Reaction of Phosphide-Bridged Palladium(I) Dimers Containing Secondary Phosphines with Ethylene and Isoprene. Coordination vs Insertion

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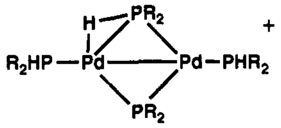
The Pd(I)–Pd(I) dimer $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PHBu^t_2)(PHBu^t_2)_2](CF_3SO_3)$ ($1(CF_3SO_3)$) reacts with excess isoprene, giving $[Pd_2(\mu\text{-}PBu^t_2)(\mu\eta^4\text{-}CH_2{=}CHC(CH_3){=}CH_2)(PHBu^t_2)_2](CF_3SO_3)$ ($2(CF_3SO_3)$). Ethylene reacts with complex 1, giving $[Pd_2(\mu\text{-}PBu^t_2)\{\mu\eta^2\text{-}O_2S(O)CF_3\}(PEtBu^t_2)_2$ (3), which arises from insertion of the olefin into the two secondary phosphine P–H bonds. Complexes 2 and 3 were characterized via X-ray diffraction and multinuclear, multidimensional NMR spectroscopy. Relevant crystallographic parameters are as follows: for 2, space group *Pbca*, $a = 17.321(4)$ Å, $b = 22.115(3)$ Å, $c = 21.531(9)$ Å, $V = 8205(4)$ Å^3, $Z = 8$; for 3, space group $Cmc2_1$, $a = 15.435(3)$ Å, $b = 18.142(9)$ Å, $c = 14.833(4)$ Å, $V = 4154(2)$ Å^3, $Z = 4$.

Introduction

There is a continuing interest[1] in the chemistry of the three-center M---H–C bonds often called "agostic". In a recent study[2] we have reported the preparation of cation 1, as the $CF_3SO_3^-$ salt, which contains the first example of an M---H–P agostic bond. This 3c–2e Pd–H–P interaction is unprecedented in phosphine coordination chemistry. Since agostic bonds are relatively weak, the reaction of 1 with a ligand could lead to complexes such as **A**, as shown in Scheme I, where the novel bond is broken and one of the bridging ligands is converted to a terminal secondary phosphine.



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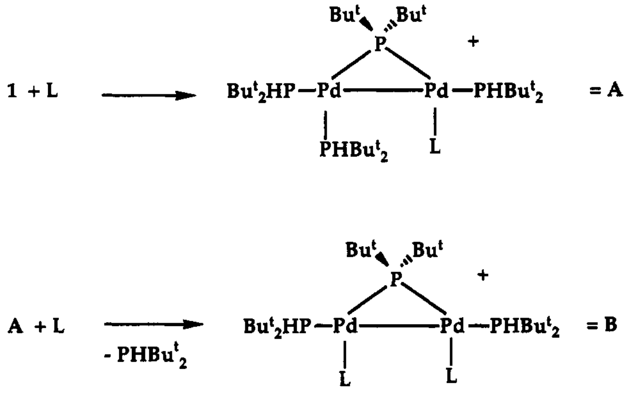
The crowding in complex **A** might lead to the transformation of **A** to **B**, also shown in Scheme I. This would effectively permit synthetic access to a wide variety of palladium(I) dimers with differing L ligands, or put in a different fashion, the agostic bridging phosphine can be viewed as a labile, 4e protecting group for the Pd–Pd bond.

Initial support for this view came from our previously reported[3] reaction of 1 with CO to afford the complex **B** (and a second isomer) with L = CO. We report here an extension of the chemistry of 1, namely reactions with the olefins ethylene and isoprene.

Scheme I



Complexes A and B as $CF_3SO_3^-$ salts

Results and Discussion

Reaction with Isoprene. The reaction of 1 with isoprene, $CH_2{=}CHC(CH_3){=}CH_2$, in dimethoxyethane, as shown in eq 1, afforded complex 2 as a yellow crystalline $CF_3SO_3^-$ salt.

$$1^+(CF_3SO_3)^- + CH_2{=}CHC(CH_3){=}CH_2 \rightarrow 2^+(CF_3SO_3)^- + PHBu^t_2 \quad (1)$$

The solution structure proof for 2 is not straightforward. The ^{31}P NMR spectrum affords an ABX spin system with chemical shifts of 41.8, 43.5, and 372.1 ppm, respectively,

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[1] Brookhart, M.; Green, M. L. H.; Wong, L.-L. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley-Interscience: New York, 1988; Vol. 36, p 1.

[2] Albinati, A.; Lianza, F.; Pasquali, M.; Sommovigo, M.; Leoni, P.; Pregosin, P. S.; Ruegger, H. *Inorg. Chem.* 1991, *30*, 4690.

[3] Leoni, P.; Pasquali, M.; Sommovigo, M.; Albinati, A.; Lianza, A.; Pregosin, P. S.; Rüegger, H. *Organometallics* 1993, *12*, 1702.

