Coordination of Ligands That Contain Thiocarbonyl, Carbonyl, or Thiolate Functionalities to Complex Fragments of Palladium in Various Oxidation States

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Dedicated to Professor *Dieter Seebach* on the occasion of his 75th birthday in recognition of his enormous contribution to chemistry

Two phosphine ligands of $[Pd(PPh_3)_4]$ were substituted by $\pi(C{=}S)$ coordination of 4-bromodithiobenzoic acid methyl ester resulting in complex **1**. The same ester, after alkylation, afforded the dicationic complex bis(μ-methanethiolato)tetrakis(triphenylphosphine)dipalladium(2+) bis(tetrafluoroborate) (**2**) from the same palladium source. A related thiolato-bridged complex, bis(μ-methanethiolato)bis(1-methylpyridin-2(1*H*)-ylidene)bis(triphenylphosphine)dipalladium(2+) bis(tetrafluoroborate) (**4**) and the trinuclear cluster tris(μ-methanethiolato)tris(triphenylphosphine)tripalladium(+)(3*Pd–Pd*) (**5**) resulted from treatment of a known cationic pyridinylidene complex with MeSLi. The double oxidative substitution reaction of $[Pd(PPh_3)_4]$ with 1,5-dichloro-9,10-anthraquinone afforded *trans*-dichloro[μ-(9,10-dihydro-9,10-dioxoanthracene-1,5-diyl)]tetrakis(triphenylphosphine)dipalladium (**6**). Some of these complexes could be fully characterized by ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy, mass spectrometry, and elemental analysis. The crystal and molecular structures of all of them, and of *trans*-bis(1,3-dihydro-1,3-dimethyl-2*H*-imidazol-2-ylidene)diiodopalladium (**3**), were determined by single-crystal X-ray diffraction.

Introduction. – So-called remote carbene complexes in which the stabilizing heteroatom is positioned at a distant position from the carbene C-atom have recently attracted much attention [1][2]. In our attempts to prepare such complexes with heteroatoms other than N-atoms, a number of foreseen and unforeseen precursors and products were isolated that are nevertheless interesting, owing to their particular structures and respective metal–ligand interactions.

Thione π-type complexes of palladium are rare. Except for the simple complex $[Pd(Ph_3P)_3CS_2]$ (**I** in *Fig. 1*) that was prepared in 1968 [3], only one other mononuclear Pd-complex with $\pi(C{=}S)$ coordination has been structurally authenticated. *Gessner* [4] isolated a thioketone complex in which $Ph_2PC({=}S)SiMe_3$ is π-bonded to a $Pd(PPh_3)_2$ fragment. *Yih* and co-workers [5] successfully employed a similar coordination mode of an [(alkylthio)thioxomethyl]phosphine ligand ($Ph_2P(CS_2Me)$ to synthesize more complicated dinuclear complexes (for example **II** in *Fig. 1*).

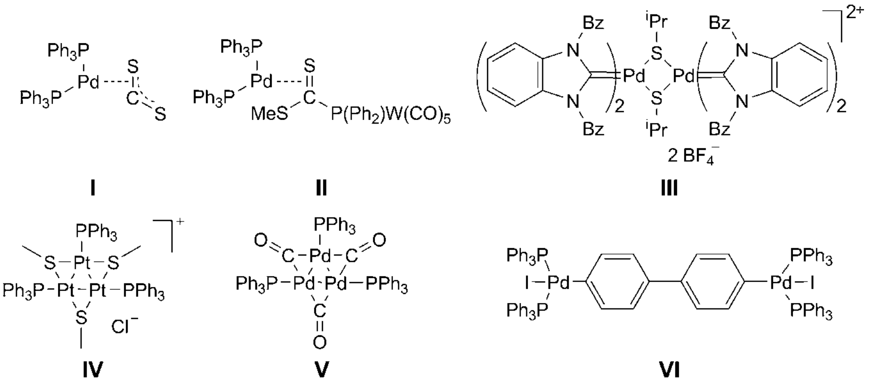


Fig. 1. *Various palladium and platinum complexes that are related to the new compounds described in this article*

Although thiolato-bridged Pd- and Pt-complexes and clusters are well known [6] [7], double bridging of [PdL_2] fragments by thiolato ligands are not known, except for two N-heterocyclic carbene (NHC) complexes recently reported by *Huynh* and co-workers [8] in which L = 2*H*-benzimidazol-2-ylidene (*cf.*, *e.g.*, **III**, in *Fig. 1*). Note that the metal=C bonds drawn in *Figs. 1* and *2* and *Scheme 2* should not be taken too literally – they only serve to clearly indicate carbene-complex formation. The dinuclear compounds [$M_2(\mu\text{-SR})_2L_4$] may theoretically be found in up to six conformations, some of which have been shown to interconvert at rates observable on the NMR time scale [7] [9].

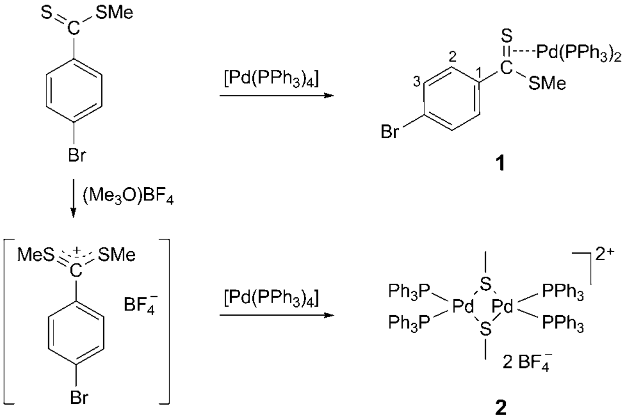
An extension of the bridging-thiolato-ligand family to include the higher nuclearity [$(LM)_3(\mu\text{-SR})_3]^+$ cluster type has been reported by *Bruhn* and co-workers [10]. They treated Pt^{II} complexes with disulfides to form cationic complexes with 44 cluster valence electrons (cve) (**IV**, in *Fig. 1*). Homologous 44 cve triangular Pd_3 clusters comprising three phosphine and three thiolato groups are not yet known, despite the fact that their neutral 42 cve CO-bridged structural analogue [$Pd_3(\mu\text{-CO})_3(PPh_3)_3$] (**V** in *Fig. 1*) has been available since 1971 [11].

Complexes that consist of more than one metal fragment attached to an aromatic ring or even σ-linked aromatic rings [12] (*cf.* **VI** in *Fig. 1*) are rare, and such carbene-complex derivatives are not known. While remote O-atoms have not yet been harnessed in preparing carbene complexes, we visualized that 'two birds could be killed with one stone' if double oxidative addition of [$Pd(PPh_3)_4$] with 1,5-dichloro-9,10-anthraquinone could be followed or preceded by mono- or bis-*O*-alkylation.

Herein, we report a number of new Pd-complexes in some of which *i*) C=S π coordination occurs, *ii*) [Pd(phosphine)$_2$] or [Pd(phosphine)(carbene)] fragments are bridged by methanethiolato ligands, *iii*) three [Pd(phosphine)] units are clustered while bridged by the same thiolato ligand, and *iv*) double oxidative addition of 1,5-dichloro-9,10-anthraquinone to Pd^0 has occurred. Finally, the crystal- and molecular-structure determination of the *trans*-isomer of a well-known carbene precursor bis(1,3-dihydro-1,3-dimethyl-2*H*-imidazol-2-ylidene)diiodopalladium(II) is described for the first time.

