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Mono- and di-nuclear palladium(II) complexes with bulky arsino(phosphino)methanes in different coordination modes

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Received 21st March 2002, Accepted 2nd May 2002
First published as an Advance Article on the web 6th June 2002

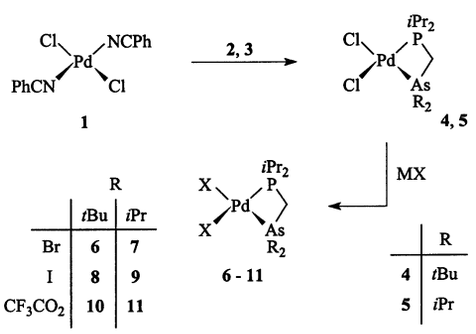
The peralkylated arsino(phosphino)methanes $R_2AsCH_2PiPr_2$ (R = *t*Bu **2**, *i*Pr **3**) react with *trans*-[$PdCl_2(NCPh)_2$] **1** to give the chelate compounds [$PdCl_2(\kappa^2\text{-}R_2AsCH_2PiPr_2)$] **4**, **5** which, *via* salt metathesis with KBr, KI (or NaI) and CF_3CO_2Ag, are converted to the dibromo-, diiodo-, and bis(trifluoracetato)-palladium(II) derivatives **6**–**11**, respectively. Whereas from **2**, **3** and [{Pd(μ-Cl)(η^3-C_3H_5)}$_2$] **12** the mono-cationic species [Pd(η^3-C_3H_5)(κ^2-$R_2AsCH_2PiPr_2$)]PF_6 **13**, **14** are obtained, treatment of **4**, **5** with $AgPF_6$ in acetonitrile affords the di-cationic complexes [Pd($NCCH_3$)$_2$(κ^2-$R_2AsCH_2PiPr_2$)](PF_6)$_2$ **15**, **16**. Compound **15** (R = *t*Bu) reacts with Na(acac) to give [Pd(κ^2-acac)-(κ^2-$R_2AsCH_2PiPr_2$)]PF_6 **17**. The reaction of **4**, **5** with $AgPF_6$ in acetone leads to the formation of the di-nuclear complexes [{Pd(μ-Cl)(κ^2-$R_2AsCH_2PiPr_2$)}$_2$](PF_6)$_2$ **18**, **19**, which in the presence of $SbiPr_3$ or pyridine undergo bridge cleavage to yield the mono-nuclear chelate derivatives [PdCl(L)(κ^2-$R_2AsCH_2PiPr_2$)]PF_6, mostly as a mixture of *cis*/*trans* isomers. The methylpalladium(II) compound [PdCl(CH_3)(κ^2-$tBu_2AsCH_2PiPr_2$)] **25**, prepared from [PdCl(CH_3)(η^4-C_8H_{12})] **24** and **2**, reacts with Na[$B(Ar_F)_4$] to afford the A-frame type complex [$Pd_2(CH_3)_2$(μ-Cl)-(μ-$tBu_2AsCH_2PiPr_2$)$_2$][$B(Ar_F)_4$] **27**. In contrast, the related precursor [PdCl(CH_3)(κ^2-$iPr_2AsCH_2PiPr_2$)], generated *in situ* from **24** and **3**, gives, upon treatment with Na[$B(Ar_F)_4$], a mixture of two products **28a**,**b** being the corresponding head-to-tail and head-to-head isomers. The mono-nuclear compounds **4** and **13** as well as the A-frame type complex **27** have been characterized by X-ray crystallography.

In the context of our studies on the coordination chemistry of unsymmetrical, possibly hemilabile, chelating systems such as $R_2PCH_2CH_2OMe$ and $R_2AsCH_2CH_2OMe$,[1,2] we recently reported the synthesis of the first representatives of arsino-(phosphino)methanes $R_2AsCH_2PR'_2$ with bulky alkyl or cycloalkyl groups R and R′ at the donor centres.[3] We first tested the bonding capabilities of these molecules towards rhodium(I) and found that mono-nuclear as well as di-nuclear complexes with either monodentate or bidentate $R_2AsCH_2PR'_2$ ligands can be obtained.[3,4] As a continuation of this work, we turned our interest to palladium(II), being isoelectronic to rhodium(I), as the metal centre and describe in this article the preparation of a series of neutral and cationic compounds, in which the bulky arsino(phosphino)methanes coordinate either in a chelating or bridging mode. Some preliminary results have already been communicated.[5]

