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Hemilabile Phosphines by Methyl Acrylate Insertion into the P−H Bonds of Palladium(I)-Coordinated Secondary Phosphines. Labile Anion (X = OTf) vs PO-Chelate Coordination (X = BF$_4$) in Pd$_2$(μ-PR$_2$)(PR$_2$R′)$_2$(X) (R = Bu^t, R′ = CH$_2$CH$_2$COOMe; X = OTf, BF$_4$)

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Methyl acrylate reacts with $[Pd_2(\mu\text{-}PR_2)(\mu\text{-}PR_2H)(PR_2H)_2]X$ (R = Bu^t; **1a**, X = CF_3SO_3; **1b**, X = BF_4) to give, after CC insertion into the PH bonds of di-*tert*-butylphosphine, $[Pd_2(\mu\text{-}PR_2)(\mu,\eta^2\text{-}O_2SOCF_3)(\eta^1\text{-}PR_2R')_2]$ (**5a**) or $[Pd_2(\mu\text{-}PR_2)(\eta^2\text{-}PR_2R')_2]$ BF$_4$ (**5b**) (R′ = CH_2CH_2COOMe). The reaction of **1a** with methyl methacrylate proceeds analogously, forming $[Pd_2(\mu\text{-}PR_2)(\eta^2\text{-}PR_2R'')_2]CF_3SO_3$ (**6**) (R″ = $CH_2CH(CH_3)COOMe$) as a mixture of diastereoisomers. The unsaturated $[Pd_2(\mu\text{-}P)(P)_2]$ core is stabilized by the coordination of the triflate anion (**5a**) or of the carbonyl groups of the functional phosphines (**5b** and **6**). The weak Pd−O interactions in **5a** and **5b** are easily displaced by CO or *p*-tolylisonitrile, yielding $[Pd_2(\mu\text{-}PBu^t_2)(L)_2\{\eta^1\text{-}PBu^t_2(CH_2CH_2COOMe)\}_2]X$ (**7a**,**b**, L = CO; **8**, L = CN−C$_6$H$_4$-*p*-Me, X = CF_3SO_3). The reaction of **5a** with an excess of *p*-tolylisonitrile gives the new triangulo cluster $Pd_3(\mu\text{-}PBu^t_2)_2(CN\text{-}C_6H_4\text{-}p\text{-}Me)_5](CF_3SO_3)_2$, (**9**). The X-ray crystal and molecular structures of **5a** and **9** are also reported.

Introduction

Primary and secondary phosphines (and PH$_3$) as well as the corresponding oxides or hydrophosphonates have been extensively employed as PH donors in hydrophosphinations of CC, CO, and CN multiple bonds.[1] The reactions are generally performed in the presence of acidic, basic, or radical catalysts; possible drawbacks were shown to be a low regioselectivity and/or the occurrence of undesired side reactions, as for example the polymerization of the unsaturated substrate. Interesting developments of these synthetic procedures have been reported in the past few years, namely, the utilization of borane adducts of the PH donors in *uncatalyzed* reactions[2] or the first examples of transition metal (Pt, Pd, Ni, Rh, Ir) catalyzed reactions.[3]

By the stoichiometric addition of Mo-bonded PH donors to phosphino- or arsino-alkynes or -allenes, a series of complexed unsymmetrical PP- or PAs-chelating ligands have been prepared.[4] Moreover, potentially hemilabile P$_n$E$_n$ ligands (n = 2, E = N, O; n = 3, E = N, O, S) have been prepared by the addition of vinyl or allyl substrates to metal-bonded secondary diphosphines[5a] or macrocyclic triphosphines.[5b,c]

During our investigations on secondary phosphine mono-,[6] di-,[7] and trinuclear[8] complexes, we found that ethylene can insert into the PH bonds of R$_2$PH (R = Bu^t, Cy) molecules of dinuclear palladium(I) derivatives, e.g., compound **2**.[7f,g]

The comparison of the reactions of eq 1a,b was of some interest and showed that these highly hindered systems can, in some cases, discriminate the ligand they bind on the basis of its dimensions. In fact, the fragment [Pd$_2$-

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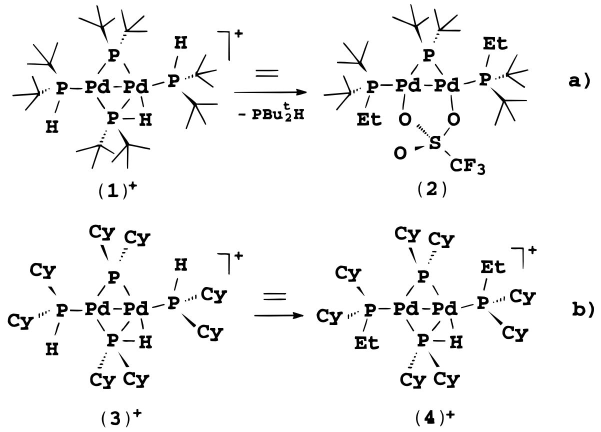

(μ-PR$_2$)(PR$_2$H)$_2$]$^+$ coordinates a bridging phosphine when R = Cy,[7f] but was found to bind the triflate anion, also in the presence of excess PBu$^t_2$H, when R is the bulkier *tert*-butyl.[7g] Given the presence of a labile triflate ligand spanning two adjacent palladium centers, complex **2** may be of relevant synthetic interest, but it was isolated in very low yields, thus preventing further investigations. As reported in the following, the reaction of [Pd$_2$(μ-PR$_2$)(μ-PR$_2$H)(PR$_2$H)$_2$]X (R = Bu^t; **1a**, X = CF$_3$SO$_3$; **1b**, X = BF$_4$) with acrylate esters proceeds analogously, giving high yields of the products arising from CC insertion into the PH bonds of the secondary phosphines. The so-formed phosphinoesters behave as hemilabile η^2-P,O-chelates, easily transformed into terminal P-bonded ligands by CO, isonitriles, and ligands as weak as the triflate ion (in some cases) or a coordinating solvent such as CH$_3$CN. Extensive rearrangement was observed in the reaction of **5a** with an excess of *p*-tolylisonitrile, which yielded the 44 e$^-$ triangulo cluster [Pd$_3$(μ-PBu$^t_2$)$_2$(CN-C$_6$H$_4$-*p*-Me)$_5$](CF$_3$SO$_3$)$_2$.

