Terminal and Bridging Bonding Modes of the Acetophenone Enolate to Palladium(II): The Structural Evidence and the Insertion of Isocyanides

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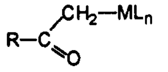
The oxidative addition of $PhCOCH_2Cl$ to $Pd(PPh_3)_4$ led to a high yield of *trans*-$[(PPh_3)_2(Cl)Pd(CH_2COPh)]$, **3**, in which the enolate is C-bonded to Pd(II), as shown by an X-ray analysis. Complex **3** reacts with Bu^{t}NC, and depending on the stoichiometric ratio, two compounds were isolated. With a 1:1 stoichiometry, the insertion of Bu^{t}NC into the Pd—C bond of **3** was observed and the crystalline solid **5** isolated, *trans*-$[(PPh_3)_2(Cl)Pd—C(NH—Bu^t)=CH—C(O)Ph]$, which contains the enolic form of a β-keto imino fragment. The reaction of **3** with 2 mol of Bu^{t}NC led to a good yield (>70%) of an organic compound **7**, which results from double insertion of Bu^{t}NC on the Pd—C bond of **3**, followed by homolytic cleavage of the Pd—C bond and dimerization of the resulting organic fragments. The ionization of the Pd—Cl bond by $AgCF_3SO_3$ in acetonitrile led not to the cationic solvated form of **3**, but rather to the dimer $[\{cis\text{-}(PPh_3)_2Pd\}_2(\mu\text{-}CH_2COPh)_2]^{2+}\cdot 2[CF_3SO_3]^-$, **9**, containing the enolato anion bridging two palladium atoms in the oxoallyl form. In coordinating solvents, **9** is a source of the expected monomeric cationic form. Crystallographic details: **3** is monoclinic, space group Pn, a = 9.845(1) Å, b = 12.119(2) Å, c = 15.432(2) Å, $\alpha = \gamma = 90°$, β = 95.29°, Z = 2, and R = 0.024; **5** is triclinic, space group $P\bar{1}$, a = 12.040(1) Å, b = 18.473(2) Å, c = 11.922(1) Å, α = 97.25(1)°, β = 109.29(1)°, γ = 81.31°, Z = 8, and R = 0.072; **9** is monoclinic, space group $I2/a$, a = 21.550(2) Å, b = 34.773(3) Å, c = 22.592(2) Å, $\alpha = \gamma = 90°$, β = 95.88(1)°, Z = 8, and R = 0.072.

Introduction

Transition metal enolate chemistry is nowadays a major feature of organic synthetic methodology.[1] An important distinction should be made, however, between carbophilic[2] and oxophilic[3] metals. The former ones prefer to bind the enolato functionality *via* the "CH_2" unit, the latter *via* the oxygen atom.

A number of examples are known for both binding modes, though the structural data are limited. The chemistry associated with the two metal enolates as well as the role played by the metal are very different.[2] In addition, the synthesis of **I** is normally achieved by an oxidative addition reaction to a low valent metal, while **II** is usually formed by a transmetalation reaction between an alkali metal enolate and a high valent transition metal halide. The reactivity of metal enolate **I** is characterized by migration of a σ-bonded alkyl group to an incoming substrate; the metal should therefore have a free coordination site. The role of the metal in **II** is that of binding an electrophilic substrate, *i.e.* a carbonyl group, in order to enhance its electrophilicity and to direct the attack by the "CH_2" nucleophile.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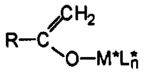
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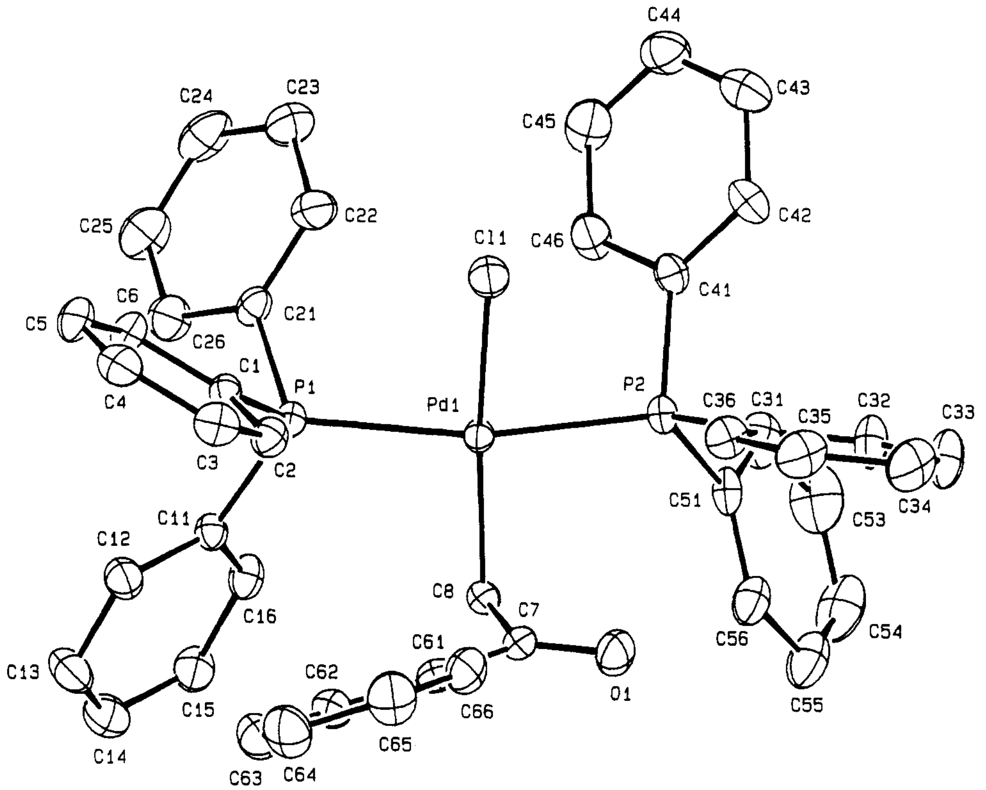


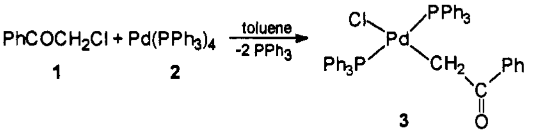
Figure 1. ORTEP view of complex **3** (30% probability ellipsoids).

Among the carbophilic metals, palladium has been widely used for asisting the reactivity of enolato species.[4,5] The number of isolated and well characterized complexes is, however, rather limited.[6] Binding modes of the enolato to Pd have been proposed without any substantial proof.[4,5,7]

In this context, we report the synthesis and structural characterization of (i) a monomeric C-bond Pd–enolate and (ii) a dimeric Pd enolate containing a bridging oxaallyl enolate; we also report on (iii) the insertion of isocyanides into a Pd–enolate[8] relevant to the synthesis of a novel organic skeleton.