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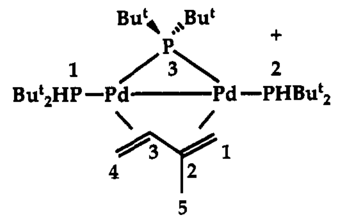


2

thereby confirming[4] the presence of one bridging and two nonequivalent terminal phosphorus ligands. Obviously, one phosphorus ligand has dissociated. The assignment of the phosphorus, proton, and carbon signals follows from detailed 2-D P,H and C,H correlations plus a ^1H 2-D NOESY study. These measurements are required for the following reasons.

1. The various isoprene protons can be assigned using NOE and C,H correlation data combined with a classical use of proton–proton vicinal and geminal coupling constants. The C,H correlation (see Figure 1) is especially valuable, as it pinpoints the methine isoprene CH= carbon, thereby providing a starting point for the assignment. These measurements show that the coordinated isoprene has the *trans* configuration and that the complex does *not* contain a π-allyl ligand.

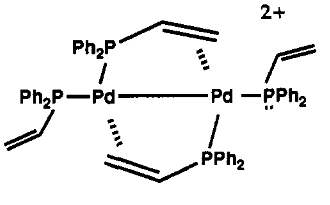
2. With these proton data and a P,H correlation, one can now assign the nonequivalent terminal phosphorus resonances, as the two ^{31}P spins couple selectively to the olefin protons H_1^E and H_4^E, respectively (see Figure 2). This allows the two (very similar, but nonetheless different) secondary phosphine protons, as well as the various *tert*-butyl groups, to be recognized by the same P,H correlation.

3. With a complete assignment of the protons, a C,H correlation identifies all of the protonated carbons.

A summary of all the multinuclear NMR data can be found in Table I; however, it is worth noting that the isoprene olefin carbons resonate at very different positions (ppm): 105.9, C2; 90.0, C3; 63.6, C1; 48.8, C4.

X-ray Structure for 2. As there are relatively few[5] olefin complexes of Pd(I), we have determined the structure of 2 by X-ray diffraction and show an ORTEP plot of the molecule in Figure 3. Selected bond lengths and bond angles for 2 are given in Table II. The immediate coordination sphere of each palladium comprises the Pd–Pd bond, a terminal secondary phosphine phosphorus, a bridging phosphide phosphorus, and one of the two double bonds of the isoprene.

The Pd–Pd bond length at 2.751(2) Å is one of the longest of its kind[4] and is comparable to that found in the vinyl phosphine complex[5]



Pd-Pd	Pd-P
2.748(2)	2.328(6) T
	2.255(2) B

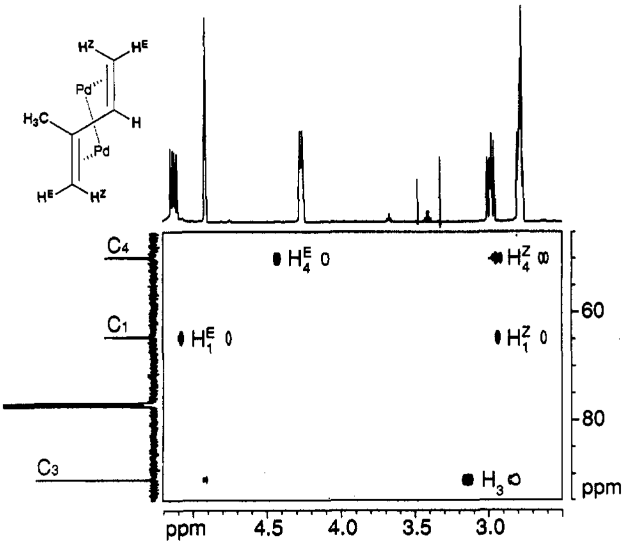


Figure 1. Section of the 11.7-T $^{13}C,^1H$ multiple quantum correlation spectrum of 2, showing the assignment of the isoprene protons. There is $^{13}C,^1H$ coupling in the ^1H direction, with the open and filled-in cross peaks indicating the phases for each of the two ^{13}C spin states. Note that C_3 correlates to a single proton at δ 2.96, whereas C_1 and C_4 each show cross peaks for two protons.

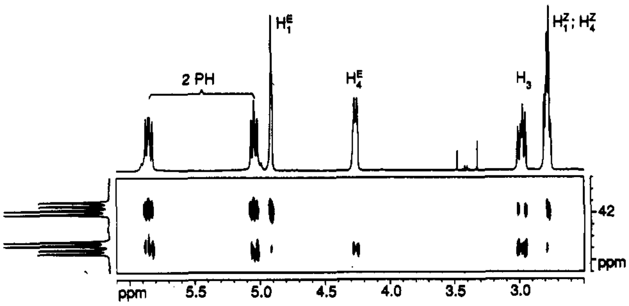


Figure 2. Section of the 9.4-T $^{31}P,^1H$ multiple quantum correlation spectrum of 2. For the annotation of the isoprene protons see Figure 1.

