P(1)–C(8)	1.836 (8)	P(1)–C(11)	1.798 (7)
P(1)–C(21)	1.818 (7)	P(2)–C(9)	1.815 (7)
P(2)–C(31)	1.818 (7)	P(2)–C(41)	1.814 (7)
C(8)–C(9)	1.319 (10)		
C(11)–C(12)	1.404 (9)	C(11)–C(16)	1.385 (10)
C(12)–C(13)	1.363 (10)	C(13)–C(14)	1.371 (11)
C(14)–C(15)	1.377 (12)	C(15)–C(16)	1.390 (12)
C(21)–C(22)	1.372 (11)	C(21)–C(26)	1.388 (12)
C(22)–C(23)	1.412 (15)	C(23)–C(24)	1.342 (16)
C(24)–C(25)	1.360 (16)	C(25)–C(26)	1.402 (16)
C(31)–C(32)	1.374 (10)	C(31)–C(36)	1.397 (10)
C(32)–C(33)	1.397 (11)	C(33)–C(34)	1.343 (13)
C(34)–C(35)	1.371 (14)	C(35)–C(36)	1.374 (12)
C(41)–C(42)	1.381 (11)	C(41)–C(46)	1.377 (10)
C(42)–C(43)	1.442 (15)	C(43)–C(44)	1.345 (17)
C(44)–C(45)	1.318 (17)	C(45)–C(46)	1.387 (13)
C(51)–C(52)	1.376 (9)	C(51)–C(56)	1.366 (9)
C(52)–C(53)	1.379 (10)	C(53)–C(54)	1.377 (10)
C(54)–C(55)	1.342 (11)	C(55)–C(56)	1.386 (10)
C(52)–F(52)	1.366 (8)	C(53)–F(53)	1.347 (9)
C(54)–F(54)	1.353 (9)	C(55)–F(55)	1.362 (10)
C(56)–F(56)	1.359 (8)		

Scheme I



Reaction Path to [2 + 3] Cycloadduct. Primarily two routes are possible to the cycloadduct **7** (Scheme I). One involves direct attack of MA at the allylic terminal to give an intermediate **8**, followed by ring closure, as suggested in analogous reactions of (η^1-allyl)iron complexes.[1] The other may proceed via initial coordination of MA to the Pd atom and subsequent insertion[13] of the olefin into the Pd–allyl bond, affording **9**. Then **9** may rearrange to **7** via **8**. Direct ring closure from **9** to **7** seems less likely, since the four-centered transition state for this insertion step

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(20) Johnson, C. K. ORTEP-II, Report ORNL-5138, 1976; Oak Ridge National Laboratory: Oak Ridge, TN.

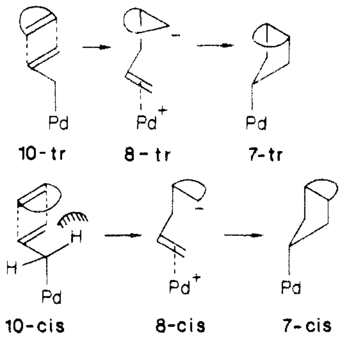
(21) Gray, L. R.; Gulliver, D. J.; Levason, W.; Webster, M. *Inorg. Chem.* **1983**, *22*, 2362.

(22) Uson, R.; Fornies, J.; Navarro, R.; Uson, M. A.; Garcia, M. P.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1984**, 345.

Table V. Bond Angles (deg) and Their Estimated Standard Deviations in Parentheses for Non-Hydrogen Atoms