Results and discussion

Mono-nuclear neutral and cationic chelate complexes with $R_2AsCH_2PiPr_2$ as ligands

Addition of a solution of *trans*-[$PdCl_2(NCPh)_2$] **1** in CH_2Cl_2 to a solution containing an equimolar amount of tBu_2AsCH_2-$PiPr_2$ **2** or $iPr_2AsCH_2PiPr_2$ **3** in CH_2Cl_2 affords the chelate complexes **4** and **5** in, respectively, 75% and 83% yield (Scheme 1). The red or red–brown air-stable compounds are readily soluble in acetone and CH_2Cl_2, nearly insoluble in ether and pentane and thermally stable up to about 185 °C. The most typical features of the ^{1}H and ^{13}C NMR spectra of **4** and **5** are the positions of the signals for the protons and carbon atoms of the bridging CH_2 groups of the ligands, which are significantly shifted to lower field compared to the arsino(phosphino)-methanes **2** and **3**. Moreover, the signal for the $AsCH_2P$ protons appears as a doublet with J(P,H) = 9.7 Hz, while in the



Scheme 1

^{1}H NMR spectra of the free ligands singlet resonances are observed.

The result of the X-ray crystal structure analysis of **4** (possessing C_s symmetry) is shown in Fig. 1. The coordination geometry around the palladium(II) centre is distorted square-planar with a Cl(1)–Pd–Cl(2) bond angle of 93.66(5)°. The As–Pd–P bite angle of 74.94(3)° is quite small and comparable to the P–Pd–P bite angle of the dppm relatives [$PdCl_2(\kappa^2\text{-}Ph_2PCH_2$-$PPh_2$)] [72.68(3)°][6] and [$PdI_2(\kappa^2\text{-}Ph_2PCH_2PPh_2$)] (73.56°).[7] The PdAsCP four-membered ring is not strictly planar, the dihedral angle between the planes [As,C,P] and [As,Pd,P] being 10.9°.

Both chelate complexes **4** and **5** undergo salt metathesis reactions in the presence of KBr and KI or NaI, respectively. In acetone or acetone–CH_2Cl_2 as solvent, substitution products **6**–**9** are formed and isolated as yellow (**6**, **7**), brown (**8**) or orange (**9**) air-stable solids in good to excellent yields (see Scheme 1). The chemical properties as well as the spectroscopic data of **6**–**9** are quite similar to those of the chloro derivatives and deserve no further comment.

DOI: 10.1039/b202879b

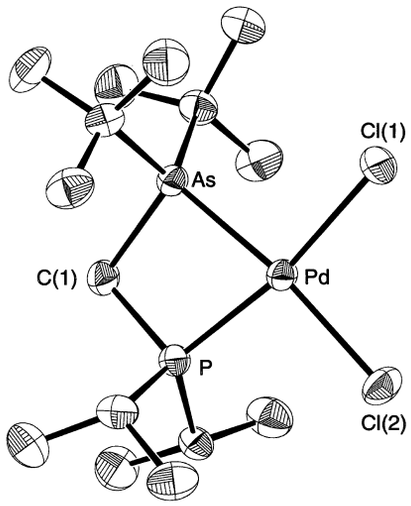
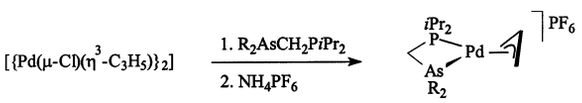


Fig. 1 Molecular structure of compound **4**. Selected bond distances (Å) and angles (°): Pd–As 2.3526(7), Pd–P 2.2427(13), Pd–Cl(1) 2.3595(14), Pd–Cl(2) 2.3657(13), As–C(1) 1.974(5), P–C(1) 1.840(5); As–Pd–P 74.94(3), As–C(1)–P 94.3(2), Cl(1)–Pd–Cl(2) 93.66(5), As–Pd–Cl(2) 170.24(4), P–Pd–Cl(1) 170.08(5), As–Pd–Cl(1) 95.23(4), P–Pd–Cl(2) 96.25(5).