In 2 the two Pd–P separations for the terminal phosphines, 2.302(6) and 2.311(6) Å, are identical within the experimental error and, again, are in good agreement with the model vinyl phosphine complex. The Pd olefin–carbon separations are as follows: Pd(2)–C(1), 2.22(3) Å; Pd(2)–C(2), 2.30(3) Å; Pd(1)–C(3), 2.28(3) Å; Pd(1)–C(4), 2.21(2) Å.

The angles about the two palladium atoms are as expected, e.g., Pd(1)–P(3)–Pd(2) = 74.5(1)°, Pd(2)–Pd(1)–P(1) = 162.7(2)°, Pd(1)–Pd(2)–P(2) = 161.9(2)°, and Pd(1)–Pd(2)–P(3) = 52.7(1)°. The two Pd atoms and the three P atoms lie in a plane, and the terminal secondary phosphine ligands bend ca. 9° toward the phosphide on isoprene coordination. As noted above, the coordinated isoprene has two double bonds in a *trans* configuration. The plane defined by the five isoprene carbons is (a) at an angle of 87.7(9)° to the plane defined by the two metals and the bridging phosphorus and (b) equidistant from both palladium atoms.

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[5] Wilson, W. L.; Nelson, J. H.; Alcock, N. W. *Organometallics* **1990**, *9*, 1699.

Table I. Selected NMR Data for the Complexes

	δ (ppm)	*J* (Hz)
		Compound **2**[a]
P^2	41.8	$J(P,P) = 25.1, 56.0$
P^3	372.1	$J(P,P) = 25.1, 27.7$
P^1	43.4	$J(P,P) = 27.7, 56.0$
HP^2	5.47	$J(P,H) = 323.8$
HP^1	5.42	$J(P,H) = 322.0$
H^{1E}	4.90	$J(P,H) = 3.0, 3.0$
H^{1Z}	2.75	$J(P,H) = 5.2$
H^3	2.96	$J(P,H) = 2.1, 2.1; J(H,H) = 14.6, 8.7$
H^{4E}	4.25	$J(P,H) = 3.2, 3.2; J(H,H) = 8.7$
H^{4Z}	2.75	$J(P,H) = 5.4; J(H,H) = 14.6$
$CH_3{}^5$	0.67	$J(P,H) = 1.5$
C^1	63.6	$J(P,C) = 10.6, 1$
C^2	105.9	
C^3	90.0	
C^4	48.8	$J(P,C) = 8.2, 1$
$CH_3{}^5$	18.3	
		Compound **3**[b]
P^1	45.2	$J(P,P) = 107.8$
P^3	306.7	$J(P,P) = 107.8$
CH_2	1.61	
CH_3	1.21	
CH_2	17.0	$\lvert {}^1J(P,C) + {}^4J(P,C) \rvert = 8.5$
CH_3	12.7	$\lvert {}^2J(P,C) + {}^5J(P,C) \rvert = 3.0$
^{19}F	−76.9	

[a] ^1H Bu^t groups: P^2, 1.35 ppm (14.7 Hz), 1.36 (14.5); P^3, 1.26 (14.0), 1.25 (14.0); P^1, 1.33 (14.6), 1.36 (14.7). ^{13}C Bu^t groups: $P^{1,2}$ quaternary, 34.6 ppm (16.2), 34.2 (16.3), 34.1 (16.8), 34.0 (17.1); CH_3, 31.3, 31.2, 31.0, 30.9 (all coupling constants are ca. 5 Hz); P^3 quaternary, 40.7 (3.5), 39.8 (3.5); CH_3 = 32.8 (5.0) for both. [b] The bridging P is defined as P^3 for consistency (a) with the X-ray data and (b) with **2**. ^1H Bu^t groups: P^1, 1.23 ppm, P^3 = 1.48. ^{13}C Bu^t groups: P^1 quaternary, 34.9 ppm (ΣJ = 6.8); CH_3, 30.4 (ΣJ = 7.2); P^3, 39.4 (6.9), CH_3, 31.8 (9.7).

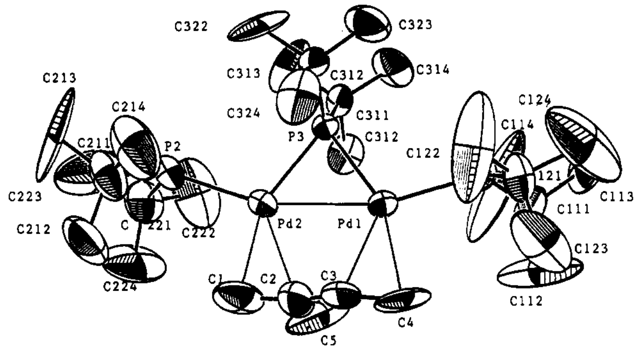
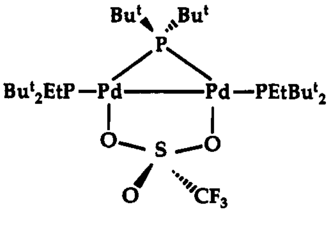


Figure 3. ORTEP plot for 2. Ellipsoids are drawn at 50% probability.