Results and Discussion

The synthesis of Pd–enolates is much better performed *via* the oxidative addition of α-chloro ketones to a Pd(0)[6,8,9] than from a transmetalation reaction involving alkali metal enolates, because the alkali metal enolate undergoes a one electron oxidation with the consequent dimerization of the enolato fragment and reduction of Pd(II).[10] The oxidative addition of **1** to Pd(0) in complex **2** proceeds cleanly, as expected, with the formation of the *trans*-Pd(II)–enolate, **3**, as yellow crystals (85%):



$$PhCOCH_2Cl + Pd(PPh_3)_4 \xrightarrow[-2\,PPh_3]{toluene} trans\text{-}[PdCl(PPh_3)_2(CH_2C(=O)Ph)] \quad (1)$$

Although Pd–enolates have been invoked and used without isolation, structural data on them are lacking.[4,5,7,8] In addition, it has been suggested that the enolate-to-palladium bonding mode occurs *via* a metal–oxygen or metal–oxoallyl bond to justify different reactivities. The structure of **3** reveals a normal carbon σ-bonded enolate, as expected for a soft metal. The structure is shown in Figure 1, and a selected list of structural parameters is in Table V. The square planar coordination around Pd shows distortions, as can be seen from the P–Pd–P [160.7(1)°] and Cl–Pd–C [162.7(1)°] angles and the displacements of atoms from the mean coordination plane: Pd1, 0.083(1) Å; P1, –0.325(1) Å; P2, –0.292(1) Å; Cl1, 0.064(1) Å; C8, 0.711(4) Å. The enolato anion is twisted with respect to the phenyl ring by 26.7(2)° and is nearly perpendicular to the mean coordination plane [dihedral angle 76.9(3)°]. The C7–C8 [1.501(6) Å] and C7–O1 [1.211(6) Å] distances correspond well to single and double bonds, respectively. The Pd–C distance [2.093(5) Å] falls within the standard range of values[11] [2.044(42) Å] for Pd–C (primary alkyls, CH_2R, R=C_{sp^2})]. Bond distances within the enolate unit are in agreement with a metal–carbon σ-bonded species. The CO band is at 1624 cm^{-1}, and the methylene protons

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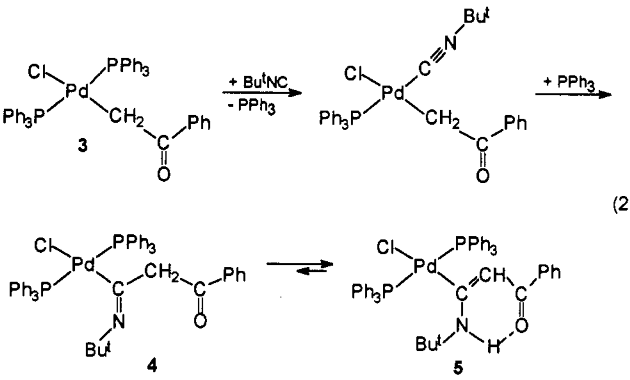
Table I. Experimental Data for the X-ray Diffraction Studies on Crystalline Compounds 3, 5, and 9

	3	5	9
chemical formula	$C_{44}H_{37}ClOP_2Pd$	$C_{49}H_{46}ClNOP_2Pd\cdot 2C_2H_3N$	$C_{88}H_{74}O_2P_4Pd_2\cdot 2CF_3O_3S$
a, Å	9.845(1)	12.040(1)	21.550(2)
b, Å	12.119(2)	18.473(2)	34.773(3)
c, Å	15.432(2)	11.922(1)	22.592(2)
α, deg	90	97.25(1)	90
β, deg	95.29(1)	109.29(1)	95.88(1)
γ, deg	90	81.31(1)	90
V, $Å^3$	1833.4(4)	2465.8(4)	16840.4(26)
Z	2	2	8
fw	785.6	950.8	1798.4
space group	*Pn* (No. 7)	$P\bar{1}$ (No. 2)	*I*2/*a* (No. 15)
t, °C	22	22	22
λ, Å	0.710 69	0.710 69	0.710 69
ρ_{calc}, g cm^{-3}	1.423	1.281	1.419
μ, cm^{-1}	6.91	5.27	6.09
transm coeff	0.784–1.000	0.871–1.000	0.943–1.000
R^a	0.024	0.038	0.061
R_w	0.024	0.039	0.068

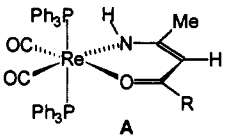
[a] $R = \sum|\Delta F|/\sum|F_o|$. $R_w = \sum w^{1/2}|\Delta F|/\sum w^{1/2}|F_o|$.

appear as a triplet, which is derived from the coupling with the two phosphines in *cis* position (J_{HP} = 6.7 Hz). The enolato functionality loses its nucleophilicity because of the binding to the metal and does not react with the conventional electrophiles of aldol reactions. It can, however, be transferred to another substrate via a conventional insertion–migration reaction, as shown by the reaction of 3 with an isocyanide. Although the reaction is a stepwise process, the product of the first insertion can be isolated, as reported in reaction 2.

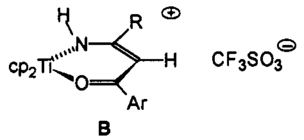


(2)

The tautomerization of 4 is driven by the formation of a stable hydrogen-bonded heterocycle in 5. The tautomerization of the β-keto imino 4 to the corresponding β-keto enamine form 5 has been observed for β-keto imino derivatives derived from the migratory insertion of nitriles into the Re–C-bonded enolate (**A**)[2] and in the reaction of cationic titanium O-bonded enolate with nitriles (**B**).[12]



A



B

The enolic proton in the NMR spectrum of 5 is a triplet at 5.83 ppm. A similar result was reported from the insertion of isocyanide into the Pd–C-bonded acetone enolate.[8]

The crystal structure of 5 consists of the packing of complex molecules and acetonitrile solvent molecules in the complex:solvent molar ratio of 1:2. An ORTEP view of the complex is given in Figure 2. Selected bond distances and angles are quoted in Table VI. The palladium atom exhibits a distorted square planar coordination, the Pd,P1,Cl1 plane being twist from that of Pd,P2,C9 by 13.7(1)°. The displacements of atoms from the mean coordination plane are Pd1, –0.058(1) Å; P1, 0.168(1) Å; P2, 0.219(1) Å; Cl1, 0.006(1) Å; and C9, 0.109(3) Å. The Pd–Cl [2.384(1) Å] and Pd–P [2.355(1), 2.356(1) Å] distances are in good agreement with those found in complex 3. The Pd–C9 distance [1.992(4) Å], which is significantly shorter than the Pd–C8 distance in complex 3, is in agreement with the values quoted in the literature[11] [mean value 1.987(32) Å]. The bond distances N1–C9 [1.325(4) Å], C8–C9 [1.399(4) Å], C7–C8 [1.409(6) Å], and C7–O1 [1.262(4) Å] along with the approximate planarity of the N1,C9,C8,C7,O1 system [maximum displacement 0.047(4) Å for C7] are consistent with a high degree of π delocalization. This conformation is determined mainly by the strong N–H···O intramolecular hydrogen bond, which gives rise to a six-membered ring: N1···O1, 2.644(4) Å; H1···O1, 1.87 Å; N1–H1···O1, 143.1°. The ring is almost coplanar with the C61···C66 phenyl ring [dihedral angle 18.7(1)°]. The values for the C7–C61 distance [1.508(6) Å] and the C–C distances within the ring (Table SIX), however, rule out a possible conjugation between the two systems. The N1,C9,C8,C7,O1 plane is tilted by 88.1(1)° with respect to the mean coordination plane. This conformation brings two hydrogen atoms (from the C8 carbon and from the C71 methyl carbon of the Bu^t group) toward the palladium atom at opposite sides with respect to the coordination plane (Pd···H8, 2.84 Å; Pd···H712, 2.59 Å). H712 lies nearly in the axial direction, the dihedral angle between the Pd···H712 line and the normal to the coordination plane being 14.1°. On the opposite side, another hydrogen atom from a PPh_3 ligand (Pd···H16, 2.82 Å) fills the coordination around palladium. The Pd···H8 and Pd···H16 lines form dihedral angles of 42.8 and 31.3°, respectively, with the normal to the coordination plane. Packing is mainly determined by van der Waals contacts. There is a short contact involving the O1 oxygen atom and the methyl carbon atom of an acetonitrile molecule which could be considered as a hydrogen bond: C75···O1, 3.219(6) Å; H751···O1, 2.24 Å; C75-H751···O1, 147.3°.