Results and Discussion

A violet suspension of [Pd$_2$(μ-PR$_2$)(μ-PR$_2$H)(PR$_2$H)$_2$]CF$_3$SO$_3$ [R = Bu^t: **1a**] in DME reacts with a 4-fold excess of CH$_2$=CHCOOCH$_3$, yielding an orange solution. After workup, the orange solid **5a** can be isolated in high yields. The ^{31}P{^{1}H} NMR spectrum (C$_6$D$_6$, 293 K) of **5a** contains only a doublet at 43.7 and a triplet at 311.5 ppm ($^2J_{PP}$ = 82 Hz), thus indicating that one of the phosphines of **1a** has been released. Moreover, these data suggest that **5a** has retained the dinuclear framework, with a single bridging-phosphide and two equivalent terminally bonded phosphines. The high-field doublet is only slightly broadened in the corresponding proton-coupled spectrum, and the absence of the usual large PH coupling ($^1J_{PH}$ ca. 300 Hz) further suggests that the phosphines are tertiary, i.e., that a hydrophosphination of the CC double bond of the ester has occurred. The hypothesis is confirmed by the ^{1}H NMR spectrum (C$_6$D$_6$, 293 K), which lacks the typical PH resonance and exhibits signals at 1.18 (virtual triplet, [$^3J_{HP} + {}^5J_{HP}$] = 6.3 Hz, 36 H), 1.48 (d, $^3J_{HP}$ = 13.6 Hz, 18 H), 2.12 (br m, 4 H), 2.81 (br m, 4 H), and 3.42 (s, 6 H) ppm, respectively assigned to the protons of the *tert*-butyl groups on the phosphines and the phosphido ligands and of the PC*H$_2$*, C*H$_2$*CO, and OC*H$_3$* moieties of the new PBu$^t_2$(CH$_2$CH$_2$COOCH$_3$) ligands. As suggested by these spectra and confirmed by elemental analyses, complex **5a** contains only two palladium atoms, a bridging phosphide, two of the new tertiary phosphines, and the triflate counterion. Since, if only the P nuclei are coordinated to the Pd$_2$ core, **5a** should be highly unsaturated (26 e$^-$), one may anticipate that there must be an interaction with the oxygen atoms of the tertiary phosphines or of the triflate anion. The latter geometry occurs in the solid state, as shown by an X-ray crystallographic study (see below) and by the IR (Nujol, KBr) spectrum. This shows an absorption at 1745 (m, $\nu_{C=O}$) cm^{-1} (close to the values observed for terminal P-bonded phosphinoesters)[9] and those pertaining to the triflate ion (1298, 1166, 1019, and 633 cm^{-1}) close to the corresponding absorptions in **2** and significantly shifted from the expected position for uncoordinated triflate ions (ca. 1269, 1145, 1032, and 637 cm^{-1}).[10] The solid-state structure is retained in solution, as indicated by the solubility of **5a** in apolar solvents [soluble in Et$_2$O and C$_6$D$_6$ and slightly soluble (0.005 M) in *n*-hexane] and by the observation of the $\nu_{C=O}$ absorption at 1741 cm^{-1} in toluene. Moreover, the appearance of the ^{1}H NMR signal at 1.18 ppm as a virtual triplet suggests that the P−Pd−Pd−P fragment is close to linear in solution, as found in the solid state (see below); an analogous splitting was observed for the resonances assigned to the functional phosphines in the ^{13}C{^{1}H} NMR spectrum (see Experimental Section). Finally the value of $^2J_{PP}$ at 82 Hz is intermediate between the values observed in [(R$_3$P)(L)Pd(μ-PR$_2$)Pd(L)$_2$]$^+$ cations (L = monodentate ligand), where the P nuclei are in pseudo-cis (6−60 Hz) or pseudo-trans (140−270 Hz) position,[7] in accord with the value of the PPdP$_\mu$ angles in the range 125−131°.

Interaction of methyl acrylate with the same dipalladium cation, taken as the fluoroborate salt (**1b**), still results in the CC insertion; however in this case, the ionic compound [Pd$_2$(μ-PR$_2$)(η^2-PR$_2$R′)$_2$]BF$_4$ (**5b**) is produced in 82% yield (Scheme 1). In fact, **5b** easily dissolves in polar solvents (acetone, CH$_2$Cl$_2$), from which it can be precipitated by the addition of Et$_2$O. The $\nu_{C=O}$ absorption was found at 1675 cm^{-1}, with a 70 cm^{-1} bathochromic shift compared to **5a**, strongly supporting the involvement of the carbonyl groups of the functional phosphines in metal coordination.

The fluoroborate ion is clearly unbound, as shown by the expected unique absorption (vs, ν_{BF}) at 1050 cm^{-1}.[11]

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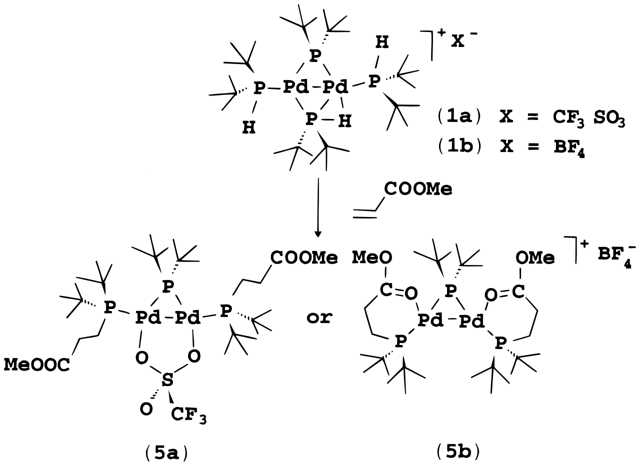
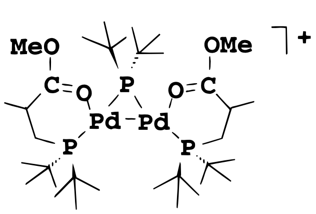
Scheme 1



The ionic structure of **5b** is confirmed by the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$, 293 K), which shows significant downfield shifts [52.4 (d), 319.5 (t) ppm] compared to the corresponding signals of the neutral **5a**. The spectrum also implies a symmetrical structure. Moreover, the value of $^2J_{PP}$ (105 Hz) is *significantly larger* than in **5a**, although still below the range given above for $^2J_{PP(trans)}$ (it is worth noting, however, that the range is referred to complexes of *monodentate alkyl- or aryl*phosphines). The increase of $^2J_{PP}$ suggests a widening of the $PPdP_\mu$ angles compared to **5a**. We therefore prefer structure **5b** (Scheme 1) over its possible isomer with P,P′-cis and O,O′-trans to P_μ; for the latter we should in fact expect a *significant decrease* of $^2J_{PP}$.