C(1)–Pd–P(1)	172.70 (16)	C(1)–Pd–P(2)	88.66 (16)
C(1)–Pd–C(51)	91.1 (3)	P(1)–Pd–P(2)	85.08 (6)
P(1)–Pd–C(51)	95.00 (16)	P(2)–Pd–C(51)	177.12 (16)
Pd–C(1)–C(2)	119.2 (5)	Pd–C(1)–C(5)	116.0 (4)
C(1)–C(2)–C(3)	103.0 (6)	C(2)–C(3)–C(4)	105.5 (6)
C(2)–C(3)–C(6)	110.5 (7)	C(4)–C(3)–C(6)	104.1 (7)
C(3)–C(4)–C(5)	106.1 (6)	C(3)–C(4)–C(7)	104.4 (6)
C(5)–C(4)–C(7)	110.4 (6)	C(1)–C(5)–C(4)	103.8 (6)
C(3)–C(6)–O(1)	111.5 (7)	C(3)–C(6)–O(2)	128.9 (9)
O(1)–C(6)–O(2)	119.5 (9)	C(4)–C(7)–O(1)	109.7 (6)
C(4)–C(7)–O(3)	130.4 (8)	O(1)–C(7)–O(3)	119.8 (7)
C(6)–O(1)–C(7)	110.1 (7)		
Pd–P(1)–C(8)	107.1 (3)	Pd–P(1)–C(11)	112.8 (3)
Pd–P(1)–C(21)	122.9 (3)	C(8)–P(1)–C(11)	104.1 (3)
C(8)–P(1)–C(21)	101.8 (4)	C(11)–P(1)–C(21)	106.0 (3)
Pd–P(2)–C(9)	109.5 (3)	Pd–P(2)–C(31)	114.5 (3)
Pd–P(2)–C(41)	117.4 (3)	C(9)–P(2)–C(31)	102.7 (3)
C(9)–P(2)–C(41)	106.1 (3)	C(31)–P(2)–C(41)	105.4 (3)
P(1)–C(8)–C(9)	119.4 (6)	P(2)–C(9)–C(8)	118.6 (6)
P(1)–C(11)–C(12)	121.1 (5)	P(1)–C(11)–C(16)	121.1 (5)
C(12)–C(11)–C(16)	117.4 (6)	C(11)–C(12)–C(13)	121.5 (7)
C(12)–C(13)–C(14)	120.4 (7)	C(13)–C(14)–C(15)	119.7 (8)
C(14)–C(15)–C(16)	120.2 (8)	C(11)–C(16)–C(15)	120.7 (7)
P(1)–C(21)–C(22)	122.5 (6)	P(1)–C(21)–C(26)	117.1 (6)
C(22)–C(21)–C(26)	120.0 (8)	C(21)–C(22)–C(23)	118.9 (9)
C(22)–C(23)–C(24)	121.1 (11)	C(23)–C(24)–C(25)	120.0 (11)
C(24)–C(25)–C(26)	120.7 (11)	C(21)–C(26)–C(25)	118.9 (9)
P(2)–C(31)–C(32)	118.8 (5)	P(2)–C(31)–C(36)	122.3 (5)
C(32)–C(31)–C(36)	118.9 (6)	C(31)–C(32)–C(33)	119.5 (7)
C(32)–C(33)–C(34)	121.1 (8)	C(33)–C(34)–C(35)	120.0 (9)
C(34)–C(35)–C(36)	120.4 (9)	C(31)–C(36)–C(35)	120.0 (7)
P(2)–C(41)–C(42)	119.1 (6)	P(2)–C(41)–C(46)	121.6 (6)
C(42)–C(41)–C(46)	119.0 (7)	C(41)–C(42)–C(43)	117.2 (9)
C(42)–C(43)–C(44)	119.9 (10)	C(43)–C(44)–C(45)	123.4 (12)
C(44)–C(45)–C(46)	117.9 (10)	C(41)–C(46)–C(45)	122.6 (8)
Pd–C(51)–C(52)	120.2 (5)	Pd–C(51)–C(56)	125.7 (5)
C(52)–C(51)–C(56)	114.1 (6)	C(51)–C(52)–C(53)	123.8 (6)
C(52)–C(53)–C(54)	118.9 (7)	C(53)–C(54)–C(55)	119.6 (7)
C(54)–C(55)–C(56)	119.5 (7)	C(51)–C(56)–C(55)	124.0 (6)
C(51)–C(52)–F(52)	119.5 (6)	C(53)–C(52)–F(52)	116.7 (6)
C(52)–C(53)–F(53)	120.6 (7)	C(54)–C(53)–F(53)	120.5 (7)
C(53)–C(54)–F(54)	119.7 (7)	C(55)–C(54)–F(54)	120.7 (7)
C(54)–C(55)–F(55)	120.2 (7)	C(56)–C(55)–F(55)	120.2 (7)
C(51)–C(56)–F(56)	119.5 (6)	C(55)–C(56)–F(56)	116.5 (6)

Scheme II



would contain very large steric constraints.[23]