The reaction of 3 with carbon monoxide or ethylene was unsuccessful. The starting material has been recovered

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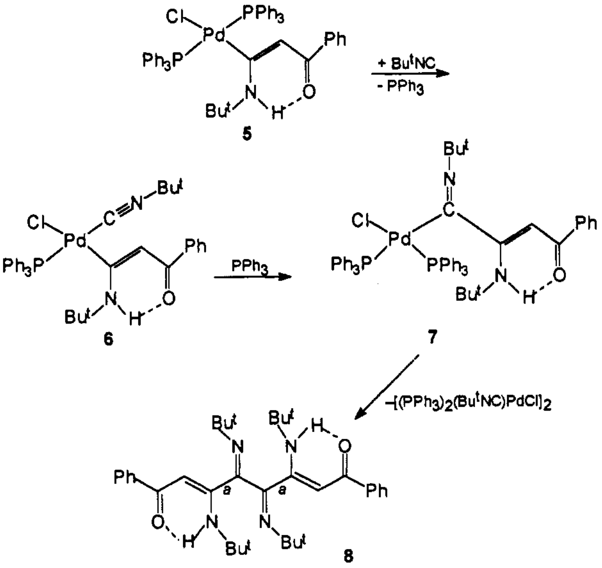
Table II. Fractional Atomic Coordinates ($\times 10^4$) for Complex 3

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Pd1	0(–)	1692.4(2)	0(–)	C31	2366(4)	3755(4)	–590(3)
Cl1	997.1(13)	2264.5(11)	1404.9(7)	C32	2765(5)	4653(4)	–1061(4)
P1	1229.7(11)	309.7(9)	642.3(7)	C33	4122(6)	4882(5)	–1109(4)
P2	574.7(10)	3409.0(9)	–556.6(7)	C34	5108(5)	4224(6)	–679(4)
O1	2014(4)	1379(3)	–1558(3)	C35	4736(4)	3344(5)	–190(4)
C1	–227(4)	–489(3)	1474(3)	C36	3372(4)	3104(4)	–143(3)
C2	1137(4)	–682(4)	1377(3)	C41	–110(5)	4368(3)	194(3)
C3	1905(5)	–1358(4)	1965(3)	C42	627(5)	5255(4)	575(4)
C4	1306(5)	–1830(4)	2649(3)	C43	74(7)	5900(4)	1198(4)
C5	–45(5)	–1620(4)	2761(3)	C44	–1196(7)	5688(5)	1437(4)
C6	–807(4)	–947(4)	2173(3)	C45	–1946(6)	4835(5)	1060(4)
C7	1209(5)	738(4)	–1287(3)	C46	–1399(5)	4178(4)	446(4)
C8	–266(4)	1037(4)	–1259(3)	C51	–139(4)	3882(4)	–1643(3)
C11	–2092(4)	–733(3)	–56(3)	C52	–1113(6)	4718(5)	–1745(4)
C12	–1931(5)	–1858(4)	89(3)	C53	–1523(7)	5108(6)	–2574(5)
C13	–2542(6)	–2616(4)	–490(4)	C54	–983(7)	4667(7)	–3297(4)
C14	–3309(6)	–2269(5)	–1234(4)	C55	–56(6)	3822(6)	–3198(4)
C15	–3503(5)	–1149(5)	–1387(3)	C56	368(5)	3435(5)	–2375(3)
C16	–2922(4)	–396(4)	–796(3)	C61	1693(5)	–373(4)	–960(3)
C21	–2638(4)	919(4)	1174(3)	C62	854(5)	–1287(4)	–950(3)
C22	–2464(6)	1894(5)	1636(4)	C63	1362(6)	–2290(4)	–643(4)
C23	–3542(7)	2383(5)	2015(4)	C64	2699(6)	–2373(5)	–307(4)
C24	–4803(6)	1892(6)	1921(4)	C65	3555(6)	–1465(5)	–309(4)
C25	–4989(5)	945(6)	1481(4)	C66	3048(5)	–473(5)	–645(4)
C26	–3928(5)	447(5)	1112(4)				

unchanged. The success of the reaction with Bu^{t}NC is perhaps due to the ability of isocyanide to displace PPh_3 in the preliminary stage of the insertion, in a position *cis* to the Pd–C bond.[13] The yield of **5** is variable from *ca.* 30 up to 80%, depending on the solvent used and the concentration of the reagents (see Experimental Section). In the case of the lowest figure this may be due to (i) reductive elimination of the C-bonded organic fragment or (ii) further insertion of Bu^{t}NC into the Pd–C bond in complex **5**. In fact, carrying out the reaction of **3** with 2 mol of Bu^{t}NC (or reacting **5** with an additional molecule of Bu^{t}NC), we observed a double insertion of isocyanide into the Pd–C bond according to reaction 3.

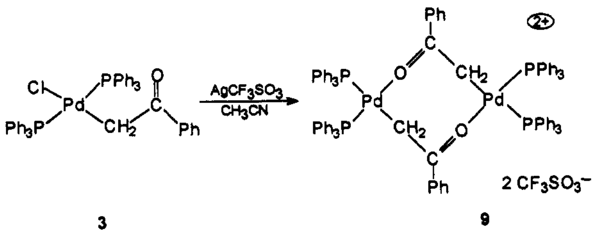


(3)

The second insertion of the isocyanide into the Pd–enolate functionality is followed by a reductive homolytic cleavage of the Pd–C bond in **7** and formation of **8**, which has been isolated as a moisture sensitive white crystalline solid, which hydrolyzes after a few hours. The IR spectrum shows the weak N–H band at 3254 cm^{-1} and a strong carbonylic band at 1694 cm^{-1}, while the iminic group is at 1160 cm^{-1}. The ^{1}H NMR spectrum showed the presence of two isomers α and β in a 3:2 ratio, having similar patterns and very close resonances: two singlets at 1.27 and 1.35 (α), 1.25 and 1.32 (β) ppm for the four Bu^t groups, a large peak at 4.14 (α) and 4.09 (β) ppm for NH, and a singlet at 5.34 (α) and 5.49 (β) ppm for the enolic proton. As temperature does not affect the ratio of the two isomers, we conclude that they form directly from the C–C coupling reaction and do not interconvert. The two isomers should be formally considered as rotamers obtained by a rotation around the C–C bond *a*, keeping the two imino groups in the same plane. One of the isomers will have all the heteroatoms above the plane; the other will have them in an alternate orientation. In reaction 3, we did not characterize the Pd compound which appeared as a yellow-orange powder, but it could be a Pd(I) derivative.

The low reactivity of **3** in insertion reactions can be related to the stable electronic and coordinate configuration of the metal, preventing the precoordination of the substrate to be inserted. This obstacle has usually been overcome in the case of chloro derivatives *via* the ionization of the Pd–Cl bond, which liberates a coordination site. Unless isomerization occurs, this should not be very helpful in our case, because the free coordination site would be *trans* to the Pd–C bond. The ionization of the Pd–Cl bond led, however, to an interesting compound with a novel bonding mode of the enolato moiety, and with the isomerization to a *cis*-bis(triphenylphosphine) derivative.