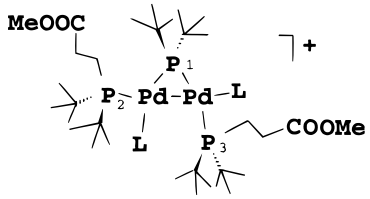
An equimolar amount of CF_3SO_3Na added to a DME solution of **5b** causes the rapid and quantitative formation of **5a**. This, however, does not necessarily mean that the coordination of the triflate is highly preferred; in fact, the solution structures of **5a** and **5b** depend strongly upon the solvent. As shown above, complex **5a** retains its structure in apolar noncoordinating solvents ($\nu_{C=O} = 1741$ cm^{-1} and $^2J_{PP} = 82$ Hz in toluene). Two $\nu_{C=O}$ absorptions were observed in CH_2Cl_2 (1737, 1673 cm^{-1}, ca. 1:1 intensity ratio), and the value $^2J_{PP}$ rises to 95 Hz. This is consistent with the presence of an equilibrium mixture of **5a** and the ionic P,O-bonded $[Pd_2(\mu\text{-}PR_2)(\eta^2\text{-}PR_2R')_2]CF_3SO_3$, the latter being stabilized by the polar solvent. Complex **5b** shows a single $\nu_{C=O}$ absorption at 1664 (DME) or 1673 (CH_2Cl_2) cm^{-1} ($^2J_{PP} = 105$ Hz), which agrees with the structure shown in Scheme 1. When the solvents (toluene, CH_2Cl_2, or DME) are removed from the above solutions, complexes **5a** or **5b** are recovered unchanged, as estimated by their IR (Nujol) spectra. On the other hand, by dissolving **5b** in the coordinating solvent CH_3CN, a single $\nu_{C=O}$ absorption was observed, shifted from ca. 1670 (solid state and DME or CH_2Cl_2 solutions) to 1738 cm^{-1}. This indicates the opening of the P,O-chelate rings and suggests the coordination of two solvent molecules, which should be positioned pseudo-cis to the phosphido ligand, since the value of $^2J_{PP}$ in the $^{31}P\{^1H\}$ NMR spectrum [324.0 (t), 51.8 (d)] was found to be 113 Hz. Identical values of $\nu_{C=O}$, δ_P, and $^2J_{PP}$ were found when **5a** was dissolved in CH_3CN, thus indicating the formation of the same cation, reasonably the P-bonded $[Pd_2(\mu\text{-}PR_2)(\eta^1\text{-}PR_2R')_2(NCCH_3)_2]^+$. Again, compounds **5a** and **5b** are recovered unchanged when the solvent is evaporated.

As clearly suggested by these data, the Pd−O interactions in **5a** and **5b** are very weak (both being displaced by the weakly coordinating solvent CH_3CN) and close in energy. This is nicely confirmed by the reaction of **1a** with methyl methacrylate, yielding a mixture of diastereoisomers of the ionic derivative $[Pd_2(\mu\text{-}PR_2)(\eta^2\text{-}PR_2R'')_2]CF_3SO_3$ (**6**) (R″ = $CH_2CH(CH_3)COOMe$, $\nu_{CO} =$ 1672, and 1266, 1143, 1032, 638 cm^{-1} for the free triflate ion; $^2J_{PP} = 100$ Hz). The other spectroscopic features are those expected for structure **6** (see Experimental Section). Here the carbonyls successfully compete with the triflate ion, as a result of the substitution on the methylene chain, which increases both the stability of the P,O-chelate ring[12] and the basicity[13] of the carbonyl groups.



(6)$^+$

As expected, both types of Pd−O interactions are easily displaced by carbon monoxide, which reacts with **5a** or **5b** to give the corresponding dicarbonyl $[Pd_2(\mu\text{-}PBu^t_2)(CO)_2\{\eta^1\text{-}PBu^t_2(CH_2CH_2COOMe)\}_2]X$ (**7a**,**b**). The reaction of **5a** with *p*-tolylisonitrile yields the analogous derivative $[Pd_2(\mu\text{-}PBu^t_2)(CN{-}C_6H_4\text{-}p\text{-}Me)_2\{\eta^1\text{-}PBu^t_2(CH_2CH_2COOMe)\}_2]CF_3SO_3$ (**8**).



(7)$^+$ L = CO
(8)$^+$ L = CN-C_6H_4-*p*-Me

The characterization of these compounds is straightforward; indeed we found (a) three resonances in the $^{31}P\{^1H\}$ NMR spectrum, one at 369.6 (**7a**,**b**) or 329.4 ppm (**8**) for the bridging nucleus P_1, and two between 50 and 60 ppm for the nonequivalent phosphines, one pseudo-cis (P_2, $^2J_{P2P1} = 22{-}24$ Hz) and one pseudo-trans (P_3, $^2J_{P3P1} = 140{-}162$ Hz) to P_1; (b) two strong ν_{CO} absorptions at ca. 2040 cm^{-1} for **7a**,**b** and a strong, broad absorption at 2137 cm^{-1} (ν_{CN}) for **8** (see Experimental Section).