The chloro ligands of **4** and **5** can also be replaced by trifluoracetate but in this case it is necessary to use instead of CF_3CO_2Na or CF_3CO_2K the corresponding silver salt. Treatment of solutions of **4** or **5** in CH_2Cl_2 with solutions of CF_3CO_2Ag in acetone at −40 °C affords, after warming to room temperature and separation of AgCl, the bis(trifluoracetato) compounds **10** and **11** as pale-yellow moderately air-sensitive solids in 56% and 90% yield, respectively. In CH_2Cl_2 or acetone, both compounds **10** and **11** are not exceedingly stable and decompose in 4–6 h to give palladium precipitates. Since in nitromethane **10** and **11** possess a molar conductivity of *ca.* 25 $cm^2\ \Omega^{-1}\ mol^{-1}$ (*i.e.*, significantly less than anticipated for 1 : 1 electrolytes),[8] we conclude that in polar solvents a partial dissociation takes place. However, owing to the positions of the asymmetric and symmetric OCO stretching vibrations in the IR spectra (in Nujol) of **10** and **11** there is no doubt that in the crystal the two CF_3CO_2 groups are covalently linked to the metal in a monodentate bonding mode.

The π-allylpalladium complexes **13** and **14** (Scheme 2)



12 **13, 14**

Scheme 2

containing **2** and **3** as chelating ligands were prepared from $[\{Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)\}_2]$ **12** following the procedure used for analogous compounds with P,N-donor groups.[9] After recrystallization from ethyl acetate, the PF_6 salts **13** and **14** were obtained as white solids revealing in nitromethane a molar conductivity typical for 1 : 1 electrolytes.[8] The ^1H NMR spectra of **13** and **14** display five well-separated signals for the allylic protons indicating that at least at room temperature a η^3-η^1-η^3 rearrangement of the C_3H_5 ligand does not take place. The assignment for these signals is based on NOE measurements (Fig. 2) as well as in the case of **13** on a C,H correlation spectrum in $CDCl_3$. From the latter it is obvious that the resonance for the carbon atom C1 of the allylic ligand (for numbering see Chart 1 in the Experimental section) at δ 66.4 correlates with the signals of the protons H^{1s} and H^{1a} and the resonance for C3 at δ 63.7 with the signals of H^{3s} and H^{3a}, respectively. Since there is no mirror plane passing through the coordinated As

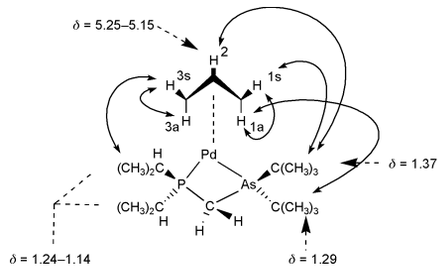
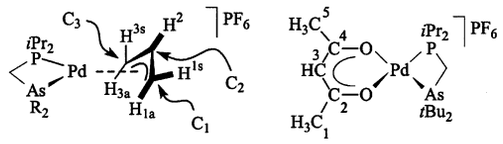


Fig. 2 Selected data of NOE measurements (in $CDCl_3$) for compound **13** (δ in ppm).



13, 14 **17**

Chart 1 Assignment of protons and carbon atoms of the C_3H_5 ligand in compounds **13** and **14**, and of carbon atoms of the acac ligand in compound **17**.

and P atoms, the two isopropyl groups at phosphorus and the two *tert*-butyl or isopropyl groups at arsenic are diastereotopic and thus give rise both in the ^1H and ^{13}C NMR spectra of **13** and **14** to two sets of signals.

To obtain information about the detailed structural aspects of the cationic π-allyl complexes, an X-ray crystal structure investigation of **13** was carried out. The molecular diagram (Fig. 3) confirms the chelating coordination mode of the

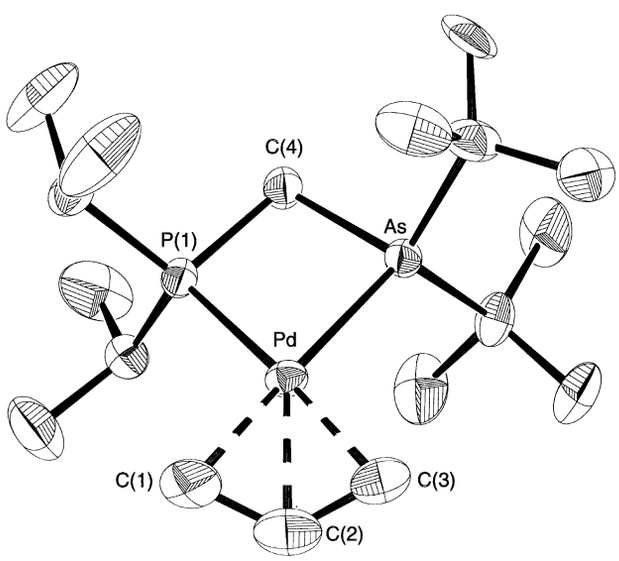
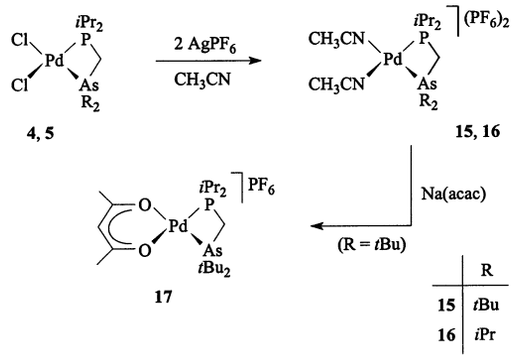