Reaction with Ethylene. When ethylene is bubbled through a dimethoxyethane suspension of **1**, a slow reaction takes place, which after workup affords red crystals of **3**, as shown in eq 2.

$$1^+(CF_3SO_3)^- + CH_2{=}CH_2 \rightarrow 3 + PHBu^t_2 \qquad (2)$$



3

The new complex **3** was readily characterized in solution via multinuclear NMR methods. The ^{31}P NMR spectrum revealed an A_2X spin system with the X spin at 306.7 ppm and the A spins at 44.2 ppm. As with **2**, these positions identify the former as a bridging phosphide[4] and the latter as terminal phosphines. Again, as there are only three ^{31}P spins, a phosphorus ligand has been displaced. In addition to the different *tert*-butyl ^1H resonances, in the ratio of 1:2 (18:36 relative to two ethyl groups), one finds CH_2 and CH_3 proton signals at 1.61 and 1.19 ppm, respectively, with the former as a multiplet and the latter (almost obscured by a *tert*-butyl signal, but resolved at 500 MHz) as a slightly distorted triplet. The *tert*-butyl protons of the $PEtBu^t_2$ ligands show the expected[6] second-order character. The presence of the ethyl group on phosphorus becomes clear from the ^{13}C data. The ^{13}C DEPT spectrum indicates a methylene and a methyl, and both of these signals appear as *triplets* as a consequence of the second-order spin system (virtual coupling).[7,8] A proton–carbon 2-D correlation ties the appropriate spins together so that the various spectra can be assigned with confidence. There is no indication of either coordinated ethylene or P–H signals from secondary phosphines. The ^{19}F spectrum shows a singlet at −76.9 ppm. Effectively, the $CH_2{=}CH_2$ molecules have been inserted into the P–H bonds of the two *coordinated* secondary phosphine ligands. If the solution structure were **3**, as written, one would expect nonequivalent Bu^t methyl signals within each PBu^t_2 moiety, and this is not observed. Consequently, it is likely that the triflate is dynamic (presumably the uncomplexed S–O oxygen exchanges with the two coordinated O atoms, thereby causing the CF_3 to change its position with respect to the Bu^t groups).

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) for 2

Pd1–Pd2	2.751(2)	Pd1–C4	2.21(2)
Pd1–P1	2.302(6)	Pd2–C1	2.22(3)
Pd1–P3	2.272(5)	Pd2–C2	2.30(3)
Pd2–P2	2.311(6)	C1–C2	1.30(4)
Pd2–P3	2.271(5)	C2–C3	1.23(4)
Pd1–C4	2.21(2)	C3–C4	1.37(4)
Pd1–C3	2.28(3)	C2–C5	1.66(4)
P1–Pd1–Pd2	162.7(2)	C1–C2–C3	137(3)
P2–Pd2–Pd1	161.9(2)	C2–C3–C4	143(3)
P1–Pd1–P3	110.0(2)	C1–C2–C3	137(2)
P2–Pd2–P3	109.1(2)	C1–C2–C5	115(3)
Pd1–P3–Pd2	74.5(2)		

X-ray Structure of 3. The structure for **3** was determined by X-ray diffraction methods, and an ORTEP view of the molecule is shown in Figure 4. The local coordination sphere about each palladium consists of a Pd–Pd bond, a terminal phosphine, a bridging phosphide phosphorus, and one of the three oxygens of the bridging $CF_3SO_3^-$ anion. The bridging nature of this last anion is obvious from the structure but could only be presumed from the ^{19}F NMR data on the basis of the observed symmetry in the ^{31}P spectrum.

The Pd–Pd bond separation (2.648(2) Å) is consistent with a metal–metal single bond and falls in the middle of the known range for this distance.[2–4,9] The terminal tertiary phosphine Pd–P bond length (2.378(6) Å) is slightly long,[10] several hundreths of an angstrom longer