However, it is worth noting the easy reversibility of the carbonylation reactions (prolonged exposure to

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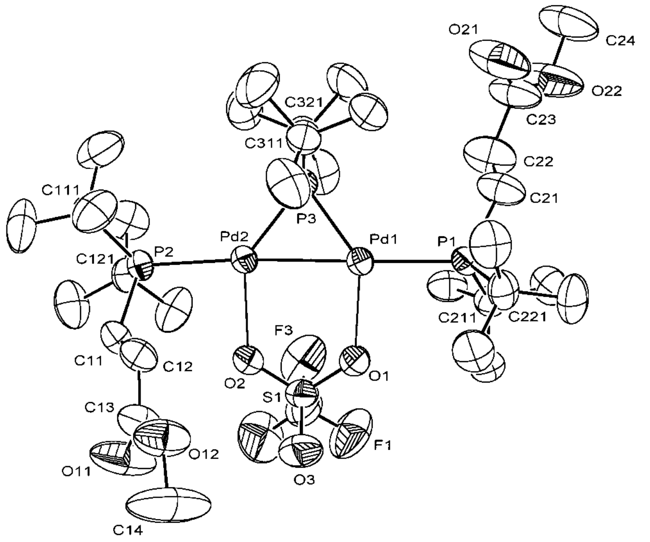
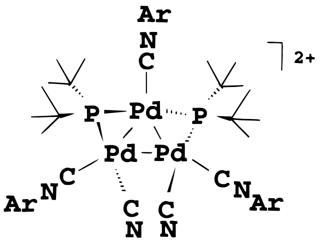


Figure 1. ORTEP view of the molecular structure of **5a**. Thermal ellipsoids are drawn at 50% probability.

vacuum restores complexes **5a**,**b**) and the formation of a single isomer of cations **7**$^+$ and **8**$^+$, tentatively attributed to the steric bulkiness of the phosphine and the phosphido ligands.

The reaction of **5a** with a higher (8:1) excess of *p*-tolylisonitrile proceeds with the unexpected formation of a new complex, shown to be the triangulo cluster [$Pd_3(\mu\text{-}PBu^t_2)_2(CN\text{-}C_6H_4\text{-}p\text{-}Me)_5](CF_3SO_3)_2$ (**9**) by an X-ray crystallographic study (see below). Complex **9**, isolated in 49% yield, shows a single $^{31}P\{^1H\}$ NMR resonance at 329.4 ppm (s) and the expected signals in the ^1H, $^{13}C\{^1H\}$ NMR and IR spectra. Both the ^1H and $^{13}C\{^1H\}$ NMR spectra show that the five isonitrile ligands rapidly equilibrate on the NMR time scale, probably through isonitrile-bridged intermediates. A similar scrambling of the isonitrile ligands was found in the related derivative $Pd_3(\mu\text{-}SO_2)_2(CNBu^t)_5$.[14]



$(\mathbf{9})^{2+}$

Crystal Structure of 5a. An ORTEP view of **5a** is given in Figure 1, and a list of selected bond lengths and angles is given in Table 1, together with those of the related compound **2**.[7g]

In both compounds (**5a** and **2**), the coordination sphere around each Pd atom consists of a M−M bond, a terminal phosphine, a bridging phosphide phosphorus, and one oxygen of a bridging $CF_3SO_3^-$ anion. Thus the overall geometry is comparable in both compounds even though in **2** a crystallographic mirror plane is present (passing through the midpoint of the Pd−Pd bond and containing the bridging P atom as well as the unbound O atom and a C−F group of the anion). As a consequence, only half of the molecule is independent.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [$Pd_2(\mu\text{-}PBu^t_2)(\mu,\eta^2\text{-}O_2SOCF_3)\{PBu^t_2(CH_2CH_2COOMe)\}_2$] (5a) and [$Pd_2(\mu\text{-}PBu^t_2)(\mu,\eta^2\text{-}O_2SOCF_3)(PBu^t_2Et)_2$] (2)[a]

	5a	2[b]
Pd1−Pd2	2.6390(3)	2.648(2)
Pd1−P1	2.3868(8)	2.378(6)
Pd2−P2	2.4044(8)	
Pd1−P3	2.2110(9)	2.227(3)
Pd2−P3	2.2141(8)	
Pd1−O1	2.290(2)	2.28(2)
Pd2−O2	2.321(2)	
S1−O1	1.441(3)	1.47(2)
S1−O2	1.453(2)	
S1−O3	1.425(3)	1.42(4)
P1−C21	1.846(4)	
P2−C11	1.848(4)	
P−C(av)	1.888(10)	
Pd1−P3−Pd2	73.22(3)	73.0(3)
P1−Pd1−Pd2	178.13(2)	180(1)
P2−Pd2−Pd1	175.15(2)	
P1−Pd1−P3	125.55(3)	126.4(4)
P2−Pd2−P3	131.07(3)	
Pd1−Pd2−O2	86.82(2)	
Pd2−Pd1−O1	87.87(6)	
P1−Pd1−O1	93.17(6)	92.5(6)
P2−Pd2−O2	88.83(6)	
Pd1−P1−C21	116.6(2)	
Pd2−P2−C11	106.1(1)	
O1−S1−O2	113.9(1)	114(1)
O1−S1−O3	114.4(2)	
O2−S1−O3	115.2	116(1)

[a] Cfr. ref 7 g. [b] The molecule lies on a crystallographic C2 axis.

The main differences between the two compounds are (a) the Pd−Pd separation shorter in **5a** than in **2** (2.6390(3) and 2.648(2) Å, respectively) and (b) the longer Pd−P(terminal) and Pd−P(bridging) distances (2.396 (av) and 2.212 Å, respectively).

These changes are consistent with the presence of different terminal tertiary phosphines with different electron-donating properties.

It may also be noted that the coordination around the two metal centers is slightly different, as can be seen from the values of the Pd1−P1 and Pd2−P2 distances (2.3868(8) and 2.4044(8) Å, respectively) and of the P1−Pd1− P3 and P2−Pd2−P3 angles (125.55(3)° and 131.07(3)°, respectively). These distortions may be due to the presence of a bulky tertiary phosphine, giving rise to different nonbonded interactions between the coordinated triflate moiety and the phosphine substituents on each side of the molecule.