The acetonitrile used in reaction 4 does not compete with the bridging bonding mode of the enolato anion, as far as the isolated solid product is concerned. Such an



(4)

3 9

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[13] Veya, P.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 253 and in press.

Table III. Fractional Atomic Coordinates (×10^4) for Complex 5

atom	*x/a*	*y/b*	*z/c*
Pd1	2339.7(2)	1911.7(1)	4282.4(2)
Cl1	2701.0(7)	849.5(4)	5354.9(7)
P1	1361.4(6)	1210.3(4)	2540.7(6)
P2	3687.4(7)	2500.6(4)	5926.7(7)
O1	2467(2)	3831(1)	1907(2)
N1	1347(2)	3317(1)	3152(2)
N2	7569(7)	4360(4)	9790(6)
N3	9499(7)	3580(5)	7136(6)
C1	584(2)	507(2)	2796(2)
C2	−173(3)	708(2)	3476(3)
C3	−874(4)	203(2)	3585(4)
C4	−811(4)	−495(2)	3042(3)
C5	−53(4)	−697(2)	2394(4)
C6	651(3)	−199(2)	2262(3)
C7	3235(3)	3284(2)	2202(3)
C8	3103(2)	2725(2)	2834(3)
C9	2191(2)	2753(2)	3328(2)
C11	2489(3)	713(2)	1922(3)
C12	2246(3)	512(2)	716(3)
C13	3124(4)	122(2)	295(4)
C14	4224(4)	−68(2)	1069(4)
C15	4479(4)	128(3)	2259(5)
C16	3607(3)	521(2)	2686(3)
C21	242(3)	1618(2)	1252(2)
C22	−889(3)	1399(2)	781(3)
C23	−1719(3)	1712(2)	−188(4)
C24	−1446(4)	2259(2)	−697(4)
C25	−346(4)	2479(2)	−257(3)
C26	521(3)	2166(2)	713(3)
C31	5180(3)	2180(2)	5854(3)
C32	5512(3)	1436(2)	5690(4)
C33	6613(4)	1171(2)	5598(5)
C34	7382(3)	1652(3)	5637(4)
C35	7087(3)	2376(2)	5792(4)
C36	5985(3)	2651(2)	5906(4)
C41	3655(3)	2238(2)	7336(3)
C42	4686(4)	2077(2)	8272(3)
C43	4593(5)	1912(2)	9351(3)
C44	3508(6)	1909(2)	9485(4)
C45	2503(4)	2067(2)	8566(4)
C46	2561(4)	2225(2)	7480(3)
C51	3660(2)	3506(2)	6196(3)
C52	3720(3)	3924(2)	5328(3)
C53	3664(3)	4684(2)	5526(4)
C54	3569(4)	5031(2)	6576(4)
C55	3508(4)	4628(2)	7444(4)
C56	3566(3)	3869(2)	7262(3)
C61	4346(3)	3251(2)	1867(3)
C62	4347(3)	3693(2)	1015(3)
C63	5341(4)	3692(2)	678(4)
C64	6344(4)	3251(3)	1210(4)
C65	6385(3)	2805(3)	2073(4)
C66	5375(3)	2806(2)	2411(3)
C70	313(3)	3532(2)	3585(3)
C71	−279(5)	2899(3)	3638(7)
C72	683(5)	3937(4)	4783(6)
C73	−522(5)	4008(5)	2720(7)
C74	7252(5)	4412(3)	8806(7)
C75	6883(5)	4506(3)	7607(5)
C76	10146(7)	3833(4)	7891(7)
C77	10988(9)	4141(5)	8861(8)

oxoallyl bonding mode for the enolato, though often invoked in Pd chemistry, has never been proven structurally.[4,5,7]

A perspective view of complex 9 is given in Figure 3. Selected bond distances and angles are quoted in Table VII. The structure consists of the packing of cations and $CF_3SO_3^-$ anions (see Experimental Section). The cation is a dinuclear unit where two enolato anions bridge two *cis*-$(PPh_3)_2Pd$ fragments through the oxygen and carbon atoms. The four coordinate Pd atoms show a slightly distorted square planar geometry, with the Pd,P,P plane twisted away from the Pd,O,C plane by 5.5(2) and 3.1(2)° for Pd1 and Pd2, respectively. The displacements of atoms from the mean coordination planes are Pd1, 0.000(1) Å; P1, −0.013(3) Å; P2, 0.012(2) Å; C10, −0.188(9) Å; O1, 0.056(5) Å; Pd2, 0.002(1) Å; P3, −0.009(3) Å; P4, 0.000(3) Å; C8, −0.105(9) Å; and O2, 0.006(7) Å. The two coordination planes in the dimer are mutually perpendicular, the dihedral angle they form being 85.6(1)°. The bridging role of the enolato ligands gives rise to an eight-membered dinuclear ring which assumes a distorted boat conformation with the rough plane of atoms (C7, C9, O1, O2) at the bottom (out-of-plane distances from −0.075(6) to 0.192(9) Å) (Figure 4). The distances of the other atoms from that plane are Pd1, 1.368(1) Å; Pd2, 1.281(1) Å; C8, 1.481(9) Å; and C10, 1.530(9) Å. The bottom of the boat forms dihedral angles of 137.8(3) and 139.4(3)° with the Pd1,O1,C10 and Pd2,O2,C8 planes, respectively. The two enolato groups are slightly rotated with respect to the Ph rings (torsion angles 12.0(3) and 6.1(3)° around C7–C121 and C9–C131, respectively). They are almost perpendicular to the mean coordination plane involving the carbon atom, as seen in the following dihedral angles: O2,C9,C10,C131 ∠ P1,P2,O1,C10,Pd1, 82.2(3)°; O2,C9,C10,C131 ∠ P3,P4,O2,C8,Pd2, 66.7(2)°; O1,C7,C8,C121 ∠ P1,P2,O1,C10,Pd1, 64.0(2)°; O1,C7,C8,C121 ∠ P3,P4,O2,C8,Pd2, 83.7(3)°.

The geometries around the two palladium atoms are practically the same. We emphasize the following points: (i) The two Pd–P distances are significantly different. The Pd1–P1 [2.372(3) Å] and Pd2–P3 [2.370(3) Å] bonds *trans* to the carbon atoms are significantly longer than the Pd1–P2 [2.243(3) Å] and Pd2–P4 [2.244(3) Å] bonds *trans* to the oxygen atoms. (ii) The Pd–C bonds [Pd1–C10, 2.162(10) Å; Pd2–C8, 2.137(10) Å] are significantly longer than the Pd–C bond in complex 3, perhaps as a consequence of the bridging role of the enolato. (iii) The phenyl rings in the *cis*-triphenylphosphine ligands around Pd2 adopt a conformation leading two pairs of hydrogen atoms (H10, H112, H76, H102; Pd···H range 2.74–3.08 Å) to cap above and below the coordination plane. Coordination around Pd1 is filled by three hydrogen atoms from the triphenylphosphine ligands and one from the C8 atom of the enolato (H8, H42, H6, H36; Pd···H range 2.74–3.05 Å). The four H atoms show tetrahedral distortions, the mean least-squares planes being nearly perpendicular to the mean coordination plane (dihedral angles: 75.6, 76.6° around Pd1 and Pd2, respectively).