As only one stereoisomeric adduct, **7-tr** (see Scheme II) was obtained in the reaction of **3** with MA, as demonstrated by X-ray structural determination of **7b**, it is possible that, among two stereoisomers of the intermediate **8** (**8-tr** and **8-cis**), **8-tr** was preferentially formed, or **8-tr** preferentially underwent the ring closure. However, it seems difficult to find a rational basis of the preferential ring closure from **8-tr**. At the moment we think that the preferential formation of **8-tr** is a more likely explanation, as discussed below, provided that the carbanion in **8** attacks at the Pd-bound C=C bond from the anti side[1] and movement of the Pd atom between two diastereo faces of the C=C bond (**8-tr** ⇌ **8-cis**) is sufficiently slow.

We propose that there occurs specific orientation of two reactants, **3** and MA, prior to the formation of **8**. Since **3** is a very good donor olefin and MA a very good acceptor, it is feasible that these first form a charge-transfer (CT) complex whose structure may be written as in **10-tr** or **10-cis** (Scheme II).[25] **10-tr** and **10-cis** would readily lead to **8-tr** and **8-cis**, respectively, where an electron-transfer step may or may not intervene. It thus seems reasonable to assume that **10-tr** is sufficiently more stable than **10-cis** to yield **8-tr** preferentially because of less steric constraints. Even though we have no evidence to support the CT complex, the formation of propene and 1-butene in various amounts in some reactions of MA with **3** and **6** described before may well be explained by the electron transfer and M–C bond homolysis which are preceded by the CT complex.[27] The higher reactivity of **6** with MA than of Pt(CH_3)(C_6F_5)(dppe) with MA is in accord with the smaller ionization potential of (η^1-allyl)metal vs. methylmetal complexes.[28]

If the cycloaddition proceeded via the intermediate **9**, then the selection of one diastereo face of the allylic C=C bond by Pd, a requirement for the preferential formation of **8-tr**, must have taken place during the rearrangement step from **9** to **8**. However, there does not appear to exist very strong steric and electronic demand for such diastereo face selection.

Conclusions. The present study has shown that the η^1-allyl group bound to Pd is more susceptible to the attack of electrophiles than the aryl group, which in turn is more reactive than the Pd-bound η^3-allyl group. This reactivity order is not surprising, since there is a change of numbers of electrons to be supplied from the allyl group to Pd ($4 \rightarrow 2$) upon the $\eta^3 \rightarrow \eta^1$-allyl conversion. Moreover, this conversion usually requires coordination of very basic donors (e.g., PR_3) which also helps enhance the electron density on Pd and hence the allylic ligand. Thus, the present results support the participation of η^1-allyl species in the reaction of **4** with proton acids[12a] and electron-deficient olefins[12b] as well as in the CN^--induced intramolecular reaction of the (η^3-allyl)palladium moiety with the C–Cl part.[29] On the other hand, a previously proposed nucleophilic substitution at the Pd-bound η^1-allyl ligand[30] seems rather unusual and may require further scrutiny.

The allylic terminus of **3** is always attacked by the electrophiles employed in this study including $CR'Cl_2$ radicals in the case of the reaction with halomethanes. This trend may have been caused by both steric and electronic effects. Those electronic causes which were mentioned in the introduction may also be responsible for

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(23) The ring closure of similar type appears also very rare in palladium-mediated olefin transformations, e.g., Heck reactions.[24]

(24) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: New York, 1985.

(25) Thermal cycloaddition between good electron-donating and -accepting olefin pairs proceeds through [2s + 2s] stereochemistry owing to dominant contribution of the CT configuration.[26]

(26) (a) Houk, K. N. *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 2, p 181. (b) Epiotis, N. D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 751.

(27) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; p 492.

(28) Fabian, B. D.; Fehlner, T. P.; Hwang, L. S. J.; Labinger, J. A. *J. Organomet. Chem.* **1980**, *191*, 409.

(29) Parra-Hake, M.; Rettig, M. F.; Wing, R. M. *Organometallics* **1983**, *2*, 1013.

(30) Akermark, B.; Akermark, G.; Hegedus, L. S.; Zetterberg, K. *J. Am. Chem. Soc.* **1981**, *103*, 3037.

the high reactivity and selectivity of the (η^1-allyl)palladium complexes.