Results and Discussion. – *Preparative Aspects.* We reasoned that *remote* carbene complexes of Pd^{II} could become available by oxidative substitution of the methyl ester of 4-bromodithiobenzoic acid (=4-bromobenzenecarbodithioic acid) onto $[Pd(PPh_3)_4]$ followed by S-alkylation. Alternatively, the alkylation could be performed first *in situ*, as we have shown previously in another context [13]. Unexpectedly, two unique complexes, **1** and **2**, were isolated (*Scheme 1*). It is clear that simple phosphine substitution to form the C=S π-coordinated complex **1** is preferred to the oxidative-substitution pathway. The ^{13}C-NMR resonance for the C=S functionality of **1** appears at δ(C) 181.0. It is interesting to note that when $[Fe^{II}(Cp)(dppm)]$ (Cp = cyclopenta-2,4-dien-1-yl; dppm = methylenebis[diphenylphosphine]) bears a dithioacetato group, two isomers can be formed, and the C-atom which is π-bonded to the metal has a lower ^{13}C-NMR chemical shift (δ(C) 187.2) than the one of the same ligand which is only coordinated through the two S-atoms (δ(C) 230.0) [14]. Inequivalence of the two *cis*-positioned phosphine ligands of **1** is shown by two *d*s at δ 25.1 and 26.0 in the ^{31}P-NMR spectra. Although the molecular ion is not observed in the FAB-MS of **1**, the highest *m/z* fragment indicates liberation of a bridging MeS group. Subsequent fragmentations involve the sequential loss of phosphine ligands.

Scheme 1. *Complexes* **1** *and* **2** *Formed from a Dithioester and Its Alkylated Analogue*



The first doubly thiolato-bridged palladium complex **2** was probably formed by C–S bond cleavage and oxidative substitution of MeS^+ to the Pd^0 precursor. Many examples of reactions in which C–S bonds are severed to form S- or SR-bridged dinuclear or polynuclear products are known for group-10 metals and also for metals in other periodic groups [15]. The ^{13}C-NMR chemical shift of the bridging MeS^- ligand of **2** at δ(C) 22.4 corresponds to the resonance at δ(C) 21.9 observed previously for μ-(methanethiolato)-μ-thioxotetrakis(triphenylphosphine)diplatinum(+) iodide ($[Pt_2(\mu\text{-}MeS)(PPh_3)_4(\mu\text{-}S)]I$ [16]. A *s* seen in the ^{31}P-NMR spectrum is consistent with the retention of the solid-state structure of **2** in solution. In the FAB-MS of the complex, one Me group is eliminated from a monocationic complex to afford a signal at *m/z* 1341.1. It is of interest that the corresponding MS of the other MeS-bridged complex (see **4** below), in addition to standard fragmentations from a monocationic complex, also exhibits an *m*/*z* signal at 508.9, corresponding to the dicationic complex.

Our attempts to further increase the number of known thiolato-bridged [PdL_2] compounds by reacting a [$PdI_2(NHC)_2$] complex with MeSLi were unsuccessful. As mentioned earlier, *Huynh* and co-workers have described a three-step approach to isolate such compounds [8]. In the course of our preliminary investigation, however, single crystals of *trans*-bis(1,3-dihydro-1,3-dimethyl-2*H*-imidazol-2-ylidene)diiodopalladium (**3**; *Fig. 2*), previously described by *Herrmann* and co-workers [17], were isolated. The crystal and molecular structure of **3** is below compared to that of its *cis*-isomer.

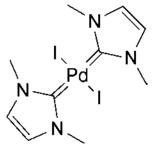
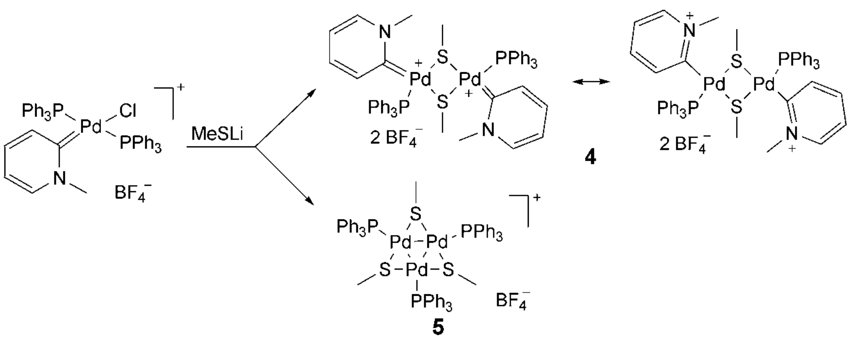


Fig. 2. *Carbene complex* **3** *previously reported by* Herrmann *and co-workers*

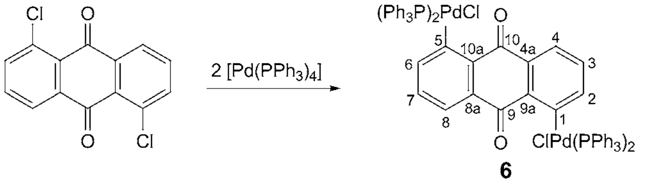
The negative results nudged us further to prepare a still lacking member of the thiolato-bridged family, **4**, in which two phosphine ligands in **2** are substituted for carbenes, as indicated in *Scheme 2*. The starting pyridinylidene complex has been reported before [18]. Separation and purification were extremely difficult but we were fortunate to obtain single crystals of **4** and of the serendipitous product **5** (*Scheme 2*) suitable for X-ray analysis. The latter previously unreported cationic cluster is formed by substitution of an anionic chloro ligand as well as neutral phosphine and carbene ligands of the pyridinylidene precursor while a 2e$^-$ reduction occurs. It is possible that dimethyl disulfide was formed initially and that cluster formation then occurred, as for the platinum analogues described by *Bruhn* and co-workers [10].

Scheme 2. *Thiolato-bridged Palladium Complexes* **4** *and* **5** *Produced from a Pyridinylidene Complex and a Thiolate*



Treatment of 1,5-dichloro-9,10-anthraquinone with [$Pd(PPh_3)_4$] afforded product **6** (*Scheme 3*) by double oxidative substitution. No alkylation occurred on subsequent treatment with (Me_3O)BF_4. Preceding alkylation of the substituted anthraquinone precursor with the same oxonium salt or CF_3SO_3Me was also unsuccessful. The bimetallic palladium complex **6**, a rare example of a dipalladated annelated aromatic ring system, was isolated and characterized. The FAB-MS data for complex **6** provided an *m*/*z* value at 769.5, which corresponds to the dicationic complex ion. Furthermore, elimination of phenyl groups, oxygen, phosphine ligands, and a Cl-atom from the monocationic complex were observed.