Fig. 3 Molecular structure of compound **13** (PF_6 counterion omitted for clarity). Selected bond distances (Å) and angles (°): Pd–As 2.4063(6), Pd–P(1) 2.3079(12), Pd–C(1) 2.169(3), Pd–C(2) 2.162(4), Pd–C(3) 2.197(4), As–C(4) 1.973(3), P(1)–C(4) 1.848(3), C(1)–C(2) 1.371(7), C(2)–C(3) 1.361(7); As–Pd–P(1) 74.81(2), As–C(4)–P(1) 97.09(14), C(4)–As–Pd 90.70(9), C(4)–P(1)–Pd 97.11(10), C(3)–C(2)–C(1) 123.7(4).

arsino(phosphino)methane with bond lengths Pd–P and Pd–As that are *ca.* 0.06 Å longer than in **4**. The distance Pd–C(1) is somewhat shorter (by 0.03 Å) than the distance Pd–C(3), probably due to the stronger *trans* influence of phosphines compared with arsines. Despite the positive charge of **13**, the As–Pd–P bite angle of 74.81° is almost identical to that of the neutral compound **4**. The plane of the allylic carbon atoms C(1)–C(3) is not exactly perpendicular to the plane containing the palladium, arsenic and phosphorus atoms, the dihedral

angle between the two planes being 116.1° with the carbon atom C^2 pointing away from the metal centre.

The reactions of **4** and **5** with *two* equivalents of $AgPF_6$ in acetonitrile at −30 °C afford the dicationic complexes **15** and **16** which were isolated as yellow solids in 83% (**15**) and 47% (**16**) yields (Scheme 3). Both the elemental analysis and conductivity



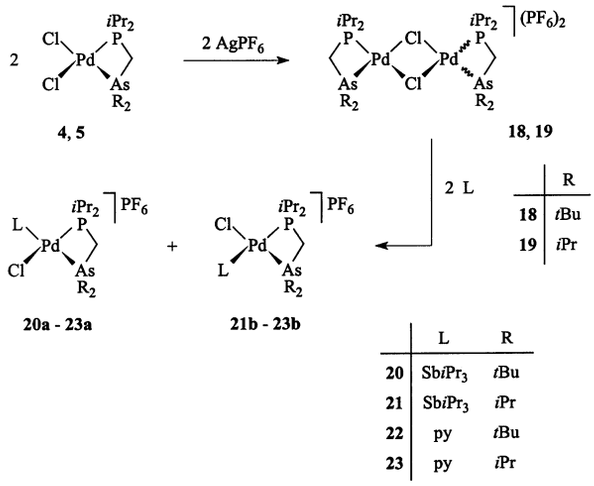
Scheme 3

measurements are in agreement with the proposed composition. Similarly to the starting material **1**, the nitrile ligands can easily be displaced by other nucleophiles and thus upon treatment of **15** with Na(acac) the mono-cationic species **17** is formed. Since the Pd(acac) unit is connected to an unsymmetrical chelating moiety, the ^{1}H NMR spectrum of **17** exhibits two signals for the methyl protons of the acetylacetonate and the ^{13}C NMR spectrum two resonances, separated only by 0.4 ppm, for the carbonyl carbon atoms of the acac ligand. The ^{13}C–^{31}P coupling constant of the signal for the ^{13}C carbon nuclei *trans* to phosphorus is rather small (1.9 Hz) and comparable to the value found for $[Pd(\kappa^2\text{-acac})(\kappa^2\text{-}Ph_2PCH_2PPh_2)]PF_6$ (1.5 Hz).[10]