Experimental Section

Preparation of Pd(η^1-C_4H_7)(C_6F_5)(dppe) (3b). Complex **4b** was prepared as colorless crystals in a manner similar to that for **4a** described before;[8] mp 130–133 °C dec. Anal. Calcd for $C_{28}H_{22}F_5PPd$ C, 56.92; H, 3.75. Found: C, 56.86; H, 3.88. Then a benzene solution (5 mL) of **4b** (200 mg, 0.34 mmol) was added dropwise to dppe (136 mg, 0.34 mmol) in benzene (5 mL) cooled at 5 °C. The color changed to pale yellow, and the solvent was evaporated under vacuum to half volume. *n*-Hexane (15 mL) was added to give an almost colorless precipitate. This was extracted with 50 mL of diethyl ether, and the ether extract was evaporated under vacuum. The residual solid was recrystallized from benzene–*n*-hexane to give pale-yellow crystals (90 mg, 36%), mp 120–123 °C dec. Anal. Calcd for $C_{36}H_{31}F_5P_2Pd$: C, 59.48; H, 4.30. Found: C, 59.37; H, 4.23.

Preparation of Pd(η^1-C_4H_7)(C_6HCl_4-2,3,5,6)(dppe) (3d). This complex was prepared in a similar manner from **4d**[19] and dppe; mp 120–123 °C dec. Anal. Calcd for $C_{36}H_{32}P_2Cl_4Pd$: C, 55.81; H, 4.16. Found: C, 55.92; H, 4.28.

Preparation of Pd(η^1-C_3H_5)(C_6F_5)(dppen) (3e). This was also prepared similarly; mp 145–148 °C dec. Anal. Calcd for $C_{35}H_{27}F_5P_2Pd$: C, 59.13; H, 3.83. Found: C, 59.55; H, 3.93. IR (benzene): 1605 cm^{-1} (C=C).

Preparation of Pt(η^1-C_3H_5)(C_6F_5)(dppe) (6). This was prepared similarly to the palladium analogues described above; mp 180–183 °C. Anal. Calcd for $C_{35}H_{29}F_5P_2Pt$: C, 52.44; H, 3.65. Found: C, 52.80; H, 3.58. ^1H NMR ($CDCl_3$): δ 2.27 (q, $J_H = J_P = 9$, $J_{Pt} = 91$ Hz, $PtCH_2$), 3.93 (d, $J_H = 17$ Hz, =CHH), 4.07 (d, $J_H = 10$ Hz, =CHH), 5.65 (m, –CH=).

Preparation of Pt(CH_3)(C_6F_5)(dppe). To a THF solution (8 mL) of C_6F_5Li (3.0 mmol) cooled at –78 °C was added Pt(CH_3)Cl(COD)[31] (550 mg, 1.56 mmol) in THF (20 mL). The mixture was stirred for 2 h at –50 °C. The temperature was then gradually raised to –20 °C, and aqueous NH_4Cl solution was added. The solvent was evaporated, and the residue was washed with water and methanol. The solids were dissolved in benzene (20 mL), and dppe (600 mg, 1.5 mmol) was added. The solution was filtered, and *n*-hexane was added to cause crystallization of a colorless powder. This was recrystallized from benzene–*n*-hexane to give colorless plates which showed no decomposition point up to 240 °C. Anal. Calcd for $C_{33}H_{27}F_5P_2Pt$: C, 51.10; H, 3.51. Found: C, 51.38; H, 3.38. ^1H NMR ($CDCl_3$): δ 0.53 (t, $J_P = 7.5$, $J_{Pt} = 66$ Hz, CH_3), 1.8–2.6 (m, PCH_2).

Reaction of 3 with Electrophiles. **3a** (50 mg, 0.07 mmol) was dissolved in chloroform (0.5 mL), and an equimolar amount of HCl in methanol (0.1 mL) was added dropwise. The color changed immediately from pale yellow to colorless. After the formation of propene had been analyzed by ^1H NMR and GLC (Sebacconitrile, 3 mm × 10 m), the solvents were evaporated under vacuum. The resulting residue was recrystallized from CH_2Cl_2–*n*-hexane to give a colorless powder of Pd(C_6F_5)Cl(dppe), mp 185 °C dec. Anal. Calcd for $C_{32}H_{24}F_5P_2ClPd$: C, 54.34; H, 3.42. Found: C, 54.43; H, 3.62. Reactions with other electrophiles shown in Tables II and III were carried out similarly. Organic products were analyzed by ^1H NMR and GLC methods. Metallic products from the reaction of NBS were treated with aqueous LiCl, and the colorless crystals obtained were identical with those of Pd(C_6F_5)Cl(dppe). Pd(C_6F_5)Br(dppe), formed from **3a** and Br_2, was identified by comparing its ^1H NMR and IR spectra with those of the corresponding chloride complex.