Scheme 3. *Dipalladation of 1,5-Dichloro-9,10-anthraquinone*



Crystal Structure Determinations of **1**·*CH$_2$Cl$_2$*, **2**·*x Solvent Molecules*, **3**, **4**, **5**·*2 CH$_2$Cl$_2$, and* **6**·*6 CH$_2$Cl$_2$*. Compound **1** crystallizes in the centrosymmetric triclinic system as a CH$_2$Cl$_2$ solvate with one complex entity and one solvent molecule in the asymmetric unit. The strongly distorted square planar geometry around the central Pd-atom is formed by a C=S moiety (π-bonded) and two P-atoms of triphenylphosphine ligands with the angles ranging from *ca.* 46° (typical value for a C=S linkage bite angle in Pd complexes [4][5]) to 149° (*Fig. 3*). The largest deviation from planarity of the P(1A),P(1B),C(21),S(20) core is 0.086(2) Å for C(21). The bond lengths between atoms forming the coordination sphere concur well with data presented in earlier reports: the Pd(1)–P(1B) distance of 2.3060(8) Å falls in the lower range of Pd–P distances for similar structural motifs (median 2.339 Å; lower/upper quartile 2.317 Å/ 2.359 Å; $n = 15$) [19]. The bond length S(20)–C(21) of 1.747(3) Å is the same as reported by *Gessner* for a coordinated thioketone [4] and indicates the partial π character of the bond. The geometry around C(21) in the dithioester ligand is distorted from its more ideal trigonal (sp^2) arrangement in the free molecule as a result of coordination (the distortion from planarity for C(21) is *ca.* -0.22 Å, whereas for C(24), S(22), and S(20), the values fall in the range of 0.07–0.08 Å). The orientation of the aromatic ring C(24) to C(29) of the methyl bromodithiobenzoate moiety is stabilized by the presence of intramolecular π–π interactions between this ring and the C(8B) to C(13B) benzene ring of a triphenylphosphine ligand (P1B). The complex units interact by C–H···π interactions (C(17A)–H(17A)···Cg1^i, where Cg1 is the centroid of C(24) to C(29), and symmetry operation $i = x, -1+y, z$; *d*(C(17A)··· Cg1) = 3.679(4) Å) forming supramolecular 1D chains extending along the *b* axis. There are no intermolecular π–π interactions present, and the packing is further stabilized by *van der Waals* interactions.

Compound **2** crystallizes in a centrosymmetric triclinic space group, $P\bar{1}$. One dinuclear cationic Pd^{II} complex, two disordered tetrafluoroborate counterions, and unidentified solvent molecules are present in the asymmetric unit (for details, see X-ray structure determination in the *Exper. Part*). There are no reports on structural data of related palladium complexes, but a similar cationic Pt^{II} complex with PF$_6^-$ counterions is known [20]. The geometry of the Pd center in **2** is disordered square planar and formed by two S-atoms originating from two thiolato bridges and two P-atoms from

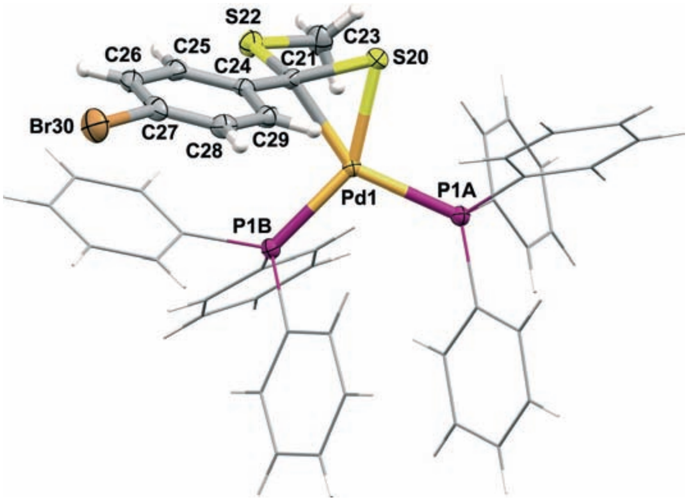


Fig. 3. *Molecular structure of* **1** *with displacement ellipsoids drawn at the 50% probability level.* PPh_3 Ligands are shown in stick representation; solvent molecule omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–C(21) 2.134(3), Pd(1)–S(20) 2.3035(8), Pd(1)–P(1B) 2.3060(8), and Pd(1)–P(1A) 2.3488(8); C(21)–Pd(1)–S(20) 46.18(9), C(21)–Pd(1)–P(1B) 102.79(9), S(20)–Pd(1)–P(1B) 148.70(3), C(21)–Pd(1)–P(1A) 148.47(9), S(20)–Pd(1)–P(1A) 102.73(3), and P(1B)–Pd(1)–P(1A) 108.53(3).

two triphenylphospine ligands (*Fig. 4*). The $[Pd_2(\mu\text{-}S)_2]$ core is somewhat bent, with a hinge angle θ of 146° (defined as the angle between the two planes, calculated from the atoms forming the central Pd^{II} geometries; the corresponding θ angle for the related Pt^{II} complex is 156° as a result of different interactions in the crystal structure). The bridging methanethiolato ligands adopt a '*syn–exo*' conformation [9] in **2**, which is stabilized by intramolecular C–H $\cdots\pi$ interactions between the Me groups of the thiolato ligands and phenyl substituents of neighboring PPh_3 ligands (C(21)–H(21B)$\cdots$Cg1, where Cg1 is the centroid of C(8A) to C(13A) with a C(21)$\cdots$Cg1 distance of 3.430(3) Å, and C(23)–H(23B)$\cdots$Cg2 where Cg2 is the centroid of C(2C) to C(7C) with a C(23)$\cdots$Cg2 distance of 3.454(3) Å). The squeezed solvent molecules do not allow full analysis of the packing; however, no π–π interactions are present. Weak H-bonding plays a dominant role in the molecular arrangement. The intermolecular C–H $\cdots\pi$ interactions between cationic complexes (such as C(3B)–H(3B)$\cdots$Cg3^i, where Cg3 is the centroid of C(2D) to C(7D) with C(3B)$\cdots$Cg3 = 3.846(3) Å, and symmetry operation $i = x,\ -1+y,\ z$; C(12A)–H(12A)$\cdots$Cg4^{ii}, where Cg4 is the centroid of C(2A) to C(7A) with C(12A)$\cdots$Cg4^{ii} = 3.475(3) Å, and symmetry operation $ii = 1-x,\ 1-y,\ -z$, and C(15A)–H(15A)$\cdots$Cg1^{ii} with C(15A)$\cdots$Cg1^{ii} = 3.673(3) Å) form 1D strands expanding along the b axis with the rows of molecules related by an inversion centre. These molecules are further interconnected through counterions (C–H$\cdots$F interactions) into a 3D supramolecular assembly.

Complex **3** crystallizes in the monoclinic space group $C2/m$ with a quarter of the Pd ion (located on a special, *Wyckoff* position 2a), half a molecule of the ligand, and half of the iodide ion (both bisected by the mirror plane, *Wyckoff* position 4i for C(2) and I(1))

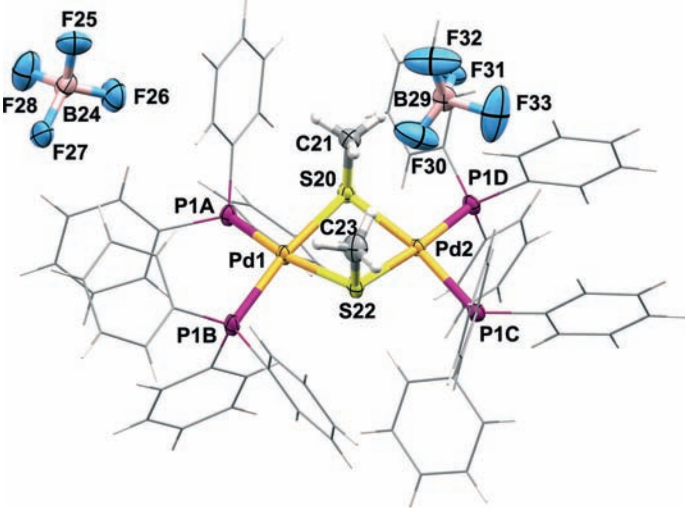


Fig. 4. *Representation of* **2** *with displacement ellipsoids drawn at the 50% probability level.* PPh$_3$ Ligands are shown in stick representation; disorder omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–P(1B) 2.3323(7), Pd(1)–P(1A) 2.3360(7), Pd(1)–S(22) 2.3558(7), Pd(1)–S(20) 2.3648(6), Pd(2)–S(20) 2.3450(7), Pd(2)–S(22) 2.3581(6), Pd(2)–P(1C) 2.3265(7), and Pd(2)–P(1D) 2.2929(6); P(1B)–Pd(1)–P(1A) 101.58(2), P(1B)–Pd(1)–S(22) 89.92(2), P(1A)–Pd(1)–S(22) 167.38(2), P(1B)–Pd(1)–S(20) 171.78(2), P(1A)–Pd(1)–S(20) 84.94(2), S(22)–Pd(1)–S(20) 83.17(2), P(1D)–Pd(2)–P(1C) 97.85(2), P(1D)–Pd(2)–S(20) 91.65(2), P(1C)–Pd(2)–S(20) 169.84(2), P(1D)–Pd(2)–S(22) 175.16(2), P(1C)–Pd(2)–S(22) 86.98(2), and S(20)–Pd(2)–S(22) 83.55(2).