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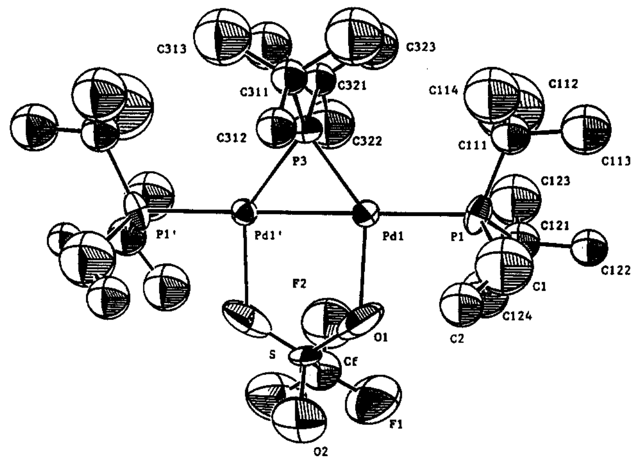
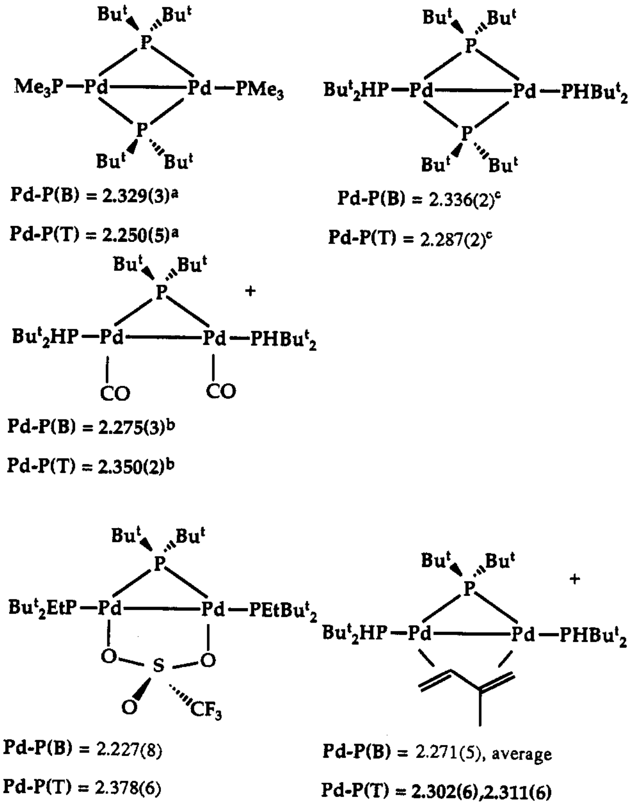


Figure 4. ORTEP plot for 3. Ellipsoids are drawn at 50% probability.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for 3

Pd1–Pd1′	2.648(2)	Pd1–O1	2.28(2)
Pd1–P1	2.378(6)	S–O(1)	1.47(2)
Pd1–P3	2.227(8)	S–O(2)	1.42(4)
P1–Pd1–P3	126.4(4)	O1–S–O2	116(1)
P1–Pd1–O1	92.5(6)	P3–Pd1–O1	141.0(4)
Pd1–P3–Pd1′	73.0(3)	Pd1–O1–S	124(1)
O1–S–O1′	114(1)	P1–Pd1–Pd1′	180(1)

Chart I. Selected Pd–P Bond Distances (Å) in Phosphide-Bridged Pd(I) Dimers



Pd-P(B) = 2.329(3)[a]

Pd-P(T) = 2.250(5)[a]

Pd-P(B) = 2.336(2)[c]

Pd-P(T) = 2.287(2)[c]

Pd-P(B) = 2.275(3)[b]

Pd-P(T) = 2.350(2)[b]

Pd-P(B) = 2.227(8)

Pd-P(T) = 2.378(6)

Pd-P(B) = 2.271(5), average

Pd-P(T) = 2.302(6),2.311(6)

B = bridging, T = terminal

[a] Data from ref 4a. [b] Data from ref 3. [c] Data from ref 15.

than the Pd–P length for the secondary phosphines in 2 (see Chart I), and interestingly, the bridging Pd–P bond distance at 2.227(8) Å is relatively short. In connection with this shortish bond length, we note the long[10] Pd–O separation (2.32(3) Å). In $K_2[Pd(NO_3)_4]$ the average Pd–O bond length is 2.000(7) Å,[11] and the three Pd–O distances in *trans*-$[Pd(NO_3)_2(OPPh_3)(PPh_3)]$ are 2.109(7), 2.031(7), and 2.031(8) Å.[12] Taken together, the Pd–O and Pd–P(bridge) distances suggest a strongly coordinated phosphide and a weakly coordinated $CF_3SO_3^-$ anion. The angles Pd–P(2)–Pd′ (73.0(3)°), P(1)–Pd–Pd′ (180(1)°), and P(1)–Pd–O (92.5(6)°) are normal. In 3 the terminal tertiary phosphines are not significantly bent toward the phosphide, in contrast to what we observed in the isoprene complex 2.