Reaction of 4 with Electrophiles. Essentially similar methods to those described for **3** above were employed for reactions of **4a** and **4b** with electrophiles. Metallic products from **4a** and NBS were recrystallized from CH_2Cl_2–*n*-hexane to give pale yellow needles of Pd(η^3-C_3H_5)(suc)(PPh_3)·CH_2Cl_2 (suc = $\overline{NCOCH_2CH_2CO}$), mp 119 °C dec. Anal. Calcd for $C_{26}H_{26}NO_2PCl_2Pd$: C, 52.68; H, 4.39; N, 2.36. Found: C, 52.86; H, 4.57; N, 2.45. ^1H NMR ($CDCl_3$):[32] δ 2.56 (d, $J_H = 12$ Hz, H^1), 3.54–3.8 (m, H^2 and H^5), 4.64 (t, $J_H = J_P = 9$ Hz, H^4), 5.72 (m, H^3), 2.14 (s, suc).

Table VI. Final Atomic Parameters and Their Estimated Standard Deviations in Parentheses for Non-Hydrogen Atoms[a]

atom	*x*	*y*	*z*	B_{eq}, Å^2
Pd	0.21939 (4)	0.23970 (3)	0.21850 (3)	3.4
C(1)	0.0846 (6)	0.2328 (4)	0.3285 (4)	3.5
C(2)	0.0437 (8)	0.1321 (5)	0.3994 (6)	5.5
C(3)	–0.0704 (8)	0.1585 (5)	0.4571 (6)	5.5
C(4)	–0.1397 (6)	0.2530 (5)	0.3842 (5)	4.9
C(5)	–0.0584 (7)	0.2832 (5)	0.2893 (5)	4.9
C(6)	–0.0030 (9)	0.1889 (6)	0.5414 (6)	6.5
C(7)	–0.1138 (8)	0.3282 (6)	0.4379 (6)	5.4
O(1)	–0.0328 (6)	0.2863 (4)	0.5285 (4)	6.3
O(2)	0.0738 (8)	0.1432 (7)	0.6118 (5)	10.8
O(3)	–0.1481 (7)	0.4112 (4)	0.4134 (5)	7.7
P(1)	0.39086 (15)	0.25047 (11)	0.11176 (11)	3.7
P(2)	0.35958 (15)	0.34653 (10)	0.27479 (10)	3.4
C(8)	0.5229 (7)	0.3422 (5)	0.1315 (5)	4.9
C(9)	0.5070 (7)	0.3853 (5)	0.1990 (5)	4.7
C(11)	0.4890 (6)	0.1370 (5)	0.1444 (4)	3.8
C(12)	0.4405 (7)	0.0598 (5)	0.1075 (5)	4.7
C(13)	0.5054 (8)	–0.0306 (5)	0.1405 (6)	5.6
C(14)	0.6207 (8)	–0.0484 (6)	0.2113 (6)	6.0
C(15)	0.6698 (8)	0.0250 (7)	0.2503 (6)	6.3
C(16)	0.6052 (7)	0.1177 (6)	0.2163 (5)	5.2
C(21)	0.3545 (7)	0.2939 (5)	–0.0250 (5)	4.6
C(22)	0.4455 (10)	0.2782 (6)	–0.0869 (5)	6.5
C(23)	0.4115 (13)	0.3173 (7)	–0.1925 (6)	8.8
C(24)	0.2956 (11)	0.3727 (8)	–0.2328 (6)	9.2
C(25)	0.2115 (10)	0.3952 (9)	–0.1718 (7)	9.8
C(26)	0.2373 (8)	0.3540 (7)	–0.0664 (6)	7.5
C(31)	0.4470 (6)	0.2919 (5)	0.4018 (5)	4.0
C(32)	0.4506 (7)	0.1897 (5)	0.4445 (5)	5.1
C(33)	0.5248 (9)	0.1465 (6)	0.5395 (6)	6.6
C(34)	0.5873 (8)	0.2031 (7)	0.5918 (6)	6.9
C(35)	0.5842 (8)	0.3051 (7)	0.5503 (6)	6.6
C(36)	0.5147 (7)	0.3501 (6)	0.4562 (5)	5.1
C(41)	0.2801 (6)	0.4604 (4)	0.2737 (5)	4.2
C(42)	0.2703 (10)	0.5415 (6)	0.1857 (6)	7.0
C(43)	0.1939 (12)	0.6269 (6)	0.1853 (8)	9.4
C(44)	0.1382 (10)	0.6258 (7)	0.2690 (9)	9.1
C(45)	0.1450 (8)	0.5484 (6)	0.3528 (8)	7.2
C(46)	0.2179 (7)	0.4652 (5)	0.3554 (6)	5.1
C(51)	0.0957 (6)	0.1356 (4)	0.1724 (4)	3.7
C(52)	0.1279 (6)	0.0358 (4)	0.2129 (5)	4.1
C(53)	0.0564 (8)	–0.0374 (5)	0.1823 (5)	5.0
C(54)	–0.0587 (7)	–0.0110 (5)	0.1108 (5)	5.3
C(55)	–0.0955 (7)	0.0853 (6)	0.0698 (5)	4.9
C(56)	–0.0185 (7)	0.1567 (5)	0.1012 (5)	4.4
F(52)	0.2359 (4)	0.0050 (3)	0.2882 (3)	5.5
F(53)	0.0961 (6)	–0.1335 (3)	0.2236 (4)	7.3
F(54)	–0.1313 (5)	–0.0819 (4)	0.0809 (4)	7.8
F(55)	–0.2080 (5)	0.1127 (4)	–0.0018 (3)	7.5
F(56)	–0.0605 (5)	0.2529 (3)	0.0559 (3)	5.8