in the asymmetric unit. The Pd-ion remains in an idealized square planar coordination environment formed by two I-ligands and two coplanar carbene ligands *trans*-orientated to each other (*Fig. 5*). The compound is isostructural with a previously reported *trans* Ni^{II} complex [21], the *cis*-form of which is not known. The crystal structure of the *cis* Pd^{II} isomer was published in 1995 [22]. It shows a more distorted geometry around Pd^{II}, with the largest deviating angles I–Pd–I and C–Pd–I equal to 93.590(9)° and 175.52(9)°, respectively; the carbene ligands are twisted by *ca.* 71° with regard to the PdI$_2$ plane. In the paper describing the *cis* isomer [22], the authors

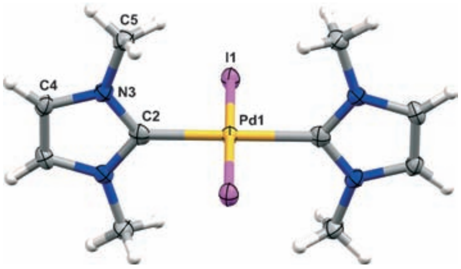


Fig. 5. *Molecular structure of* **3** *with displacement ellipsoids drawn at the 50% probability level.* Selected bond lengths [Å] and angles [°]: I(1)–Pd(1) 2.6081(10) and Pd(1)–C(2) 2.033(6); C(2)–Pd(1)–C(2) 180.000, C(2)–Pd(1)–I(1) 89.77(16), C(2)–Pd(1)–I(1) 90.23(16) and I(1)–Pd(1)–I(1) 180.000.

compared it with $[Pd(PR_3)_2X_2]$ (X = halogen) complexes exhibiting *trans*-configurations that were isolated earlier. The appearance of the *cis*-form was explained in terms of lower steric demands of the 1,3-dihydro-1,3-dimethyl-2*H*-imidazol-2-ylidene ligands than required by the bulkier phosphine ligands. However, such a conclusion does not exclude the possibility that both isomers could crystallize, and indeed, we now obtained crystals of the *trans*-isomer **3**. The patterns in the fingerprint plots (*Fig. 6*, [23]) even suggest the presence of stronger intermolecular interactions in the *trans*-isomer **3** [23]. These mainly π–π associations – absent in the *cis* isomer – form supramolecular zig-zag 1D chains between 2*H*-imidazol-2-ylidene moieties, expanding along the *c* axis with a centroid–centroid distance of 3.566(4) Å.

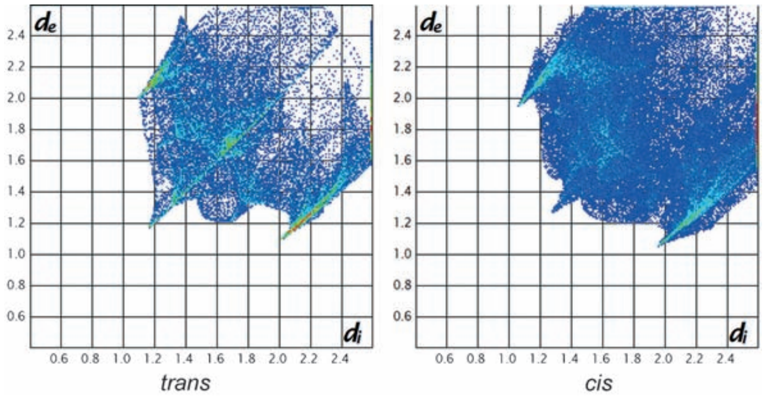


Fig. 6. *Two-dimensional fingerprint plots for* trans- *and* cis-*bis(1,3-dihydro-1,3-dimethyl-2*H-*imidazol-2-ylidene)diiodopalladium complexes indicating stronger intermolecular interactions in the* trans-*isomer* **3** (the green area near 1.7 – 1.8 Å reveals the presence of π–π interactions).

Complex **4** is related to **2** with two triphenylphosphine ligands replaced by pyridinylidene moieties in a '*trans*'-arrangement. It crystallizes in the $Pna2_1$ orthorhombic space group with one dinuclear cationic Pd^{II}–carbene complex and two disordered tetrafluoroborate counterions in the asymmetric unit. Each Pd-atom shows a disordered square planar geometry formed by two S-atoms from two distinct methanethiolato bridges, a P-atom from triphenylphosphine, and a C-atom from a pyridinylidene ligand (*Fig. 7*). The thiolato-bridge ligands adopt a '*syn–endo*' conformation [9] as a result of the presence of the less bulky pyridinylidene ligand. There is much more bending of the $[Pd_2(\mu\text{-}S)_2]$ core than in **2**, with a hinge angle θ of 115°, which is stabilized by intra- and inter-molecular C–H ··· S interactions involving phenyl substituents of the same or adjacent Pd^{II} complexes, namely C(13A)–H(13A) ··· S36 with C ··· S = 3.575(8) Å and C(6B)–H(6B)) ··· $S34^i$, symmetry operation $i = x, -1 + y, z$, with C ··· S = 3.535(7) Å respectively. Pd ··· Pd Interactions are also present at a distance of 3.121 Å, which is *ca.* 0.3 Å shorter than in **2**. The conformation adopted by complex **4** is further stabilized in the crystal by intramolecular C–H ··· π interactions between a Me group of the bridging ligands and neighboring phenyl substituents of triphenylphosphine ligands such as C(35)–H(35A) ··· Cg1, where Cg1 is the centroid of C(2B) to C(7B) with C(35) ··· Cg1 = 3.660(8) Å, and C(37)–H(37A) ··· Cg2, where