As expected, the S−O separations are different, the longest being those of the metal-coordinated oxygen atoms; however their values (1.447 Å av) suggest a weakly coordinated $CF_3SO_3^-$ anion.

It should also be noted that the terminal phosphines are not significantly bent; all other bond distances and angles fall in the expected range for this class of compounds (see ref 7g).

Crystal Structure of 9. An ORTEP view of **9** is shown in Figure 2, and a selection of bond lengths and angles is given in Table 2.

The cation $(\mathbf{9})^{2+}$ lies on a crystallographic C_2 axis (bisecting the Pd(1)−Pd(1)′ bond and passing through atoms Pd(2), C12, N12, and C211). Therefore only half

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(14) Otsuka, S.; Tatsuno, Y.; Miki, M.; Aoki, T.; Matsumoto, M.; Yoshioka, H.; Nakatsu, K. *J. Chem. Soc., Chem. Commun.* **1973**, 445.

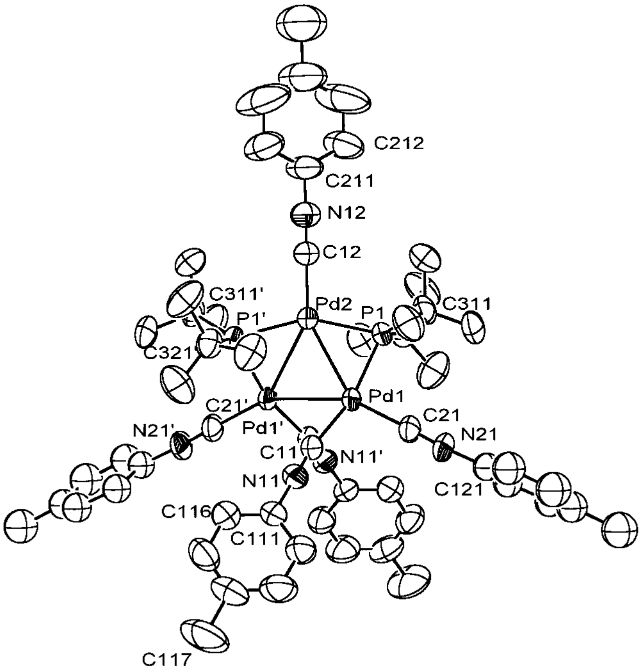

Figure 2. ORTEP view of the molecular structure of the cation $\mathbf{9}^{2+}$. Only one conformation of the C111−C116 ring is shown for clarity. Thermal ellipsoids are drawn at 50% probability; primed atoms are obtained by those unprimed by the symmetry operations 0.5 + *x*; *y*; 0.5 − *z* (C_2 axis).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Pd$_3$(*μ*-PBu$^t{}_2$)$_2$(CN-C$_6$H$_4$-*p*-Me)$_5$](CF$_3$SO$_3$)$_2$ (9)[a]

Pd1−Pd1′	2.7410(5)	Pd1′−Pd1−Pd2	60.614(7)
Pd1−Pd2	2.7930(4)	Pd1−Pd2−Pd1′	58.77(1)
Pd1−P1	2.281(1)	Pd1−P1−Pd2	75.43(3)
Pd2−P1	2.2849(9)	Pd1−Pd2−P1	52.22(3)
Pd1−C21	1.967(4)	Pd2−Pd1−P1	52.35(2)
Pd1−C11	2.064(4)	Pd1−Pd2−C12	150.614(7)
Pd2−C12	1.945(6)	Pd2−Pd1−C21	145.8(1)
N11−C11	1.146(5)	Pd2−Pd1−C11	113.8(1)
N11−C111	1.402(5)	Pd1′−Pd1−C21	151.7(1)
N12−C12	1.152(7)	Pd1′−Pd1−C11	71.4(1)
N12−C211	1.394(8)	P1−Pd1−C11	163.4(1)
N21−C21	1.148(5)	P1−Pd1−C21	95.8(1)
N21−C121	1.398(6)	C11−N11−C111	177.2(1)
		C21−N21−C121	174.4(5)

[a] Primed atoms are obtained by those unprimed by the following symmetry operation: 0.5 − *x*, *y*, 0.5 − *z*.

of the geometric parameters defining the coordination spheres are independent.

The three Pd atoms form a trimetallic unit with slightly different Pd−Pd separations (Pd(1)−Pd(1)′ = 2.7410(5), Pd(1)−Pd(2) = 2.7930(4) Å), with the longer Pd−Pd edges bridged by the PBu$^t{}_2$ ligands. The coordination geometry around the metal centers is completed by one (on Pd(2)) or two isocyanide ligands terminally bonded in an approximately linear fashion (C−N−C angles 177.2° (av)). All other bond distances and angles are unexceptional.

The phenyl ring bound to the C21−N21 group is disordered between two different positions (cfr. Experimental Section), showing a high degree of conformational flexibility.

The overall structure of this 44 e$^-$ cation highly resembles those reported for the isoelectronic palladium ([Pd$_3$(μ-SO$_2$)$_2$(CNBu^t)$_5$])[14] and [Pd$_3$(μ-SO$_2$)$_2$(PPh$_3$)$_3$(CNC$_8$H$_9$)$_2$])[15] and platinum ([Pt$_3$(μ-SO$_2$)$_2$ (PCy$_3$)$_3$(CNC$_8$H$_9$)$_2$])[16] derivatives.

Experimental Section

General Data. The reactions were carried out under a nitrogen atmosphere, by using standard Schlenk techniques. Complexes **1a**,**b** were prepared as previously described.[7h]

Solvents were dried by conventional methods and distilled under nitrogen prior to use. IR spectra (Nujol mulls, KBr) were recorded on a Perkin-Elmer FT-IR 1725X spectrometer. NMR spectra were recorded on a Varian Gemini 200 BB instrument; frequencies are referenced to the residual resonances of the deuterated solvent (H, ^{13}C) and 85% H$_3$PO$_4$ (^{31}P).