Table IV. Experimental Data for the X-ray Diffraction Study of 2 and 3

	2	3
formula	$C_{30}H_{64}F_3O_3P_3Pd_2S$	$C_{29}H_{64}F_3O_3P_3Pd_2S$
mol wt	867.62	855.61
crystal dimens, mm	0.30 × 0.20 × 0.10	0.40 × 0.30 × 0.08
data collecn T, °C	23	23
cryst syst	orthorhombic	orthorhombic
space group	*Pbca*	$Cmc2_1$
a, Å	17.231(4)	15.435(3)
b, Å	22.115(3)	18.142(9)
c, Å	21.531(9)	14.833(4)
V, Å^3	8205(4)	4154(2)
Z	8	4
ρ(calcd), g cm^{-3}	1.405	1.368
μ, cm^{-1}	10.683	10.541
radiation	Mo Kα (graphite monochromated, λ = 0.710 69 Å)	
measd rflns	$+h,+k,+l$	$\pm h,+k,+l$ ($2.5 < \theta < 15.0°$); $+h,+k,+l$ ($15.0 < \theta < 25.0°$)
θ range, deg	$2.5 < \theta < 25.0$	$2.5 < \theta < 25.0$
scan type	$\omega/2\theta$	$\omega/2\theta$
scan width, deg	$1.10 + 0.35 \tan \theta$	$1.10 + 0.35 \tan \theta$
max counting time, s	90	75
bkgd time, s	0.5 × scan time	0.5 × scan time
prescan rejection limit	0.55 (1.82σ)	0.55 (1.82σ)
prescan acceptance limit	0.025 (40.00σ)	0.025 (40.00σ)
no. of data collected	7009	2384
no. of indep data collected		1974
no. of obsd of obsd rflns (n_o)	2097 ($\lvert F_o\rvert^2 > 3.0\sigma(\lvert F\rvert^2)$)	996 ($\lvert F_o\rvert^2 > 3.5\sigma(\lvert F\rvert^2)$)
transmission coeff	0.9836–0.9015	0.9907–0.7028
decay cor	1.1220–0.9758	1.3674–0.9964
no. of params refined (n_v)	339	126
fudge factor f	0.070	0.060
R_{av}[a]		0.037
R[b]	0.071	0.069
R_w[c]	0.085	0.083
GOF[d]	1.923	1.769

[a] $R_{av} = \sum_i \lvert F_{o,av} - F_{o,i}\rvert / \sum_i \lvert F_{o,av}\rvert$. [b] $R = \sum \lVert F_o\rvert - (1/k)\lvert F_c\rVert / \sum \lvert F_o\rvert$. [c] $R_w = [\sum w(\lvert F_o\rvert - (1/k)\lvert F_c\rvert)^2 / \sum w\lvert F_o\rvert^2]^{1/2}$, where $w = [\sigma^2(F_o)]^{-1}$ and $\sigma(F_o) = [\sigma^2(F_o^2) + f^2(F_o^2)^2]^{1/2}/2F_o$. [d] $\mathrm{GOF} = [\sum w(\lvert F_o\rvert - (1/k)\lvert F_c\rvert)^2/(n_o - n_v)]^{1/2}$.

Comment

Given the very different behavior of the two olefins with respect to 1, a comment seems in order. For 3, it is reasonable to assume that one or two ethylene ligands

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Table V. Final Positional and Isotropic Equivalent Displacement Parameters for Compound 2 (Esd's in Parentheses)

atom	x	y	z	B (Å^2)^a
Pd1	0.82755(9)	0.08677(7)	0.72090(7)	4.21(3)
Pd2	0.80797(9)	0.17599(7)	0.63324(7)	4.21(3)
P1	0.8634(4)	−0.0015(3)	0.7697(3)	5.0(1)
P2	0.8155(4)	0.2302(2)	0.5417(3)	5.6(1)
P3	0.8734(3)	0.0875(2)	0.6219(2)	3.5(1)
C1	0.742(2)	0.244(1)	0.687(1)	10.1(8)
C2	0.733(2)	0.195(1)	0.719(1)	9.2(8)
C3	0.766(2)	0.169(1)	0.761(1)	11.4(8)
C4	0.760(2)	0.121(1)	0.801(1)	9.8(8)
C5	0.651(2)	0.158(2)	0.705(1)	14(1)
C111	0.781(1)	−0.055(1)	0.789(1)	7.4(7)
C112	0.726(2)	−0.032(1)	0.837(2)	21(1)
C113	0.820(2)	−0.119(1)	0.801(1)	14(1)
C114	0.747(2)	−0.065(2)	0.723(2)	29(1)
C121	0.930(1)	0.008(1)	0.835(1)	7.3(7)
C122	0.993(2)	0.051(2)	0.813(1)	21(1)
C123	0.896(3)	0.029(2)	0.896(1)	20(1)
C124	0.967(2)	−0.051(2)	0.859(2)	22(1)
C211	0.871(1)	0.303(1)	0.547(1)	8.5(8)
C212	0.829(2)	0.354(1)	0.584(2)	11(1)
C213	0.905(3)	0.327(2)	0.489(1)	23(2)
C214	0.944(2)	0.289(1)	0.583(2)	14(1)
C221	0.720(1)	0.238(1)	0.497(1)	8.4(7)
C222	0.686(2)	0.173(2)	0.496(2)	15(1)
C223	0.727(2)	0.263(2)	0.427(1)	19(2)
C224	0.660(2)	0.275(2)	0.528(2)	14(1)
C311	0.831(1)	0.0305(7)	0.5689(8)	4.0(4)
C312	0.745(1)	0.033(1)	0.584(1)	6.5(6)
C313	0.843(2)	0.047(1)	0.4988(9)	9.6(8)
C314	0.861(2)	−0.0315(9)	0.582(1)	7.6(7)
C321	0.982(1)	0.0941(9)	0.6117(9)	4.6(5)
C322	1.005(1)	0.118(2)	0.549(1)	12(1)
C323	1.024(2)	0.039(1)	0.628(2)	9.7(9)
C324	1.003(1)	0.147(1)	0.659(1)	9.3(8)
S	0.9627	0.3389	0.8461	4*
O1	0.9232	0.3097	0.7968	27*
O2	0.9419	0.3115	0.9034	21*
O3	0.9419	0.4009	0.8474	27*
C(F)	1.0703	0.3317	0.8342	12*
F1	1.1071	0.3589	0.8801	27*
F2	1.0896	0.2739	0.8330	28*
F3	1.0898	0.3572	0.7810	29*