The dimer 9 should, however, be considered as a source of coordinatively unsaturated species $[(PPh_3)_2Pd(CH_2COPh)]^+$. This is indirectly supported by the ^1H and ^{31}P NMR spectra in different solvents. In noncoordinating CD_2Cl_2, the methylene (AB) is observed as two quartets with two different H–P coupling constants, J_{AP} and J_{BP} of 5.7 and 6.5 Hz (J_{AB} = 10.6 Hz), while it appears as a large peak in CD_3CN. On the other hand, in the ^{31}P NMR spectrum, two singlets for P are present in CD_2Cl_2, but only one singlet in CD_3CN. Such spectroscopic data suggest a dissociation of the dimer 9 into solvated monomers. This is further supported by the IR spectrum, which does not show any carbonyl band in the solid state nor in CH_2Cl_2 solution, while there is a CO band at 1643 cm^{-1} in acetonitrile solution.

Table IV. Fractional Atomic Coordinates (×10^4) for Complex 9

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Pd1	−435.8(3)	585.7(2)	2591.6(3)	C76	1016(3)	2206(2)	2986(3)
Pd2	39.8(3)	1717.2(2)	1950.0(3)	C81	−798(4)	2244(2)	2825(4)
P1	101.5(12)	−7.0(7)	2541.1(11)	C82	−1359(4)	2108(2)	2537(4)
P2	−1404.7(11)	344.2(7)	2544.9(10)	C83	−1854(4)	2021(2)	2867(4)
P3	−164.1(12)	2319.7(7)	2380.9(11)	C84	−1788(4)	2069(2)	3483(4)
P4	−14.3(12)	1900.2(8)	993.6(11)	C85	−1227(4)	2205(2)	3770(4)
O1	477(2)	812(2)	2605(2)	C86	−732(4)	2293(2)	3441(4)
O2	88(3)	1549(2)	2847(2)	C91	−8(4)	1526(2)	435(3)
C1	608(3)	−67(2)	3222(2)	C92	557(4)	1409(2)	243(3)
C2	914(3)	−416(2)	3344(2)	C93	574(4)	1093(2)	−137(3)
C3	1312(3)	−461(2)	3867(2)	C94	27(4)	895(2)	−324(3)
C4	1403(3)	−156(2)	4268(2)	C95	−538(4)	1012(2)	−131(3)
C5	1097(3)	193(2)	4147(2)	C96	−556(4)	1327(2)	249(3)
C6	699(3)	237(2)	3624(2)	C101	683(4)	2200(2)	851(4)
C7	674(4)	1019(2)	2209(4)	C102	1113(4)	2268(2)	1307(4)
C8	286(4)	1150(3)	1695(4)	C103	1612(4)	2506(2)	1206(4)
C9	−288(4)	1332(3)	3080(4)	C104	1636(4)	2677(2)	649(4)
C10	−812(4)	1151(3)	2731(4)	C105	1161(4)	2609(2)	194(4)
C11	−253(3)	−478(2)	2438(3)	C106	662(4)	2371(2)	295(4)
C12	−542(3)	−639(2)	2905(3)	C111	−735(4)	2149(3)	812(4)
C13	−834(3)	−996(2)	2834(3)	C112	−1267(4)	1966(3)	979(4)
C14	−837(3)	−1193(2)	2295(3)	C113	−1850(4)	2140(3)	863(4)
C15	−548(3)	−1032(2)	1828(3)	C114	−1901(4)	2497(3)	580(4)
C16	−257(3)	−675(2)	1900(3)	C115	−1370(4)	2680(3)	413(4)
C21	602(3)	37(2)	1941(3)	C116	−787(4)	2506(3)	529(4)
C22	1230(3)	−69(2)	2016(3)	C121	1317(3)	1151(2)	2319(3)
C23	1594(3)	−37(2)	1542(3)	C122	1614(3)	1116(2)	2895(3)
C24	1331(3)	100(2)	993(3)	C123	2221(3)	1253(2)	3027(3)
C25	703(3)	206(2)	918(3)	C124	2530(3)	1426(2)	2583(3)
C26	339(3)	174(2)	1391(3)	C125	2233(3)	1461(2)	2008(3)
C31	−1546(3)	76(2)	3204(2)	C126	1626(3)	1323(2)	1876(3)
C32	−2106(3)	−120(2)	3239(2)	C131	−167(4)	1256(2)	3719(2)
C33	−2201(3)	−325(2)	3752(2)	C132	394(4)	1388(2)	4012(2)
C34	−1737(3)	−335(2)	4230(2)	C133	541(4)	1312(2)	4616(2)
C35	−1177(3)	−139(2)	4195(2)	C134	126(4)	1104(2)	4928(2)
C36	−1082(3)	67(2)	3681(2)	C135	−435(4)	972(2)	4635(2)
C41	−1525(3)	52(2)	1883(2)	C136	−582(4)	1048(2)	4031(2)
C42	−1357(3)	215(2)	1359(2)	S1[a]	2557(5)	3666(3)	355(4)
C43	−1472(3)	17(2)	821(2)	C1S	2166(8)	3694(5)	−56(9)
C44	−1756(3)	−344(2)	809(2)	O1F	2935(4)	3315(3)	501(4)
C45	−1925(3)	−507(2)	1334(2)	O2F	1926(4)	3658(2)	553(4)
C46	−1809(3)	−309(2)	1871(2)	O3F	2962(5)	4009(3)	482(5)
C51	−2054(3)	679(2)	2478(3)	S2	7269(3)	3737(2)	156(3)
C52	−2292(3)	808(2)	2995(3)	O4F	7110(6)	4109(4)	464(5)
C53	−2784(3)	1071(2)	2956(3)	O5F	6695(7)	3776(4)	−314(6)
C54	−3037(3)	1205(2)	2402(3)	O6FA	7373(11)	3340(6)	361(9)
C55	−2799(3)	1077(2)	1886(3)	O6FB	6933(12)	3568(7)	595(11)
C56	−2307(3)	814(2)	1924(3)	S3	2656(5)	1249(3)	202(5)
C61	−346(4)	2762(2)	1980(3)	C3S	2436(7)	1439(4)	410(6)
C62	142(4)	2942(2)	1728(3)	O7F	3089(4)	1457(2)	660(4)
C63	26(4)	3269(2)	1374(3)	O8F	2088(5)	1058(3)	380(4)
C64	−578(4)	3415(2)	1273(3)	O9FA	2248(10)	1909(6)	147(11)
C65	−1067(4)	3235(2)	1524(3)	O9FB	2128(7)	1775(4)	539(7)
C66	−951(4)	2908(2)	1878(3)	S4	7664(7)	832(3)	121(7)
C71	506(3)	2453(2)	2894(3)	C4F	7667(7)	1229(4)	230(6)
C72	512(3)	2804(2)	3194(3)	O10F	7133(5)	606(3)	348(5)
C73	1028(3)	2907(2)	3585(3)	O11F	7135(5)	1454(3)	342(5)
C74	1538(3)	2660(2)	3677(3)	O12F	8077(8)	1156(5)	714(8)
C75	1532(3)	2309(2)	3377(3)	O13F	8154(8)	917(5)	561(7)

[a] The atoms labeled with the symbols S and C*n*S (*n* = 1, 3, 4) were refined as occupied at the same time by sulfur and carbon with the following site occupation factors: 0.6 for S1 and 0.4 for C1S; 1.0 for S2, 0.5 for S3, C3S, S4, C4S. The atoms labeled with the symbols O*n*F (*n* = 1–13) were refined as occupied at the same time by oxygen and fluorine with the following site occupation factors: 1.0 for O1F, O2F, O3F, O4F, O5F, O7F, O8F, O10F, and O11F; 0.5 for O6AF, O6BF, O9AF, O9BF, O12F, and O13F.