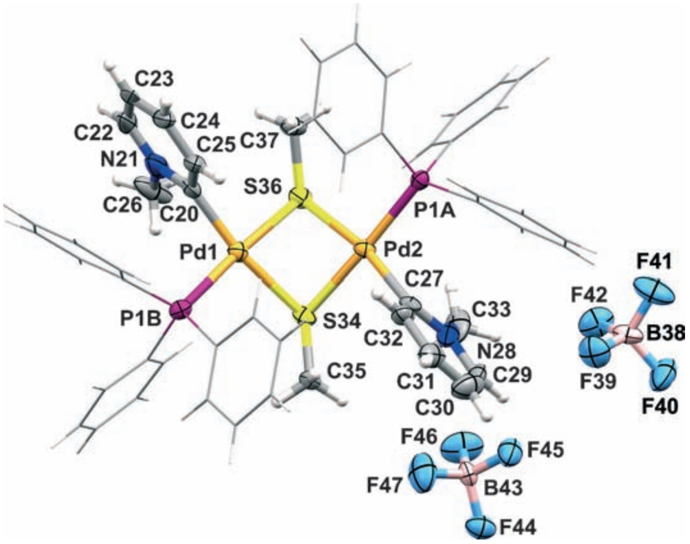


Fig. 7. *Representation of* **4** *with displacement ellipsoids drawn at the 50% probability level.* PPh_3 Ligands are shown in stick representation; disorder omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–C(20) 2.002(7), Pd(1)–P(1B) 2.270(2), Pd(1)–S(36) 2.351(2), Pd(1)–S(34) 2.370(2), Pd(2)–C(27) 1.998(7), Pd(2)–P(1A) 2.278(2), Pd(2)–S(34) 2.344(2), and Pd(2)–S(36) 2.369(2); C(20)–Pd(1)–P(1B) 90.3(2), C(20)–Pd(1)–S(36) 92.8(2), P(1B)–Pd(1)–S(36) 176.92(7), C(20)–Pd(1)–S(34) 169.9(2), P(1B)–Pd(1)–S(34) 99.69(7), S(36)–Pd(1)–S(34) 77.25(6), C(27)–Pd(2)–P(1A) 90.9(2), C(27)–Pd(2)–S(34) 92.1(2), P(1A)–Pd(2)–S(34) 176.77(7), C(27)–Pd(2)–S(36) 169.4(2), P(1A)–Pd(2)–S(36) 99.60(7), and S(34)–Pd(2)–S(36) 77.41(6).

Cg2 is the centroid of C(14A) to C(19A) with C(37) ··· Cg2 = 3.696(7) Å, as well as through intramolecular π–π interactions involving pyridinylidene and phenyl moieties. Intermolecular C–H ··· π interactions lead to the formation of supramolecular 1D chains along the *b* axis (C(12)–H(12A) ··· $Cg2^{ii}$, symmetry operation $ii = x, 1 + y, z$, with C(12) ··· Cg2 = 3.772(7) Å), which are interconnected by a net of C–H ··· F interactions involving the counterions into a 3D assembly.

The CH_2Cl_2 solvate of **5** crystallizes in the orthorhombic space group $P2_12_12_1$ with one cationic, triangular Pd-cluster (*Fig. 8*), one disordered BF_4^- counterion and two disordered solvent molecules in the asymmetric unit. The Pd_3 cluster formed resembles a reported chloroform solvate of a related Pt_3 cluster [10]. It shows differences in orientation of the benzene rings of the PPh_3 ligands as a result of other interactions in the crystal, because of the change in counterion (Cl^- in Pt) and solvent. The $[M_3S_3P_3]$ (M = Pd, Pt) cores in both compounds are almost planar, with the largest deviations from planarity of 0.275(1) Å seen for P(1B) and 0.145(1) Å for one of the S-atoms. The Pd–Pd bond lengths 2.8653(9) – 2.9023(8) Å remain in the range observed for 44 electron clusters [24]. The methyl groups of the thiolato bridges are arranged upwards on the same side of the Pd_3 plane, the orientation of which is stabilized by intramolecular C–H ··· π interactions involving all methyl groups of the thiolato bridges and the adjacent phenyl substituents of PPh_3, as was observed in **2**. No π–π interactions are present between adjacent clusters in **5**, but weak intermolecular H-

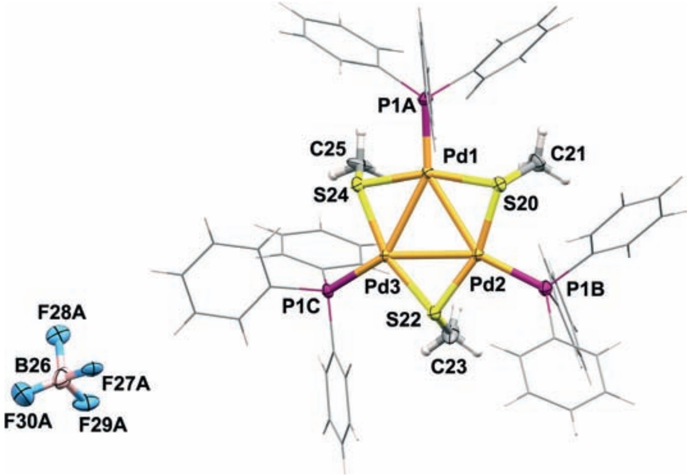


Fig. 8. *Representation of* **5** *with displacement ellipsoids drawn at the 50% probability level.* PPh_3 Ligands are shown in stick representation; solvent molecules and disorder omitted for clarity. Selected bond lengths [Å]: Pd(1)–S(24) 2.264(2), Pd(1)–P(1A) 2.267(2), Pd(1)–S(2) 2.289(19), Pd(3)–P(1C) 2.288(2), Pd(2)–S(22) 2.276(2), Pd(2)–S(20) 2.284(2), Pd(3)–S(22) 2.280(2), and Pd(3)–S(24) 2.288(2).

bonds are abundant. C–H ··· π Interactions between adjacent phenyl moieties form zigzag 1D supramolecular chains of clusters expanding along the *b* axis (C(11C)–H(11C) ··· Cg1^i where Cg1 is the centroid of C(14B) to C(19B), symmetry operation $i = 1 - x$, $-1/2 + y$, $1/2 - z$, with C(11) ··· Cg1 = 3.549(9) Å), which are further linked by means of weak H-bonds involving the counterion and solvent molecules (C–H ··· F and C–H ··· Cl interactions) into a 3D supramolecular assembly.

The dinuclear Pd^{II} complex **6** crystallizes as a CH_2Cl_2 solvate in a centrosymmetric triclinic system, with half of the Pd^{II} complex and three solvent molecules in the asymmetric unit. This is the first report of a dimetallated anthraquinone-derived complex. A slightly distorted square planar geometry is established around each of the two Pd-ions, formed by two P-atoms of triphenylphosphine ligands, a C-atom of the dioxoanthracenediyl ligand, and a Cl-ligand¹) (*Fig. 9*). The bond lengths between atoms forming the coordination geometry correspond well with those from related structural reports. No π–π interactions are present in the molecular packing. Instead, weak C–H ··· π and C–H ··· Cl H-bonds are formed, involving the Pd^{II} complex and CH_2Cl_2 (C32) molecules, namely C(32)–H(32A) ··· Cg2^i, where Cg2 is the centroid of C(14B) to C(19B), symmetry operation $i = x, y, 1 + z$, with C(32) ··· Cg2 = 3.501(3) Å, C(16A)–H(16A) ··· Cl(34), C(16A) ··· Cl(34) = 3.556(3) Å, and C(24)–H(24) ··· Cl(33)^{ii}, symmetry operation $ii = -1 + x, y, z$, with C(24) ··· Cl(33) = 3.707(3) Å, resulting in the formation of 2D supramolecular corrugated layers in the *ac* plane. The

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¹) The Pd–O separation of 2.785(2) Å is somewhat long for this association to be considered a proper coordination.