Preparation of [Pd$_2$(μ-PR$_2$)(μ,η^2-O$_2$SOCF$_3$)(η^1-PR$_2$R′)$_2$] (5a). Methyl acrylate (535 μL, 3.71 mmol) was added to a violet DME (30 mL) suspension of **1a** (877 mg, 0.927 mmol). The suspension was stirred 3 h at 50 °C. The resulting orange solution was evaporated to dryness, and the residue was suspended in Et$_2$O (10 mL). Some insoluble polyolefin was filtered off, and the filtrate was evaporated. The residue was suspended in *n*-hexane (5 mL), and the orange solid was isolated by filtration and vacuum-dried (792 mg, 88%). Anal. Calcd for C$_{33}$H$_{68}$F$_3$O$_7$P$_3$Pd$_2$S: C, 40.7; H, 7.05. Found: C, 40.6, H, 7.25. See Results and Discussion for IR, ^{31}P NMR, and ^{1}H NMR spectra. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K): 19.6 (vt, $^1J_{CP} + {}^4J_{CP} = 4.3$ Hz; [t, $^1J_{CH} = 130$ Hz], P*C*H$_2$), 30.4 (vt, $^2J_{CP} + {}^5J_{CP} = 3.6$ Hz; [q, $^1J_{CH} = 127$ Hz], PC*C*H$_3$), 32.0 (d, $^2J_{CP} = 9.5$ Hz; [q, $^1J_{CH} = 126$ Hz], μ-PC*C*H$_3$), 32.5 (vt, $^2J_{CP} + {}^5J_{CP} = 3.4$ Hz; [t, $^1J_{CH} = 128$ Hz], *C*H$_2$CO), 35.0 (vt, $^1J_{CP} + {}^4J_{CP} = 3.7$ Hz; [br s], P*C*CH$_3$), 39.7 (d, $^2J_{CP} = 8.9$ Hz; [br s], μ-P*C*CH$_3$), 51.4 (s; [q, $^1J_{CH} = 146$ Hz], *C*H$_3$O), 173.4 (br s; [br s], *C*O) (features from the corresponding proton-coupled spectrum are given in square brackets).

Preparation of [Pd$_2$(μ-PR$_2$)(η^2-PR$_2$R′)$_2$]BF$_4$ (5b). Methyl acrylate (163 μL, 1.8 mmol) was added to a violet DME (30 mL) suspension of **1b** (160 mg, 0.181 mmol). The suspension was stirred 3 h at 70 °C. The resulting brown solution was concentrated to ca. 2 mL, and complex **5b** was precipitated as a red powder by adding Et$_2$O (15 mL), isolated by filtration, and vacuum-dried (134 mg, 82%). Anal. Calcd for C$_{32}$H$_{68}$BF$_4$O$_4$P$_3$Pd$_2$: C, 42.3; H, 7. 54. Found: C, 42.4, H, 7.60. ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): δ (ppm) 52.4 (d, $^2J_{PP} = 105$ Hz), 319.5 (t, $^2J_{PP} = 105$ Hz). ^{1}H NMR (CDCl$_3$, 293 K): δ(ppm) 1.39 (d, $^3J_{HP} = 14$ Hz, 36 H, PCC*H*$_3$), 1.57 (d, $^3J_{HP} = 15$ Hz, 18 H, μ-PCC*H*$_3$), 2.05 (m, 4 H, PC*H*$_2$), 2.88 (m, 4 H, C*H*$_2$CO) and 3.82 (s, 6 H, OC*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K): δ (ppm) 20.2 (s, [t, $^1J_{CH} = 133$ Hz], P*C*H$_2$), 34.4 (s, [q, $^1J_{CH} = 125$ Hz], PC*C*H$_3$), 36.3 (s, [q, $^1J_{CH} = 126$ Hz], μ-PC*C*H$_3$), 38.3 (s, [t, $^1J_{CH} = 134$ Hz], *C*H$_2$CO), 39.9 (s, [br s], P*C*CH$_3$), 46.6 (s, [br s], P*C*CH$_3$), 58.1 (s, [q, $^1J_{CH} = 150$ Hz], *C*H$_3$O), 182.2 (s, [br s], *C*O) (features from the corresponding proton-coupled spectrum are given in square brackets).

Preparation of [Pd$_2$(μ-PR$_2$)(η^2-PR$_2$R″)$_2$]CF$_3$SO$_3$ (6). Methyl methacrylate (2 mL, 18.7 mmol) was added to a violet suspension of **1a** (300 mg, 0.317 mmol) in DME (20 mL). After stirring for 4 h at 60 °C, the brown solution was concentrated to ca. 5 mL and Et$_2$O (20 mL) was added. The relevant amount of the polyolefin that precipitated was filtered off. The filtrate was evaporated, and the residue was suspended in Et$_2$O. The brown solid was isolated by filtration and vacuum-dried (206 mg, 65%). Anal. Calcd for C$_{35}$H$_{73}$F$_3$O$_7$P$_3$Pd$_2$S: C, 42.0, H, 7.26. Found: C, 41.2; H, 6.99. ^{31}P{^{1}H} NMR (acetone-*d*$_6$, 293 K): δ (ppm) 55.5 (d, $^2J_{PP} = 100$ Hz), 55.7 (d, $^2J_{PP} = 100$ Hz), 320.3 (t, $^2J_{PP} = 100$ Hz), 322.4 (t, $^2J_{PP} = 100$ Hz). ^{1}H NMR (acetone-*d*$_6$, 293 K): δ (ppm) 1.5 (br m, 60 H, PCC*H*$_3$ + CHC*H*$_3$), 2.6 (br m, 4 H, PC*H*$_2$), 3.1 (br m, 2 H, C*H*CH$_3$), 3.8 (s, 3 H, OC*H*$_3$),

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(15) Burrows, A. D.; Machall, J. C.; Mingos, D. M. P.; Powell, H. R. *J. Chem. Soc., Dalton Trans.* **1992**, 1521.

(16) Mingos, D. M. P.; Williams, I. D.; Watson, M. J. *J. Chem. Soc., Dalton Trans.* **1988**, 1509.

3.9 (s, 3 H, OCH_3). IR (Nujol, KBr): 1672 ($\nu_{C=O}$), 1266, 1143, 1032, 638 (uncoordinated triflate)[10] cm^{-1}.