In order to test the potential utility of the cations $[Pd(NCCH_3)_2(\kappa^2\text{-}R_2AsCH_2PiPr_2)]^{2+}$ as pre-catalysts for the generation of polyketones, a solution of **15** (10 mg) in methanol (10 cm^3) was treated in an autoclave with CO and ethene (10 bar, ratio 1 : 1). After stirring the reaction mixture at 80 °C, an off-white precipitate is formed which proved to be insoluble in all common organic solvents and decomposes at 150 °C. While the IR spectrum of the product shows a strong ν(C=O) absorption at 1692 cm^{-1} (for comparison see ref. 11), the ^{13}C NMR spectrum (CP-MAS) displays two singlet resonances at δ 209.3 and 35.4 assigned to the carbonyl and methylene (and methyl) carbon atoms. In agreement with published data,[12] these chemical shift values indicate that the polymeric material is built up by alternating CO and C_2H_4 units. The average molecular mass of the polyketone is 42390, determined by GPC (gel permeation chromatography) measurements.

Preparation and substitution reactions of di-nuclear chelate complexes

Both compounds **4** and **5** react with *one* equivalent of $AgPF_6$ in acetone–CH_2Cl_2 to give instead of $[PdCl(acetone)(\kappa^2\text{-}R_2\text{-}AsCH_2PiPr_2)]PF_6$ the di-nuclear complexes **18** and **19** in 70–80% yields (Scheme 4). Even in the presence of acetonitrile, the solvent-free di-cationic species are formed, which is noteworthy insofar as treatment of **4** and **5** with *two* equivalents of $AgPF_6$ in CH_3CN affords the mononuclear compounds **15** and **16** (see Scheme 3). The chloro-bridged dimers **18** and **19** are yellow solids, which are air-stable and readily soluble in polar solvents such as acetone, chloroform and dichloromethane. The molar conductivity of **18** (132.7 cm^2 Ω^{-1} mol^{-1}) is almost the same as that of the structurally related platinum(II) complex $[\{Pt(\mu\text{-}I)(\kappa^2\text{-}Ph_2PCH_2PPh_2)\}_2](BF_4)_2$ (129.2 cm^2 Ω^{-1} mol^{-1}),[13] both values being determined in nitromethane. The ^{31}P NMR spectra of **18** and **19** display the resonance for the coordinated



Scheme 4

phosphorus atom at δ −12.1 (**18**) and −4.7 (**19**) which is exactly 4 ppm downfield compared with the monomeric di-cations **15** and **16**.

Treatment of **18** with a slight excess of $SbiPr_3$ (molar ratio 1 : 2.3) in CH_2Cl_2 leads to bridge cleavage and formation of the mono-nuclear compound **20a** in 74% yield. Both the elemental analysis and the mass spectrum (FAB) confirm the proposed composition of the product. In contrast, the reaction of **19** with $SbiPr_3$ under the same conditions affords a mixture of two isomers **21a** and **21b**, one of which contains the stibine ligand *trans* to the $AsiPr_2$ and the other *trans* to the $PiPr_2$ unit. According to the intensity of the signals for the $AsCH_2P$ methylene protons in the ^{1}H NMR spectrum at δ 3.39 and 3.24, the ratio of **21a** to **21b** is approximately 2 : 1.

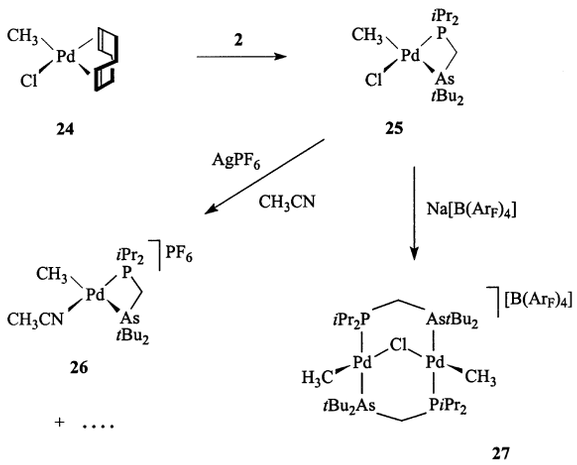
The question which of the isomers **21a** or **21b** dominates has been answered on the basis of the ^{13}C NMR data as well as DEPT 90 and DEPT 135 measurements. The most conclusive result is that the signal for the $SbCHCH_3$ carbon atom of the major isomer **21a** appears at δ 23.6 as a slightly broadened singlet while that of the minor isomer **21b** at δ 22.0 is a doublet with a ^{13}C–^{31}P coupling constant of 6.9 Hz. The assignment of the resonance at δ 23.6 to isomer **21a** is supported by the observation that the ^{13}C NMR spectrum of **20a** exhibits for the $SbCHCH_3$ carbon nuclei a single resonance at δ 23.4, *i.e.*, at practically the same position as for **21a**. In this context it should be mentioned that the chloro-bridged complex $[\{Pd(\mu\text{-}Cl)(\kappa^2\text{-}Ph_2AsCH_2CH_2PPh_2)\}_2](ClO_4)_2$ reacts with tertiary phosphines PR_3 to give also a mixture of two isomers *cis*,*trans*-$[PdCl(PR_3)(\kappa^2\text{-}Ph_2AsCH_2CH_2PPh_2)]ClO_4$ in which that with PR_3 in *trans*-disposition to $AsPh_2$ dominates.[14]