[a] Positional parameters in fraction of the cell edges and B_{eq}[36] in the form of $\exp(-B((\sin\theta)/\lambda)^2)$.

Reaction of 3a and 3e with Maleic Anhydride. To a dichloromethane solution (3 mL) of **3a** (140 mg, 0.20 mmol) kept at 0 °C was added, with vigorous stirring, a solid sample of maleic anhydride (30 mg, 0.30 mmol). The solid dissolved gradually, and the color of the solution changed from pale yellow to almost colorless. After 10 min, *n*-hexane (10 mL) was added to cause deposition of oily substances. The solution was decanted and kept in a refrigerator for 2 days. A colorless powder gradually formed. This was recrystallized from CH_2Cl_2–*n*-hexane to give 49 mg (30%) of 1:1 adduct **7a**, mp 120–125 °C dec. Anal. Calcd for

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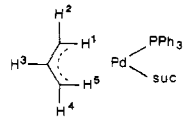
(31) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

(32) Proton numbering scheme:



$C_{39}H_{31}O_3F_5P_2Pd$: C, 57.76; H, 3.85. Found: C, 58.39; H, 4.08. ^1H NMR ($CDCl_3$):[33] δ 3.00 (d, J_H = 7.5 Hz, H^4). The other ring and dppe protons overlapped at 1.4–2.5 ppm. Approximate amounts of **7a** formed in solutions before the isolation process could be evaluated by making use of the H^4 proton resonance.

Another adduct **7b** was prepared in a similar way; mp 165–168 °C dec. Anal. Calcd for $C_{39}H_{29}O_3F_5P_2Pd$: C, 57.90; H, 3.61. Found: C, 57.42; H, 3.61. ^1H NMR ($CDCl_3$, 360 MHz):[33] δ 1.60 (m, H^3), 1.73 (m, H^1), 1.96 (dd, J_H = 4.7 and 12.5 Hz, H^2), 3.01 (d, J_H = 6.9 Hz, H^4).

X-ray Crystal Structure Determination of 7b. Crystal data: triclinic, $P\bar{1}$, a = 9.526 (3) Å, b = 14.218 (5) Å, c = 14.122 (5) Å, α = 70.47 (3)°, β = 96.48 (3)°, γ = 92.64 (3)°; U = 1719.0 (10) Å^3; Z = 2, D_{calcd} = 1.500 Mg m^{-3}; μ(Mo Kα) = 6.66 cm^{-1}; F(000) = 816.