Conclusions

Simple nonfunctionalized enolates[14] bind to Pd(II) essentially *via* the carbon atom forming the Pd–C σ-bonding functionality. By this bonding mode the classical reactivity of the enolate fragment does not hold any more. Such a kind of Pd–enolates is insensitive to electrophiles but is able to insert unsaturated functionalities into the metal–carbon σ-bond. Owing to the weakness or lability of the Pd–C bond, interesting organic fragments are formed *via* reductive elimination processes. This study allowed entry into two well defined and structurally characterized classes of Pd(II)–enolates: (i) the monomeric, neutral Pd(II) complexes containing a Pd–C σ bond, like **3**; (ii) the dimeric, cationic Pd(II) complexes, like **9**, containing the enolate as a bridging ligand in the oxallyl form (such complexes can be the source of monomeric cationic Pd(II)–enolate fragments in the presence of appropriate binding solvents).

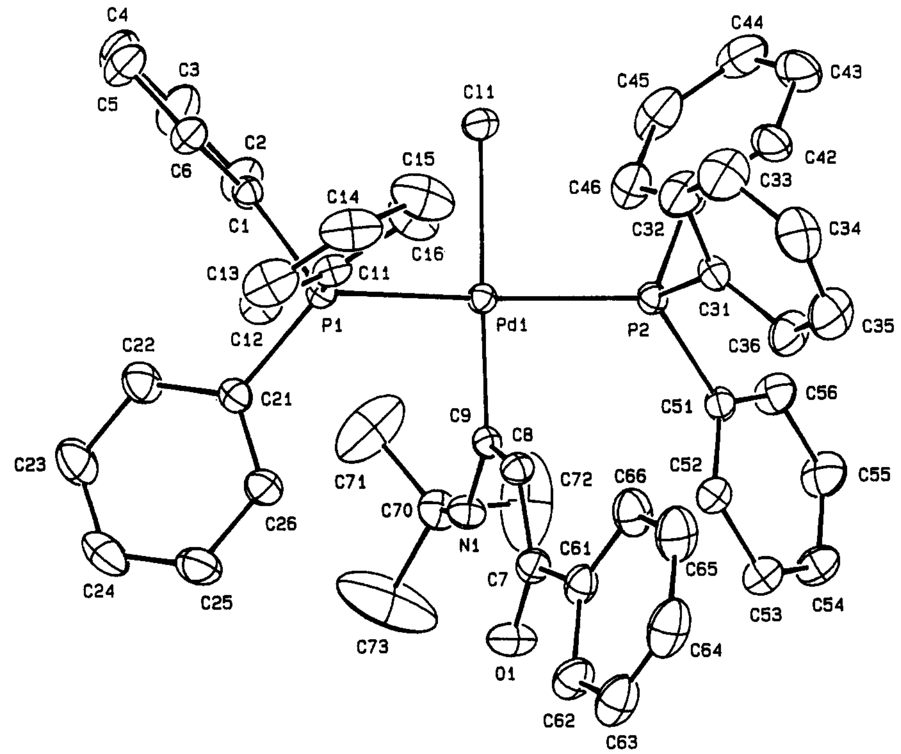

Figure 2. ORTEP view of complex **5** (30% probability ellipsoids).

Table V. Selected Bond Distances (Å) and Angles (deg) for Complex 3

Pd1–Cl1	2.398(1)	P2–C31	1.818(4)
Pd1–P1	2.340(1)	P2–C41	1.814(5)
Pd1–P2	2.340(1)	P2–C51	1.848(5)
Pd1–C8	2.093(5)	O1–C7	1.211(6)
P1–C1	1.823(4)	C7–C8	1.501(6)
P1–C11	1.819(4)	C7–C61	1.500(7)
P1–C21	1.830(5)		
P2–Pd1–C8	90.6(1)	Cl1–Pd1–P1	90.5(1)
P1–Pd1–C8	95.5(1)	O1–C7–C61	119.6(4)
P1–Pd1–P2	160.7(1)	O1–C7–C8	121.4(4)
Cl1–Pd1–C8	162.7(1)	C8–C7–C61	119.0(4)
Cl1–Pd1–P2	89.0(1)	Pd1–C8–C7	94.6(3)

Experimental Section

General Procedure. All operations were carried out under an atmosphere of purified nitrogen using modified Schlenk techniques or in a Braun drybox. Solvents were dried and distilled before use by standard methods. The compound [Pd(PPh$_3$)$_4$][15] was prepared as reported in the literature. Infrared spectra were recorded on a Perkin-Elmer 883 spectrometer and NMR spectra on a Bruker AC 200 instrument. Microanalytical (C, H, N) data have been obtained using a Carlo Erba EA 1108 elemental analyzer. The samples were sealed in a drybox under a rigorously inert atmosphere.

Table VI. Selected Bond Distances (Å) and Angles (deg) for Complex 5

Pd1–Cl1	2.384(1)	P2–C41	1.821(4)
Pd1–P1	2.355(1)	P2–C51	1.842(4)
Pd1–P2	2.356(1)	O1–C7	1.262(4)
Pd1–C9	1.992(4)	N1–C9	1.325(4)
P1–C1	1.820(4)	N1–C70	1.482(5)
P1–C11	1.829(4)	C7–C8	1.409(6)
P1–C21	1.833(3)	C7–C61	1.508(6)
P2–C31	1.832(4)	C8–C9	1.399(4)
P2–Pd1–C9	89.8(1)	O1–C7–C61	117.0(3)
P1–Pd1–C9	90.3(1)	O1–C7–C8	123.1(3)
P1–Pd1–P2	167.7(1)	C8–C7–C61	119.9(3)
Cl1–Pd1–C9	173.7(1)	C7–C8–C9	124.3(3)
Cl1–Pd1–P2	89.9(1)	N1–C9–C8	119.4(3)
Cl1–Pd1–P1	88.7(1)	Pd1–C9–C8	114.1(2)
C9–N1–C70	133.1(2)	Pd1–C9–N1	126.5(2)

Synthesis of 3. [Pd(PPh$_3$)$_4$] (1.63 g, 1.40 mmol) was added to a toluene (30-mL) solution of PhCOCH$_2$Cl (0.28 g, 1.80 mmol) and then stirred until the solid completely dissolved. The solution was kept at room temperature and gave **3** as a crystalline yellow solid (0.94 g, 85%). Crystals suitable for X-ray analysis were obtained by running the reaction in a mixture of thf (20 mL) and dimethoxyethane (30 mL). IR (Nujol): ν(C=O) 1624 (s) cm^{-1}. Anal. Calcd for C$_{44}$H$_{37}$ClOP$_2$Pd: C, 67.27; H, 4.75. Found: C, 67.35; H, 4.84. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.69 (t, CH$_2$—Pd, 2 H, J_{HP} = 6.7 Hz), 7.0–7.7 (m, Ph, 35 H). ^{13}C NMR (CD$_2$Cl$_2$): δ 30.5 (s, CH$_2$Pd), 128.1–140.9 (m, Ph), 204.5 (s, CO).