^{a} Starred values denote atoms refined isotropically; coordinates were kept fixed. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table VI. Final Positional and Isotropic Equivalent Displacement Parameters for Compound 3 (Esd's in Parentheses)

atom	x	y	z	B (Å^2)^a
Pd1	0.08578(7)	0.14544(6)	0.750	2.49(2)
S	0.000	0.2389(5)	0.5789(7)	4.2(2)
P1	0.2398(3)	0.1457(3)	0.751(1)	3.41(9)
P3	0.000	0.0933(4)	0.8525(7)	3.0(2)
F1	0.072(2)	0.372(1)	0.590(3)	11.6(8)
F2	0.000	0.342(2)	0.698(3)	10(1)
O1	0.080(1)	0.207(1)	0.616(2)	5.9(4)
O2	0.000	0.251(2)	0.484(3)	8(1)
C(F)	0.000	0.333(2)	0.613(4)	6(1)
C1	0.285(4)	0.116(3)	0.648(5)	11(2)*
C2	0.237(4)	0.095(3)	0.572(6)	6(1)*
C111	0.286(2)	0.081(2)	0.835(3)	5.2(6)*
C112	0.28(1)	0.111(6)	0.91(1)	17(5)*
C113	0.385(3)	0.085(3)	0.847(4)	8(1)*
C114	0.268(3)	0.015(3)	0.847(5)	10(1)*
C121	0.286(2)	0.240(2)	0.773(3)	5.7(7)*
C122	0.382(2)	0.247(1)	0.770(2)	4.8(5)*
C123	0.272(3)	0.262(3)	0.861(5)	10(1)*
C124	0.234(3)	0.292(2)	0.721(4)	9(1)*
C311	0.000	−0.010(2)	0.856(3)	4.2(7)*
C312	0.000	−0.035(2)	0.753(8)	5.0(7)*
C313	0.089(3)	−0.040(3)	0.899(5)	11(1)*
C321	0.000	0.134(3)	0.975(3)	5.6(8)*
C322	0.000	0.216(9)	0.96(1)	16(5)*
C323	−0.071(3)	0.112(3)	1.024(5)	9(1)*

^{a} See footnote *a* in Table V.

coordinate[13] and that, as with the isoprene reaction, a secondary phosphine is lost. The details of the insertion which follows are unknown;[14] however, whatever the mechanism, we believe that the coordinated olefin must have freedom of movement. This is not the case in the η^4-isoprene complex where, due to the coordination of both double bonds, there is much less motional flexibilty for the diene. A chelate effect would also contribute to the stability of 2 relative to a hypothetical bis(ethylene) complex. The net result is that, for 2, a relatively stable diene complex can be isolated, whereas for 3 the reaction proceeds further.

Experimental Section

General Data. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Complex 1 was prepared as described previously.[15] Solvents were dried by conventional procedures and distilled prior to use. IR spectra (Nujol mulls, KBr or CaF$_2$ plates) were recorded on a Perkin-Elmer FT IR 1725X spectrometer. NMR spectra were measured using Bruker AMX 400 and AMX 500 NMR spectrometers. ^{1}H-NOESY and X,H correlations (X = ^{31}P, ^{13}C) were measured using standard pulse sequences as described previously.

Preparation of 2. Isoprene (0.2 mL, 20 mmol) was added to a suspension of 1 (64 mg, 0.66 mmol) in DME and the resulting suspension stirred at room temperature for 3 days. After this time the violet solid had reacted to afford a yellow suspension. The solution was then concentrated to ca. 2 mL and diethyl ether added. The yellow crystalline solid which precipitated was collected by filtration and dried to afford 25 mg (44%) of the product. Anal. Calcd for $C_{30}H_{64}F_3O_3P_3Pd_2S$: C, 41.50; H, 7.38; P, 10.70; Pd, 24.50. Found: C, 41.09; H, 7.31; P, 10.50; Pd, 24.62. IR (Nujol, cm^{-1}): 1271 vs, 1143 s, 1032 s, 637 m.