Preparation of [$Pd_2(\mu\text{-}PBu^t{}_2)(CO)_2(\eta^1\text{-}PBu^t{}_2R')_2$]$CF_3SO_3$ (7a). An orange solution of **5a** (70 mg, 0.072 mmol) in *n*-heptane (20 mL) was cooled at −70 °C. The flask was evacuated and filled with carbon monoxide; the solution quickly turned yellow and a yellow solid started to precipitate; half of the solvent was evaporated and the solid was isolated by filtration and vacuum-dried (40 mg, 54%). Anal. Calcd for $C_{35}H_{68}F_3O_9P_3Pd_2S$: C, 40.9; H, 6.67. Found: C, 40.6; H, 6.49. $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectra were identical to those given for **7b** (next preparation). IR (Nujol, KBr): 2046, 2042 (ν_{CO}), 1745 ($\nu_{C=O}$), 1265, 1156, 1030, 638 (uncoordinated triflate)[10] cm^{-1}.

Preparation of [$Pd_2(\mu\text{-}PBu^t{}_2)(CO)_2(\eta^1\text{-}PBu^t{}_2R')_2$]$BF_4$ (7b). Carbon monoxide was bubbled into a brown acetone (20 mL) solution of **5b** (120 mg, 0.132 mmol). The solution quickly turned orange and was concentrated to ca. 3 mL; the addition of Et_2O caused the precipitation of an orange powder, which was isolated by filtration and vacuum-dried (48 mg, 39%). Anal. Calcd for $C_{34}H_{68}BF_4O_6P_3Pd_2$: C, 42.3; H, 7.10. Found: C, 42.7; H, 6.89. $^{31}P\{^1H\}$ NMR (acetone-d_6, 273 K): δ (ppm) 59.3 (dd, $^2J_{PP} = 140$, $^3J_{PP} = 7$ Hz), 59.6 (dd, $^2J_{PP} = 22$, $^3J_{PP} = 7$ Hz), 369.6 (dd, $^2J_{PP} = 140$, 22 Hz). ^1H NMR ($CDCl_3$, 293 K): δ (ppm) 1.35 (d, $^3J_{PH} = 14$ Hz, 36 H, PCCH_3), 1.43 (d, $^3J_{PH} = 15$ Hz, 18 H, μ-PCCH_3), 2.65 (m, 4 H, PCH_2), 2.84 (m, 4 H, CH_2CO), 3.72 (s, 6 H, OCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ (ppm) 23.6 (s, [t, $^1J_{CH} = 135$ Hz], PCH_2), 30.2 (d, $^2J_{CP} = 5$ Hz [q, $^1J_{CH} = 134$ Hz], PCCH_3), 32.7 (d, $^2J_{CP} = 5$ Hz [q, $^1J_{CH} = 126$ Hz], _μ-PCCH_3), 35.8 (s [s], PCCH$_3$), 37.2 (s [s], PCCH$_3$), 42.9 (s [t, $^1J_{CH} = 140$ Hz], CH_2CO), 52.4 (s [q, $^1J_{CH} = 148$ Hz], OCH_3), 171.9 (s [s], C=O) (values in square brackets from the proton-coupled spectrum, resonances due to the carbonyl ligands were not observed). IR (Nujol, KBr): 2037 (br, ν_{CO}), 1739 ($\nu_{C=O}$), 1059 (ν_{BF}) cm^{-1}.

Preparation of [$Pd_2(\mu\text{-}PBu^t{}_2)(\eta^1\text{-}PBu^t{}_2R')_2(CN\text{-}C_6H_4\text{-}p\text{-}Me)_2$]$CF_3SO_3$ (8). An orange solution of **5a** (95 mg, 0.0978 mmol) in CH_2Cl_2 (10 mL) quickly turned yellow after the addition of a toluene (2 mL) solution of *p*-tolylisonitrile (23 mg, 0.196 mmol). The solvents were evaporated, and the oily residue was suspended in Et_2O and vigorously stirred for 15 min. The yellow solid obtained was isolated by filtration, washed with Et_2O, and vacuum-dried (85 mg, 72%). Anal. Calcd for $C_{49}H_{82}F_3N_2O_7P_3Pd_2S$: C, 48.8; H, 6.85, N, 2.82. Found: C, 48.7; H, 6.68, N, 2.66. $^{31}P\{^1H\}$ NMR (acetone-d_6, 293 K): δ (ppm) 52.1 (dd, $^2J_{PP} = 24$, $^3J_{PP} = 12$ Hz), 57.0 (dd, $^2J_{PP} = 162$, $^3J_{PP} = 12$ Hz), 329.4 (dd, $^2J_{PP} = 162$, 24 Hz). ^1H NMR (acetone-d_6, 293 K): δ (ppm) 1. 5 (m, 54 H, PCCH_3), 2.4 (br s, 6 H, C_6H_4−CH_3), 2.8 (br m, 8 H, PCH_2 + CH_2CO), 3.7 (s, 3 H, OCH_3), 3.8 (s, 3 H, OCH_3), 7.5 (m, 8 H, C_6H_4). IR (Nujol, KBr): 2137 (br, ν_{CN}), 1729 ($\nu_{C=O}$), 1268, 1147, 1032, 639 (uncoordinated triflate)[10] cm^{-1}.