Synthesis of 5. One equivalent of Bu^{t}NC (0.21 mL, 1.92 mmol) was added with a syringe to a benzene (40 mL) suspension of **3** (1.50 g, 1.91 mmol). The solid dissolved in a few minutes and gave a yellow solution. The solution was then concentrated to 10 mL, and ether (25 mL) was added. Complex **5** crystallized as a pale yellow crystalline solid (81%). The yield is strongly dependent on the solvents used and on the concentration. In a mixture of THF/ether and more diluted solutions, the yield was only 27%. IR (Nujol): ν(C=C) 1583 (m), 1520 (s) cm^{-1}. Anal. Calcd for C$_{49}$H$_{46}$ClNOP$_2$Pd: C, 67.75; H, 5.36; N, 1.61. Found: C, 67.34; H, 5.62; N, 1.51. ^{1}H NMR (CD$_2$Cl$_2$): δ 0.96 (s, Bu^t, 9 H), 5.83 (t, =CH, 1 H), 7.1–7.7 (m, Ph, 35 H). ^{13}C NMR (CD$_2$Cl$_2$): δ 29.1 and 30.8 (2s, Bu^t), 101.3 (s, =CH), 127.3–141.9 (m, Ph), 185.7 (s, C=O). ^{31}P NMR (CD$_2$Cl$_2$): δ 18.8 (s).

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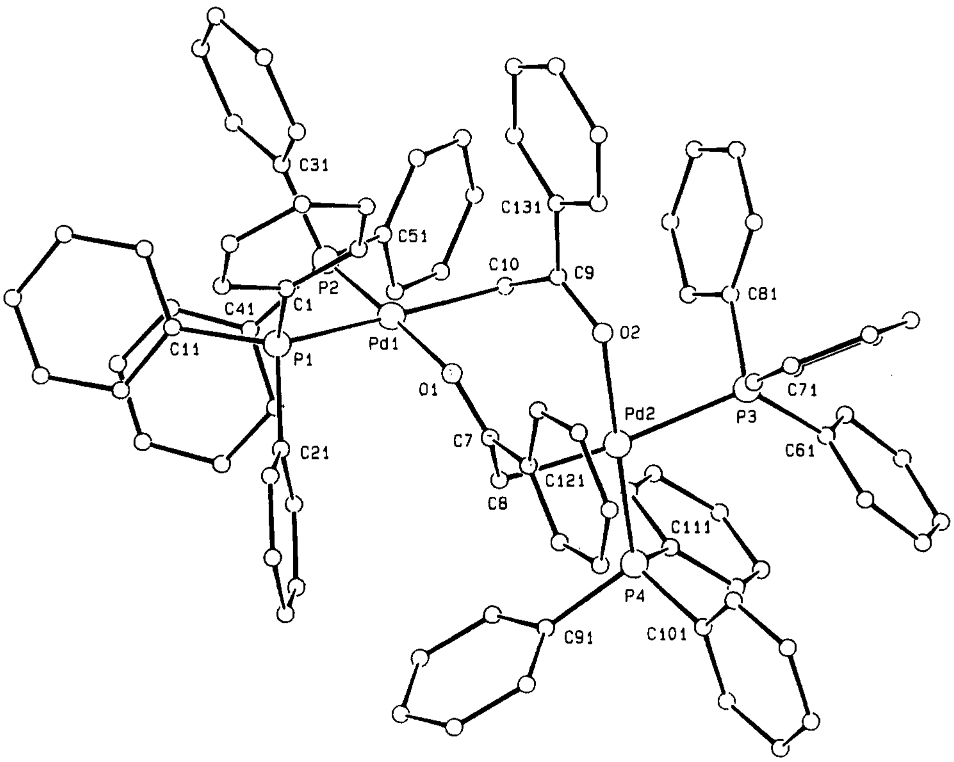

Figure 3. SCHAKAL drawing of complex 9.

Table VII. Selected Bond Distances (Å) and Angles (deg) for Complex 9

Pd1–P1	2.372(3)	P2–C51	1.815(7)
Pd1–P2	2.243(3)	P3–C61	1.807(7)
Pd1–O1	2.116(5)	P3–C71	1.817(7)
Pd1–C10	2.162(10)	P3–C81	1.795(10)
Pd2–P3	2.370(3)	P4–C91	1.814(7)
Pd2–P4	2.244(3)	P4–C101	1.805(9)
Pd2–O2	2.101(5)	P4–C111	1.788(9)
Pd2–C8	2.137(10)	O1–C7	1.256(10)
P1–C1	1.805(6)	O2–C9	1.261(12)
P1–C11	1.812(7)	C7–C121	1.457(11)
P1–C21	1.823(8)	C7–C8	1.434(12)
P2–C31	1.809(6)	C9–C131	1.464(10)
P2–C41	1.804(6)	C9–C10	1.453(12)
O1–Pd1–C10	91.2(3)	O2–Pd2–C8	90.8(3)
P2–Pd1–C10	89.2(2)	P4–Pd2–C8	89.5(3)
P2–Pd1–O1	178.1(1)	P4–Pd2–O2	179.6(2)
P1–Pd1–C10	171.5(3)	P3–Pd2–C8	171.2(3)
P1–Pd1–O1	82.3(1)	P3–Pd2–O2	81.0(1)
P1–Pd1–P2	97.4(1)	P3–Pd2–P4	98.7(1)
Pd1–O1–C7	125.8(5)	Pd2–O2–C9	126.8(5)
O1–C7–C121	116.4(7)	O2–C9–C131	117.5(7)
C121–C7–C8	120.2(7)	C131–C9–C10	120.4(8)
O1–C7–C8	123.2(7)	O2–C9–C10	122.0(8)
Pd2–C8–C7	102.4(6)	Pd1–C10–C9	101.0(6)

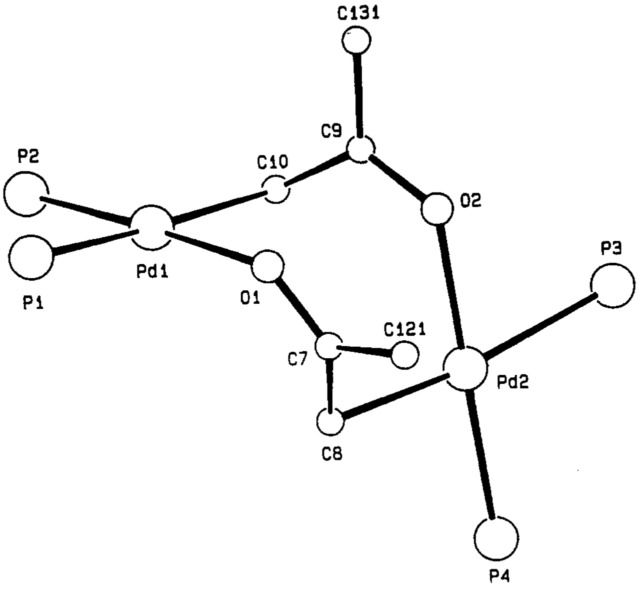

Figure 4. SCHAKAL drawing of the dimetallacycle in complex 9.

Synthesis of 8. Three equivalents of Bu^{t}NC (0.65 mL, 5.73 mmol) were added with a syringe to a benzene (40 mL) suspension of **3** (1.50 g, 1.93 mmol). The solution was stirred over a few minutes and turned dark yellow. After 1 h of stirring, the solvent was evaporated to dryness, and the orange-yellow solid was washed with *n*-hexane (3 × 50 mL). Evaporation of the hexane solution gave **8** as a white microcrystalline solid (65%).