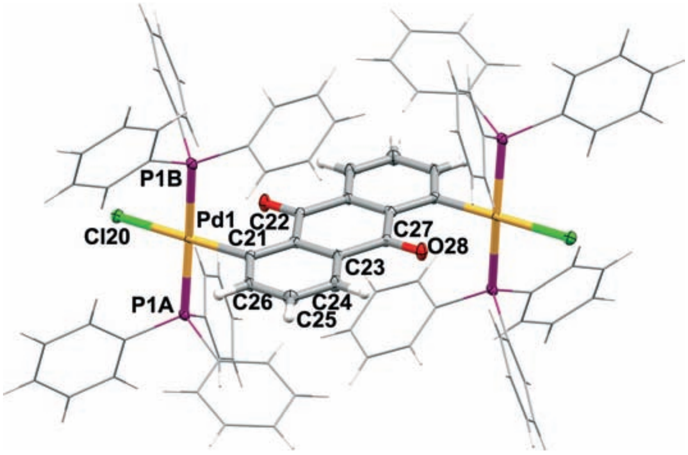

Fig. 9. *Molecular structure of* **6** *with displacement ellipsoids drawn at the 50% probability level.* PPh_3 Ligands are shown in stick representation; solvent molecules omitted for clarity; the unlabeled atoms are related to the labelled ones by an inversion center. Selected bond lengths [Å] and angles [°]: Pd(1)–C(21) 2.002(3), Pd(1)–P(1A) 2.3219(7), Pd(1)–P(1B) 2.3406(7), and Pd(1)–Cl(20) 2.3969(7); C(21)–Pd(1)–P(1A) 88.95(7), C(21)–Pd(1)–P(1B) 89.31(7), P(1A)–Pd(1)–P(1B) 174.29(2), C(21)–Pd(1)–Cl(20) 178.82(7), P(1A)–Pd(1)–Cl(20) 90.93(3), and P(1B)–Pd(1)–Cl(20) 90.92(3).

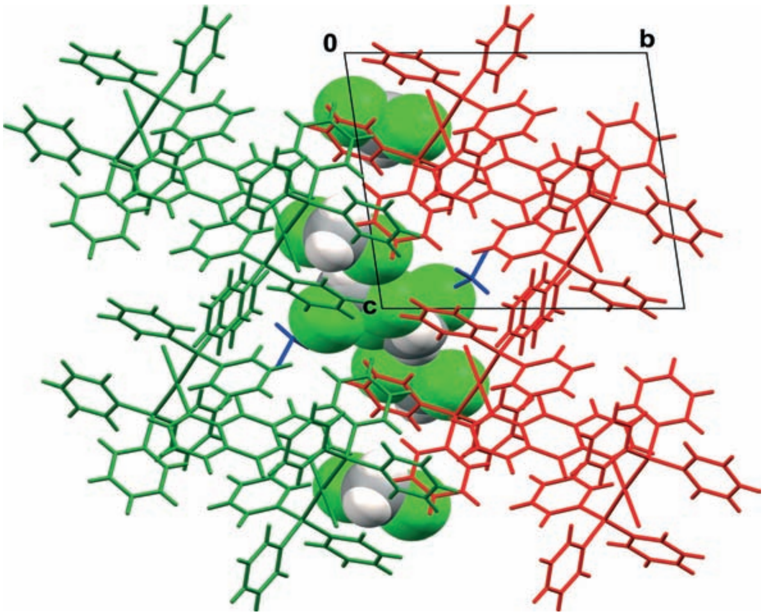

Fig. 10. *Packing representation of* **6** *shown down the* a *axis.* The supramolecular layers formed are in red and green, the CH_2Cl_2 molecule C(32) is in blue, and the remaining solvent molecules are shown as space filling depiction.

remaining solvent molecules (C(29) and C(35)) are sandwiched between these layers (*Fig. 10*).

Conclusions. – This study demonstrates that the preparation of remote carbene complexes from precursors in which bicovalent S- (C=S) or O-atoms (C=O) act as nucleophilic heteroatoms to be alkylated, is not always straightforward, and complications may arise by virtue of π(C=S) coordination, C–S bond cleavage (enabled by alkylation), or unsuccessful alkylation.

Thiolates can be installed as bridging ligands between $[Pd^{II}L_2]$ fragments by employing a pyridinylidene (an NHC ligand) as one of the L ligands and treating $[Pd(PPh_3)_2(NHC)Cl]BF_4$ with MeSLi. However, simultaneous trinuclear-cluster formation does sometimes complicate the reaction.

A dihaloanthraquinone readily reacts with $[Pd(PPh_3)_4]$ by double oxidative substitution, which could be further exploited in deliberate polynuclear-complex preparation.

The key features emerging from the molecular-structure determinations of a variety of new Pd-complexes by X-ray diffraction are the significant differences observed in Pd–S and Pd–C(carbene) separations. With a π–bonded thione, the Pd–S distance of *ca.* 2.30 Å is shorter than in the thiolato-bridged dinuclear compounds (*ca.* 2.34–2.37 Å) and longer than in the Pd-cluster (*ca.* 2.26–2.29 Å). The Pd–C(carbene) distances in a pyridinylidene complex (*ca.* 2.00 Å) are somewhat shorter than in an 2*H*-imidazol-2-ylidene compound (2.03 Å) and essentially the same as the Pd–C(aryl) bond length in the dioxoanthracenediyl complex (2.002(3) Å). The diffraction studies also indicate potential stabilization of particular conformations of ligands or even isomers of complexes by weak interations.

The authors thank the *National Research Foundation of South Africa*, *Sasol Technology*, and the *Research Foundation Flanders – FWO* (*LD*) for financial support.

Experimental Part

General. Starting materials used in the synthesis of the ligands and complexes were purchased from commercial suppliers and used without further purification. The compounds $4\text{-}BrC_6H_4CS_2Me$ [25], $[Pd(PPh_3)_4]$ [26], bis(1,3-dihydro-1,3-dimethyl-2*H*-imidazol-2-ylidene)diiodopalladium [17], and *trans*-chloro(1-methylpyridin-2(1*H*)-ylidene)bis(triphenylphosphine)palladium(+) tetrafluoroborate [18] were synthesized according to literature procedures. Reactions were carried out under an inert atmosphere by means of standard *Schlenk* techniques. All glassware were dried at 110° and cooled under vacuum before use. All solvents were freshly distilled under an inert atmosphere before use. THF, Et_2O, pentane, and hexane were dried (KOH) and distilled over Na-wire. Benzophenone and diethylene glycol dimethyl ether (= diglyme = 1,1′-oxybis[2-methoxyethane]) were used as dryness indicators for pentane and hexane, and benzophenone for THF and Et_2O. CH_2Cl_2 was dried (KOH) and distilled over CaH_2. Acetonitrile was distilled over CaH_2. M.p.: *Stuart-SMP3* melting-point apparatus; uncorrected. IR Spectra: *Perkin-Elmer-1600* or *Nicolet Avatar-330-FTIR* spectrophotometer; $\tilde{\nu}$ in cm^{-1}. ^1H-, ^{13}C-, and ^{31}P-NMR Spectra: *Varian-300-FT* or *-Inova-600* spectrometer at 300 or 600 (^1H), 75 or 151 (^{13}C), and 121.5 or 243 (^{31}P) MHz; CD_2Cl_2 solns.; δ in ppm rel. to Me_4Si according to the residual deuterated solvent (^1H and ^{13}C) and rel. to an external 85% H_3PO_4 soln. (^{31}P), *J* in Hz; atom numbering refers to *Schemes 1* and *3*. FAB-MS: *VG-70SEQ* mass spectrometer in a 2-nitrobenzyl alcohol matrix; measured at the University of Witwatersrand, South Africa. Elemental analyses: Department of Chemistry, University of Cape Town, South Africa; crystals were dried under vacuum for 5 h before analyses were carried out.