Preparation of [$Pd_3(\mu\text{-}PBu^t{}_2)_2(CN\text{-}C_6H_4\text{-}p\text{-}Me)_5$]$(CF_3SO_3)_2$ (9). An orange solution of **5a** (80 mg, 0.0823 mmol) in acetone (20 mL) quickly turned red after the addition of a toluene (5 mL) solution of *p*-tolylisonitrile (78 mg, 0.664 mmol). The solvents were evaporated and the oily residue was suspended in Et_2O and vigorously stirred for 10 min. The yellow solid obtained was isolated by filtration, washed with Et_2O, and vacuum-dried (40 mg, 49%). Anal. Calcd for $C_{58}H_{71}F_6N_5O_6P_2Pd_3S_2$: C, 46.6; H, 4.79, N, 4.69. Found: C, 47.4; H, 4.79, N, 4.77. $^{31}P\{^1H\}$ NMR (acetone-d_6, 293 K): δ (ppm) 329.4 (s). ^1H NMR (acetone-d_6, 293 K): δ (ppm) 1. 5 (d, $^2J_{HP} = 14$ Hz, 36 H, PCCH_3), 2.4 (s, 15 H, C_6H_4−CH_3), 7.4 (m, 20 H, C_6H_4). $^{13}C\{^1H\}$ NMR (acetone-d_6, 293 K): δ (ppm) 21.4 (s, C_6H_4−CH_3), 32.3 (d, $^2J_{CP} = 8$ Hz, PCCH_3), 40.6 (d, $^1J_{CP} = 4$ Hz, PCCH$_3$), 123.9 (s, C), 125.8 (s, CH), 130.3 (s, CH), 140.9 (s, C). IR (Nujol, KBr): 2138 (br, ν_{CN}), 1262, 1147, 1031, 637 (uncoordinated triflate)[10] cm^{-1}.

Crystallography. Deep orange crystals of **5a**, suitable for X-ray diffraction, were obtained by crystallization from *n*-heptane and are air stable. Air stable, light red crystals of **9** were obtained from $CDCl_3/Et_2O$.

Table 3. Experimental Data for the X-ray Diffraction Study of [$Pd_2(\mu\text{-}PBu^t{}_2)(\mu,\eta^2\text{-}O_2SOCF_3)\{PBu^t{}_2(CH_2CH_2COOMe)\}_2$] (5a) and [$Pd_3(\mu\text{-}PBu^t{}_2)_2(CN\text{-}C_6H_4\text{-}p\text{-}Me)_5$]$(CF_3SO_3)_2$ (9)

	5a	9
fw	971.64	1493.46
data coll. *T*, K	298(2)	298(2)
radiation	Mo Kα (graphite monochromated $\lambda = 0.71069$ Å)	
cryst syst	orthorombic	monoclinic
space group	*Pbca*	*C*2/*c*
a, Å	23.3300(10)	26.4218(1)
b, Å	16.3780(10)	18.9675(1)
c, Å	23.6090(10)	17.7025(1)
β, deg		124.1938(1)
V, Å^3	9021.0(8)	6923.69(9)
Z	8	4
$\rho_{(calcd)}$, g cm^{-3}	1.431	1.433
μ, cm^{-1}	10.01	9.40
no. indep data	9904	8756
no. obsd reflns	7493 [$\lvert F_o\rvert > 4.0\sigma(\lvert F\rvert)$]	5749 [$\lvert F_o\rvert > 4.0\sigma(\lvert F\rvert)$]
no. params refined	442	354
R, $R_w{}^2$ (obsd reflns)	0.0394, 0.1002	0.0459, 0.1131
R, $R_w{}^2$ (all data)[a]	0.0618, 0.1056	0.0849, 0.1275
GOF	1.179	0.956

[a] $R = \sum(|F_o - (1/k)F_c|)/\sum|F_o|$; $R_w{}^2 = [\sum w(F_o{}^2 - (1/k)F_c{}^2)^2/\sum w|F_o{}^2|^2]$. [b] GOF $= [\sum_w(F_o{}^2 - (1/k)F_c{}^2)^2/(n_o - n_v)]^{1/2}$.

Prismatic single crystals of both compounds were mounted, for the data collection, on a glass fiber at a random orientation, on a Bruker SMART CCD diffractometer.

The space groups were unambiguously determined from the systematic absences, while the cell constants were refined, at the end of the data collection with the data reduction software SAINT[17] using 12 854 reflections for **5a** and 23 819 for **9**. Data were collected by using an ω scan in steps of 0.3 deg; more experimental details on the data collection are listed in Table 3 and Supplementary Table S1.

The collected intensities were corrected for Lorentz and polarization factors[17] and empirically for absorption using the SADABS program.[18]The standard deviations on intensities were calculated in term of statistics alone, while those on $F_o{}^2$ were calculated as shown in Table 3 and Supplementary TableS1, where crystallographic and other relevant data are also listed.

Structural Studies. The structure of **5a** was solved by direct and Fourier methods and refined by full matrix least squares,[19] minimizing the function $[\sum w(F_o{}^2 - (1/k)F_c{}^2)^2]$. Anisotropic displacement parameters were used for all atoms. The contribution of the hydrogen atoms, in their calculated position, (C−H = 0.95 (Å), B(H) = 1.5 × $B(C_{bonded})$ (Å^2)), was included in the refinement using a riding model. No extinction correction was deemed necessary. Upon convergence (see Supplementary Table S1) the final Fourier difference map showed no significant peaks. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[20]

The structure of **9** was solved by direct and Fourier methods. The Pd2 atom lies on a crystallographic C_2 axis passing also through C12, N12, C211, and C214 atoms; thus only one-half of the resulting trinuclear cluster is independent. Moreover the carbon atoms of the ring in the Me-C_6H_5 group, bound to

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[17] *SAINT: SAX Area Detector Integration*; Siemens Analytical Instrumentation, 1996.

[18] Sheldrick, G. M. *SADABS*; Universität Göttingen. To be published.

[19] Sheldrick, G. M. *SHELX-97. Structure Solution and Refinement Package*; Universität Göttingen, 1997.

[20] *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publisher: Dordrecht, The Netherlands, 1992; Vol. C.

N21, are disordered between two possible orientations that were both refined (with occupancy factors of 0.3 and 0.7, respectively).

The data were refined by full matrix least squares, as described above, using anisotropic displacement parameters for all atoms except for the disordered carbons, which were treated isotropically. The contribution of the hydrogen atoms, in their calculated position (C−H = 0.95 (Å), B(H) = 1.5 × B(C_{bonded}) (Å^2)), was included in the refinement using a riding model. All calculations were carried out by using the PC version of the SHELX-97 programs.[19]

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Supporting Information Available: Text giving experimental details and a full listing of crystallographic data for **5a** and **9**, including tables of positional and isotropic equivalent displacement parameters, calculated positions of the hydrogen atoms, anisotropic displacement parameters, and bond distances and angles. ORTEP figures showing the full numbering schemes. This material is available free of charge via the Internet at http://pubs.acs.org

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