Preparation of 3. A suspension of 1 (140 mg, 0.418 mmol) in DME (35 mL) was saturated with ethylene. After the mixture was allowed to stand for 1 day, an orange solution had formed. This was concentrated to ca. 3 mL and then treated with ca. 5 mL of diethyl ether. Storage overnight at −30 °C gave 44 mg (35%) of 3. Anal. Calcd for $C_{29}H_{64}F_3O_3P_3Pd_2S$: C, 40.71; H, 7.49; Pd, 24.90. Found: C, 41.03; H, 7.70; P, 10.74; Pd, 25.01. IR (Nujol, cm^{-1}): 1296 vs, 1168, 1018 s, 631 m.

Crystallography. Yellow crystals suitable for X-ray diffraction of 2 were obtained by crystallization from DME/ether. Red crystals of compound 3 were obtained from the same solvent mix; 2 and 3 are only moderately stable in the air. Crystals of both compounds (for 2 a small fragment was cut from a larger crystal) were mounted on glass fibers (covered for protection with acrylic resin) at a random orientation. An Enraf-Nonius CAD4 diffractometer was used for the unit cell and space group determinations and for the data collection. Unit cell dimensions were obtained by a least-squares fit of the 2θ values of high-order reflections ($9.3 < \theta < 14.4°$ and $9.9 < \theta < 17.8°$, respectively) using the CAD4 centering routines. Selected crystallographic and other relevant data are listed in Table IV.

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[13] There are several possible intermediates, e.g. two ethylenes complexed, one ethylene and one secondary phosphine, etc., and we have not attempted to observe any of these intermediates.

[14] Uncoordinated secondary phosphine may also react with free olefin to give tertiary phosphine. See: King, R. B.; Kapoor, P. N. *Acc. Chem. Res.* **1972**, *5*, 177 and references therein. An interesting new contribution in this area is: Pringle, P. G.; Smith, M. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1701.

[15] Pasquali, M.; Sommovigo, M.; Leoni, P.; Sabatino, P.; Braga, D. *J. Organomet. Chem.* **1992**, *423*, 263.

Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities. Three standard reflections were used to check the stability of the crystal and of the experimental conditions and measured every 1 h. Data have been corrected for Lorentz and polarization factors and for decay, using the data reduction programs of the MOLEN package.[16] Empirical adsorption corrections were applied by using azimuthal (ψ) scans of two "high"-χ-angle reflections ($\chi > 87°$, $10.3 < \theta < 12.4°$ for **2** and $\chi > 86°$ for **3**). The standard deviations on intensities were calculated in terms of statistics alone, while those on F_o were calculated as shown in Table IV.

The structures were solved by a combination of Patterson and Fourier methods and refined by full-matrix least squares,[16] the function minimized being $\sum[w(F_o - 1/kF_c)^2]$. No extinction correction was applied.

For the refinement of **2**, anisotropic displacement parameters were used for all the atoms of the cation. Moreover, the refinement of the triflate counterion led to an unreasonable geometry. Therefore, a model was constructed assuming an idealized geometry for the "CF_3" group; only the isotropic displacement parameters were refined, while distances and angles were kept fixed.

The structure of **3** was refined using anisotropic displacement parameters for the Pd and P atoms and for those of the CF_3SO_3 group. The handedness of the crystal was tested by refining the two possible sets of coordinates and choosing that solution giving the lowest R_w factor.[17]

For both structures the contributions of the hydrogen atoms in calculated positions (C–H (Å) = 0.95, B(H) (Å^2) = 1.3B(C_{bonded})) were taken into account but not refined. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from ref 18. All calculations were carried out using the Enraf-Nonius MOLEN package.[16]

As can be seen from the relevant number of unobserved reflections and the high values of the displacement parameters of certain atoms (e.g., the carbon atoms of the phosphine ligands in **2** and **3**, the isoprene moiety in **2**), both structures are disordered. As a result, the precision of the determinations is limited.

Final atomic coordinates and equivalent thermal factors are given in Table V for **2** and Table VI for **3**.

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Supplementary Material Available: Tables of calculated positional parameters for the hydrogen atoms and anisotropic displacement parameters, extended lists of bond lengths and bond angles, and tables of torsion angles for **2** and **3** (18 pages). Ordering information is given on any current masthead page.

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[16] MOLEN: Molecular Structure Solution Procedure; Enraf-Nonius, Delft, The Netherlands, 1990.

[17] Hamilton, W. C. *Acta Crystallogr.* **1965**, *13*, 502.

[18] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.