A colorless, prismatic crystal with approximate dimensions of 0.20 × 0.20 × 0.35 mm was mounted on a Rigaku automated, four-circle diffractometer. Unit-cell parameters were determined by a least-squares fit of 24 centered reflections. Intensities were collected with graphite-monochromatized Mo Kα radiation, by the θ–2θ scan technique, scan range $\Delta 2\theta = (1.8 + 0.70 \tan \theta)°$, and scan speed = 4° min^{-1}. Background intensities were measured for 7.5 s at both ends of a scan. Four standard reflections (056, 080, 006, 300) measured after each 60 reflections showed that intensity variation over period of data collection was less than 1%. The usual Lp correction was made, but absorption (maximum μR = 0.15) and extinction corrections were ignored, even though this might have limited the accuracy of the present structure determination. A total of 7792 independent reflections, 1515 of which with $F < 3\sigma(F)$ were classified as unobserved, were collected up to 2θ = 54.0°. R_{int} ($\sum||F_o| - \langle|F_o|\rangle|/|F_o|$) was 0.023, where $\langle|F_o|\rangle$ is the average value of two or more symmetry-equivalent reflections.

The structure was solved by the heavy-atom method. The Pd atom was easily located from the Patterson map. The remaining non-hydrogen atoms were found on a subsequent Fourier map. The refinement was performed by the block-diagonal, least-squares procedure.[34] All the hydrogen atoms were located from a difference Fourier map after convergence with anisotropic thermal parameters of non-hydrogen atoms. Subsequent refinement was continued with isotropic thermal parameters for hydrogen atoms. The weighting scheme used is $w = (\sigma_{cs}{}^2 + a|F_o| + b|F_o|^2)^{-1}$, where σ_{cs} is the standard deviation obtained from the counting statistics and a = 0.0049 and b = 0.0010 were used in the final cycle, although unit weights were employed only at the early stage. Atomic scattering factors were taken from ref 35. The final R and R_w indices were 0.054 and 0.076 for 6277 observed ($|F_o| > 3\sigma(|F_o|)$) reflections, respectively, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2\}^{1/2}$. Final atomic parameters are listed in Table VI.

All the computations were done on an ACOS 850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University. ^1H NMR spectra were obtained on JEOL PS-100 and Bruker WM-360 spectrometers.

Registry No. **3a**, 62415-26-3; **3b**, 103836-51-7; **3c**, 62415-25-2; **3d**, 103851-05-4; **3e**, 99510-85-7; **4a**, 62415-33-2; **4b**, 103836-55-1; **4d**, 63249-53-6; **6**, 103836-52-8; **7a**, 99510-87-9; **7b**, 99510-88-0; $Pt(CH_3)(C_6F_5)$(dppe), 103836-53-9; $Pd(C_6F_5)Cl$(dppe), 65856-99-7; $Pd(C_6F_5)Br$(dppe), 65139-00-6; $Pd(\eta^3\text{-}C_3H_5)$(suc)(pph$_3$), 103836-54-0; $Pt(CH_3)Cl$(COD), 50978-00-2; $CH_2{=}CHCH_3$, 115-07-1; $CH_2{=}CHCH_2Br$, 106-95-6; $CH_2{=}CHCH_2CH_3$, 106-98-9; $CH_2{=}CHCH(CH_3)Br$, 22037-73-6; C_6F_5H, 363-72-4; C_6F_5Br, 344-04-7; $CH_2{=}CHCH_2CCl_3$, 13279-84-0; $CH_2{=}CHCH(CH_3)CCl_3$, 57082-94-7; $CH_2{=}CHCH_2CHCl_2$, 4279-19-0; $CH_2{=}CHCH(CH_3)CHCl_2$, 88226-91-9; C_6F_5Li, 1076-44-4; maleic anhydride, 108-31-6.

Supplementary Material Available: Tables of coordinates of hydrogen atoms, anisotropic temperature factors for non-hydrogen atoms, and equations of least-squares planes (3 pages); a listing of observed and calculated structure factors (16 pages). Ordering informaiton is given on any current masthead page.

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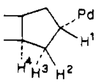
[33] Proton numbering scheme:



[34] Ashida, T. The Universal Crystallographic Computing System-Osaka, The Computation Center, Osaka University, 1979, p 53.

[35] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. 4.

[36] Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.