(*Methyl* η^2*-4-Bromobenzenecarbodithioate)bis(triphenylphosphine)palladium* (**1**). A soln. of 4-$BrC_6H_4CS_2CH_3$ (0.253 g, 1.03 mmol) and $[Pd(PPh_3)_4]$ (1.18 g, 1.03 mmol) in toluene was stirred overnight at 60°. The product mixture was allowed to cool down to r.t. and dried *in vacuo.* The resulting residue was dissolved in CH_2Cl_2, absorbed on silica gel *60* (SiO_2) and transferred to a small filtration column. Unreacted ligand was washed out with hexane and the complex was eluted with Et_2O/hexane 1:4 as a yellow fraction which afforded, after complete removal of solvent, 0.341 g (37.7%) of **1**. Yellow solid. M.p. 115° (dec.). ^{1}H-NMR: 7.23 (*m*, 20 H, Ph, H–C(3), H–C(5)); 7.06 (*m*, 12 arom. H); 6.98 (*d*, $^3J = 8.8$, H–C(2), H–C(6)); 2.31 (*s*, MeS). ^{13}C-NMR: 181.0 (*s*, C=S); 148.3 (*s*, C(4)); 135.6 (*s*, C(2), C(6)); 134.7 (*d*, ^2J(C,P) = 8.6, C_o (Ph)); 133.6 (*d*, ^1J(C,P) = 13.8, C_{ipso} (Ph)); 130.5 (*s*, C(3), C(5)); 130.1 (br. *s*, C_p (Ph)); 128.5 (*m*, C_m (Ph)); 118.7 (*s*, C(4)); 19.6 (*s*, MeS). ^{31}P-NMR: 26.0 (*d*, ^2J(P,P) = 23.6, 1 PPh_3); 25.1 (*d*, ^2J(P,P) = 23.6, 1 PPh_3). FAB-MS: 830.9 ($[M - MeS]^+$), 629.7 ($[Pd(PPh_3)_2 - H]^+$), 568.7 ($[M - MeS - PPh_3]^+$). Anal. calc. for $C_{44}H_{37}BrP_2PdS_2$ (878.1): C 60.18, H 4.25; found: C 60.40, H 4.20.

Bis(μ-methanethiolato)tetrakis(triphenylphosphine)dipalladium(2+) Bis(tetrafluoroborate) (**2**). To 4-$BrC_6H_4CS_2Me$ (0.30 g, 1.2 mmol), $(Me_3O)BF_4$ (0.22 g, 1.5 mmol) in a CH_2Cl_2/MeCN mixture was added dropwise within 1.5 h. Workup was performed as described for similar compounds in [27] to produce the alkylated salt. The alkylated mixture (0.072 g, 0.21 mmol) and $[Pd(PPh_3)_4]$ (0.24 g, 0.21 mmol) were stirred for 22 h at 60° in toluene. The soln. was filtered and pentane added to afford a yellow precipitate that was filtered and dried *in vacuo.* The filtrate contained unreacted $[Pd(PPh_3)_4]$ and **1**. Dissolution of the yellow solid and layering with pentane yielded yellow crystals (0.080 g, 4.2%) of **2** · *x* solvent molecules, suitable for X-ray determination. Complete removal of solvent under vacuum afforded **2** (0.080 g, 4.2%). M.p. 120° (dec.). ^{1}H-NMR: 7.29 (*m*, 30 arom. H); 2.57 (*s*, MeS). ^{13}C-NMR: 134.8 (br. *s*, C_o); 132.6 (*s*, C_p); 129.8 (br. *s*, C_m); 129.2 (*d*, ^1J(C,P) = 61.2, C_{ipso}); 22.4 (*s*, MeS). ^{31}P-NMR: 31.5 (*s*, PPh_3). FAB-MS: 1341.1 ($[M - 2\,BF_4 - Me]^+$), 1171.9 ($[M - 2\,BF_4 - 2\,Me - 2\,Ph]^+$), 1112.8 ($[M - 2\,BF_4 - Me - 3\,Ph]^+$), 1092.8 ($[M - 2\,BF_4 - PPh_3]^+$), 830.7 ($[M - 2\,BF_4 - 2\,PPh_3]^+$), 629.8 ($[Pd(PPh_3)_2 - H]^+$). Anal. calc. for $C_{74}H_{66}B_2F_8P_4Pd_2S_2$ (1529.78): C 58.10, H 4.35; found: C 57.91, H 4.22.

trans-*Bis(1,3-dihydro-1,3-dimethyl-2*H*-imidazol-2-ylidene)diiodopalladium* (**3**). Bis(1,3-dihydro-1,3-dimethyl-2*H*-imidazol-2-ylidene)diiodopalladium (0.10 g, 0.18 mmol), prepared according to the *Herrmann* procedure [17], and MeSLi (0.020 g, 0.37 mmol) were suspended in THF (10 ml) and stirred for 17 h at r.t. The solvent was evaporated, the resulting residue dissolved in CH_2Cl_2, the soln. filtered through *Celite*, the filtrate evaporated, and the residue redissolved in a minimum amount of MeCN and layered with pentane. No new product was formed but yellow X-ray-quality crystals of **3**, the *trans*-isomer of the starting compound, were obtained.

*Bis(μ-methanethiolato)bis(1-methylpyridin-2(1*H*)-ylidene)bis(triphenylphosphine)dipalladium(2+) Bis(tetrafluoroborate)* (**4**) *and Tris(μ-methanethiolato)tris(triphenylphosphine)tripalladium(+)(3*Pd–Pd*) Tetrafluoroborate* (**5**). To MeSSMe (0.45 g, 0.42 ml, 4.7 mmol) in Et_2O, 1.6M BuLi (3.0 ml, 4.7 mmol) was added. The soln. was stirred for 2 h and filtered and the solid MeSLi washed with Et_2O (2 × 20 ml). A suspension of MeSLi (0.007 g, 0.13 mmol) and *trans*-chloro(1-methylpyridin-2(1*H*)-ylidene) bis(triphenylphosphine)palladium(+) tetrafluoroborate (0.085 g, 0.10 mmol) in THF (15 ml) was stirred for 20 h at r.t. The solvent was evaporated, the resulting residue dissolved in CH_2Cl_2, the soln. filtered, and the filtrate evaporated. Dissolution of the solid in CH_2Cl_2 and layering with pentane afforded in low yields yellow crystals of **4** and orange-red crystals of **5** · 2 CH_2Cl_2, suitable for X-ray studies. The crystals were separated mechanically, and the solvents removed under vacuum.

Data of **4**: M.p. 210° (dec.). MS: 831.6 ($[M - 2\,BF_4 - 2\,C_6H_4N - 2\,Me]^+$), 756.0 ($[M - 2\,BF_4 - Ph]^+$), 738.0 ($[M - 2\,BF_4 - Me - PPh_3])^+$, 662.1 ($[M - 2\,BF_4 - C_6H_4N - Me - PPh_3]^+$), 508.9 ($[M - 2\,BF_4]^{2+}$). Anal. calc. for $C_{50}H_{50}B_2F_8N_2P_2Pd_2S_2$ (1191.47): C 50.41, H 4.23; found: C 50.62, H 4.12.