The orange-yellow solid, insoluble in hexane, gave orange-yellow crystals when extracted with ether; these were insoluble in CH_2Cl_2 or deuterated acetone, but slowly reacted with these solvents. The IR spectrum does not show any band for C=O, O—H, and C=N, but one NC band at 2226 (m) cm^{-1} (corresponding to a coordinated isonitrile molecule) and another at 2136 (m) cm^{-1} (corresponding to a free isonitrile molecule). Analytical data for **8**: IR (Nujol) ν(N—H) 3254, ν(C=O) 1694, ν(C=N) 1660 cm^{-1}; ^{1}H NMR (C_6D_6) (two isomers 3/2) δ α 1.27 and 1.35 (2s, Bu^t, 36 H), 4.14 (broad s, NH, 2 H), 5.34 (s, =CH, 2 H), 7.18 (m, Ph, 10 H) β 1.25 and 1.32 (2s, Bu^t, 36 H), 4.09 (broad s, NH, 2 H), 5.49 (s, =CH, 2 H), 7.18 (m, Ph, 10 H); ^{13}C NMR (CD_2Cl_2) δ 29.1 and 30.6 (2s, C*Me*), 50.8 (s, *C*Me), 101.0 (s, =CH), 127.6–136.4 (m, Ph), 140.9 and 141.3 (2s, Ph), 154.7 and 155.0 (2s, C=N). MW (cryoscopy in benzene) 594 (calcd 570). Anal. Calcd for $C_{36}H_{50}N_4O_2$: C, 75.75; H, 8.83; N, 9.82. Found: C, 75.80; H, 9.08; N, 9.81. Complex **8** was also obtained by reacting **5** with 2 equiv of Bu^{t}NC under the conditions above.

Synthesis of 9. A MeCN (20-mL) solution of $AgOSO_2CF_3$ (0.37 g, 1.40 mmol) was added dropwise to a CH_2Cl_2 (50 mL) solution of **3** (1.12 g, 1.40 mL) containing MeCN (2.0 mL). A white precipitate suddenly formed and was filtered out. The solvent mixture was evaporated to 5 mL, and then Et_2O (50 mL) was added. The solution was kept at 0 °C and gave a yellow crystalline solid (1.03 g, 80%). Crystals suitable for the X-ray analysis were obtained by recrystallizing the solid from a 1:1 CH_2Cl_2/Et_2O mixture. Anal. Calcd for $9{\cdot}0.5(Et_2O)$, $C_{92}H_{79}F_6O_{8.5}P_4Pd_2S_2$: C, 60.47; H, 4.36. Found: C, 60.09; H, 4.08. ^1H NMR (CD_3CN): δ 1.18 (t, ether), 2.91 (large peak, CH_2Pd, 2 H), 3.47 (q, ether), 7.15 (d, Ph, 3 H), 7.35 (m, Ph, 2 H), 7.45–7.8 (m, PPh, 30 H). ^{31}P NMR (CD_3CN): δ 30.6 (s). ^1H NMR (CD_2Cl_2): δ 1.15 (t, ether), 2.67 (q, CH_2Pd, 1 H, J_{AP} = 6.50 Hz, J_{AB} = 10.60 Hz), 2.97 (q, CH_2Pd, 1 H, J_{BP} = 5.80 Hz), 3.44 (q, ether), 6.5–7.9 (m, Ph, 35 H). ^{13}C NMR (CD_2Cl_2): δ 26.3 (s, THF), 40.5 and 41.7 (2s, CH_2Pd), 68.5 (s, THF), 127.3–138.4 (m, Ph), 207.5 (s, CO). ^{31}P NMR (CD_2Cl_2): δ 24.7 and 37.9 (2s). The IR spectrum of **9** in the solid state (Nujol) and in CH_2Cl_2 solution does not show any carbonyl band, while in acetonitrile a CO band appears at 1643 cm^{-1}.

Crystal Structure Determination of Complexes 3, 5, and 9. The crystals of compounds **3**, **5**, and **9** were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with the use of TRACER.[16] Crystal data and details associated with structure refinement are given in Table I. Data were collected at room temperature (295 K) on a single-crystal diffractometer [Nonius CAD4 for **3** and Philips PW1100 for **5** and **9**, respectively]. For intensities and background, individual reflection profiles were analyzed.[17] The intensity data for complex **9** were corrected for crystal decay detected by two standard reflections monitored during the data collection. The structure amplitudes were obtained after the usual Lorentz and polarization corrections, and the absolute scale was established by the Wilson method.[18] The crystal quality was tested by ω scans, showing that crystal absorption effects could not be neglected for complex **3**. The data for complexes **3** and **5** were then corrected for absorption using ABSORB.[19] The function minimized during the least-squares refinement was $\sum w|\Delta F|^2$. A weighting scheme $w = k/[\sigma^2(F_0) + |g|F_0)^2]$ based on counting statistics was applied for complexes **5** and **9**.[20] For complex **3** unit weights were applied since these gave the most satisfactory analysis of variance and agreement factors. Anomalous scattering corrections were included in all structure factor calculations.[21b] Scattering factors for neutral atoms were taken from ref 21a for non–hydrogen atoms and from ref 22 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary. All calculations were carried out on an IBM-AT personal computer equipped with an INMOS T800 transputer using SHELX-76.[20] Solution and refinement were based on the observed reflections. The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map.

Complex 3. Refinement was first done isotropically and then anisotropically by full-matrix least squares for all non-H atoms. All the hydrogen atoms were located from difference Fourier maps and introduced in the final refinement as fixed atom contributions (isotropic *U*'s fixed at 0.08 Å^2). The final difference map showed no unusual feature, with no significant peak above the general background. Since the space group is acentric, the crystal chirality was tested by inverting all the coordinates ($x, y, z \rightarrow -x, -y, -z$) and refining to convergence once again. The resulting *R* values (R = 0.026, R_G = 0.029 *vs* R = 0.024, R_G = 0.026) indicated the original choice should be the correct one.

Complex 5. Refinement was first done isotropically and then anisotropically by blocked full-matrix least squares for all non-H atoms. All the hydrogen atoms were located from difference Fourier maps and introduced in the final refinement as fixed atom contributions (isotropic *U*'s fixed at 0.10 Å^2). The final difference map showed no unusual feature, with no peak having significant meaning above the general background.

Complex 8. Refinement was first done isotropically and then anisotropically by blocked full-matrix least squares for all the non-H atoms except for the $CF_3SO_3^-$ anions which were found to be affected by a severe disorder. In the asymmetric unit there are four half independent $CF_3SO_3^-$ anions giving a cation: anion molar ratio of 1:2. Each anion was found to be statistically distributed around a 2-fold axis interchanging the CF_3 and SO_3 groups. The anions are affected by different kinds of disorder which was solved for three of them considering the sulfur (carbon) atom statistically distributed over two positions sharing the oxygen (fluorine) atoms. The fourth group possesses a crystallographic C_2 symmetry with the 2-fold axis running through the middle point of the S2–S2″ bond (″ = $1.5 - x, y, -z$). In addition the O6F oxygen (fluorine) atom was split over two positions (A and B). The best fit was found by refining isotropically the atomic positions with the site occupation factors given in Table IV. The hydrogen atoms were put in geometrically calculated positions and introduced as fixed contributors prior to the last stage of refinement (U_{iso} = 0.08 Å^2). During the refinement, the phenyl rings were constrained to be regular hexagons (C–C, 1.395 Å). The final difference map showed no unusual feature, with no significant peak above the general background.

Final atomic coordinates are listed in Tables II–IV for non-H atoms and in Tables SII–SIV for hydrogens. Thermal parameters are given in Tables SV–SVII; bond distances and angles, in Tables SVIII–SX.[23]

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Supplementary Material Available: Tables of experimental details associated with data collection and structure refinement (Table SI), hydrogen atom coordinates (Tables SII–SIV), thermal parameters (SV–SVII), and bond distances and angles (Tables SVIII–SX) and Figure S1 (ORTEP drawing of complex **9**, 30% probability ellipsoids) (17 pages). Ordering information is given on any current masthead page.

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