Data of **5**: M.p. 230° (dec.). Anal. calc. for $C_{57}H_{54}BF_4P_3Pd_3S_3$ (1334.21): C 51.31, H 4.08; found: C 50.91, H 4.22.

trans-*Dichloro[μ-(9,10-dihydro-9,10-dioxoanthracene-1,5-diyl)]tetrakis(triphenylphosphine)dipalladium* (**6**). A suspension of 1,5-dichloro-9,10-anthraquinone (0.004 g, 0.015 mol) and $[Pd(PPh_3)_4]$ (0.040 g, 0.035 mmol) in toluene (30 ml) was stirred for 17 h at 90°. The colorless solid in a light yellow soln. was allowed to cool to r.t. and filtered through *Celite.* The solid on the filter was washed with toluene (4 × 5 ml) and the product dissolved in CH_2Cl_2, the soln. filtered, and the filtrate concentrated and layered with pentane to afford orange crystals of **6** · 6 CH_2Cl_2. The solvent-free product **6** was obtained

Table. *Crystallographic Data and Structure Refinement Details for* **1** · *CH_2Cl_2*, **2** · x *Solvent Molecules*, **3**, **4**, **5** · *2 CH_2Cl_2*, *and* **6** · *6 CH_2Cl_2*

	1 · CH_2Cl_2	**2** · *x* Solvent molecules[a])	**3**	**4**	**5** · 2 CH_2Cl_2	**6** · 6 CH_2Cl_2
Chemical formula	$C_{44}H_{37}BrP_2PdS_2 \cdot CH_2Cl_2$	$C_{74}H_{66}P_4Pd_2S_2 \cdot (BF_4)_2$	$C_{10}H_{16}I_2N_4Pd$	$C_{50}H_{50}N_2P_2Pd_2S_2 \cdot (BF_4)_2$	$C_{57}H_{54}P_3Pd_3S_3 \cdot BF_4 \cdot 2\ CH_2Cl_2$	$C_{86}H_{66}Cl_2O_2P_4Pd_2 \cdot 6\ CH_2Cl_2$
M_r	963.03	1529.69[b])	552.47	1191.40	1503.95	2048.52
Crystal size [mm]	0.20 × 0.20 × 0.10	0.38 × 0.17 × 0.12	0.20 × 0.06 × 0.05	0.24 × 0.19 × 0.16	0.31 × 0.15 × 0.13	0.17 × 0.13 × 0.12
Crystal system	triclinic	triclinic	monoclinic	orthorhombic	orthorhombic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/m$	$Pna2_1$	$P2_12_12_1$	$P\bar{1}$
a [Å]	10.7573(10)	13.5292(14)	13.605(4)	27.773(9)	15.962(3)	12.9085(19)
b [Å]	12.3674(12)	13.8535(14)	8.586(3)	8.248(3)	18.360(3)	13.549(2)
c [Å]	15.5256(15)	22.584(2)	8.591(3)	21.945(7)	20.720(4)	13.775(2)
α [°]	92.040(2)	86.566(2)	90.00	90.00	90.00	82.650(2)
β [°]	90.174(2)	88.994(2)	128.218(4)	90.00	90.00	66.581(2)
γ [°]	93.764(2)	80.781(2)	90.00	90.00	90.00	89.249(2)
Unit cell volume [Å^3]	2059.7(3)	4170.5(7)	788.4(4)	5027(3)	6072.3(19)	2190.7(6)
Temperature [K]	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
$D_{calc.}$ [g cm^{-3}]	1.553	1.218	2.327	1.574	1.645	1.553
No. of formula units per unit cell, Z	2	2	2	4	4	1
Radiation type	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α
Absorption coefficient, μ [mm^{-1}]	1.762	0.611	5.079	0.929	1.288	0.960
$(\sin\theta/\lambda)_{max}$ [Å^{-1}]	0.6097	0.6677	0.6280	0.6318	0.6258	0.6254
No. of reflections measured	15758	41416	2255	23132	33283	23537
No. of independent reflections	7728	18963	854	9481	12141	8861
R_{int}	0.0212	0.0285	0.0211	0.0549	0.0482	0.0391
Param. refined	479	978	45	701	790	514
Final R_1 values ($I > 2\sigma(I)$)	0.0364	0.0396	0.0282	0.0566	0.0492	0.0374
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0944	0.0933	0.0670	0.1207	0.0988	0.0901
Final R_1 values (all data)	0.0425	0.0504	0.0317	0.0657	0.0561	0.0445
Final $wR(F^2)$ values (all data)	0.0982	0.0973	0.0685	0.1258	0.1039	0.0935
Goodness of fit on F^2	1.042	1.031	1.086	1.046	1.141	1.037
Largest diff. peak and hole [e Å^{-3}]	1.180; – 0.826	1.140; – 0.404	1.047; – 0.764	1.226; – 0.460	0.958; – 0.753	1.321; – 0.397

[a]) For details, see X-ray structure determination in the *Exper. Part.* [b]) Solvent molecules not taken into account.

after solvent removal *in vacuo* (0.020 g, 87%). M.p. 204° (dec.). ^{1}H-NMR: 8.14 (*dd*, $^3J = 7.8$, $^4J = 1.47$, 1 H, H–C(2)); 7.78 (*dm*, $^3J = 7.8$, 1 H, H–C(3)); 7.65 (*m*, 4 H, Ph, H–C(4)); 7.57, 7.48 (2*m*, 12 arom. H). ^{13}C-NMR: 183.1 (*s*, C(1)); 141.0 (*t*, ^4J(C,P) = 4.3, C(3)); 136.8 (*s*, C(9a)); 136.8 (*s*, C(10)); 136.4 (*s*, C(4)); 134.8 (*t*, ^2J(C,P) = 6.2, C_o (Ph)); 130.9 (*t*, ^1J(C,P) = 19.6, C_{ipso} (Ph)); 130.2 (*s*, C_p (Ph)); 129.5 (*s*, C(4a)); 128.4 (*t*, ^3J(C,P) = 4.8, C_m (Ph)); 126.4 (*s*, C(2)). ^{31}P-NMR: 24.1 (*s*, PPh_3). MS: 1368.8 ([*M* – 2 Ph – O]$^+$), 1055.1 ([*M* – PPh_3 – 2 Ph – 2 O – Cl]$^+$), 1024.9 ([*M* – 6 Ph – 2 Cl]$^+$), 769.5 (M^{2+}). Anal. calc. for $C_{86}H_{66}Cl_2O_2P_4Pd_2$ (1539.11): C 67.11, H 4.32; found: C 66.90, H 4.36.

X-Ray Structure Determination. Single-crystal X-ray diffraction data were collected at 100 K with a *Bruker-Smart-Apex* [28a] diffractometer equipped with graphite monochromated MoK_α radiation (λ 0.71073 Å). The cell refinement and data reduction were performed with the program SAINT+ [28b], and the empirical absorption corrections were performed with SADABS [29]. The structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-squares methods based on F^2 with SHELXL-97 [30]. All non-H-atoms were refined anisotropically, and the H-atoms were placed in calculated positions with temperature factors fixed at 1.2 times U_{eq} of the parent atoms (C) and 1.5 times U_{eq} for Me groups. A summary of the data-collection and structure-refinement parameters is provided in the *Table*.

Crystals of **1** · CH_2Cl_2 suitable for X-ray analysis were grown by recrystallization from Et_2O/hexane at – 20°.

In the structure of **2** · *x* solvent molecules, both counterions were found to be disordered and modelled in two orientations, as well as one of the phenyl substituents at P(1D). The solvent molecules could not be assigned because of diffuse electron density. Therefore, the electron density was subtracted and the SQUEEZE instruction of PLATON was applied [31]. As the crystals were grown from a mixture of solvents, it was difficult to make any assumptions regarding the exact nature of these molecules. Consequently, the tabulated relative molecular mass M_r, F(000), and absorption coefficient (*Table*) are not correct since solvent molecules were not taken into account in these calculations. Anisotropic displacement parameter restraints were applied to C(14E).

Structure **4** was a racemic twin with a contribution of the second component of 18%. Both counterions were disordered and modelled in two orientations. The anisotropic displacement parameters for B(43), B(43A), and F(39A) were restrained.

In structure **5** · 2 CH_2Cl_2, the counterion and two solvent molecules were disordered and modelled in two orientations. Geometric restraints were applied to the BF_4^- ion. The anisotropic displacement parameters of its atoms as well as those of C(40) were restrained.

The program Mercury [32] was used to prepare molecular graphic images. CCDC-888739 – 888744 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* http://www.ccdc.cam.ac.uk/data_request/cif.

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