The reaction of **18** and **19** with pyridine proceeds analogously to that of **19** with $SbiPr_3$ and affords a mixture of **22a**,**b** and **23a**,**b**, respectively (see Scheme 4). In contrast to the NMR spectra of **21a**,**b**, which at room temperature show for most of the ^{1}H, ^{13}C and ^{31}P nuclei sharp resonances, the corresponding spectra of **22a**,**b** and **23a**,**b** display at 295 K rather broad signals indicating that in solution a relatively fast (on the NMR time scale) rearrangement takes place. The ^{1}H NMR spectrum of **22a**,**b** at 353 K in CD_3NO_2 shows sharp resonances (the number of which is about half of that at 295 K) while the ^{31}P NMR spectrum of **22a**,**b** at 353 K exhibits a broad bump at *ca.* δ −12. At 295 K, the ^{31}P NMR spectrum of **22a**,**b** displays two broadened singlets at δ −6.5 and −18.4. A high-temperature ^{13}C NMR spectrum of **22a**,**b** could not be obtained due to continuing decomposition of both isomers under these conditions in nitromethane. Regarding the isomeric mixture **23a**,**b**, the ^{13}C NMR spectrum shows at 213 K in CD_2Cl_2 rather sharp signals which suggests that at this temperature the dynamic process is significantly slowed down. Whether this process consists of an intramolecular *cis*/*trans* isomerization or a dissociation of the

pyridine–palladium bond cannot be decided on the basis of the present data.

A-Frame complexes with Pd–CH_3 bonds and $R_2AsCH_2PiPr_2$ as bridging ligands

In contrast to the reaction of [PdCl(CH_3)(η^4-C_8H_{12})] **24** with **3**, which leads to a mixture of products, treatment of **24** with an equimolar amount of **2** in toluene affords cleanly the chelate complex **25** (Scheme 5). The pale-yellow slightly air-sensitive



Scheme 5

solid was isolated in 83% yield. Owing to the NMR spectroscopic data of **25**, there is no doubt that only one of the two possible stereoisomers is formed. Since the doublet resonances of the protons and the carbon atom of the Pd–CH_3 moiety in the ^{1}H and ^{13}C NMR spectra show rather small ^{1}H–^{31}P and ^{13}C–^{31}P couplings (0.9 and 5.7 Hz, respectively), we assume, in agreement with data from the literature,[15] that the metal-bonded methyl group and the P*i*Pr$_2$ unit are in *cis*-disposition.

The methylpalladium(II) complex **25** reacts with $AgBF_4$ in acetonitrile at −30 °C to give, after warming to room temperature and removal of the solvent, a white solid which due to the ^{1}H, ^{13}C and ^{31}P NMR spectra consists of [Pd(CH_3)($NCCH_3$)-(κ^2-*t*Bu$_2$AsCH$_2$P*i*Pr$_2$)]BF_4 **26** as the main product. Diagnostic features are the broadened singlet at δ −0.4 [with J(P,C) = 5.5 Hz] for the corresponding Pd–CH_3 methyl carbon atom in the ^{13}C NMR and the singlet resonance at δ 24.3 for the P*i*Pr$_2$ phosphorus atom in the ^{31}P NMR spectrum.

If instead of $AgBF_4$, the sodium salt of Brookhart's acid Na[B(Ar_F)$_4$] [Ar_F = $C_6H_3(CF_3)_2$-3,5] is used as substrate for the reaction with **25**, quite unexpectedly the A-frame type complex **27** is isolated in 74% yield (see Scheme 5). The composition of the light red, moderately air-sensitive solid has been confirmed by elemental analysis and mass spectra (FAB). The NMR data of the di-nuclear cation indicate that only the head-to-tail isomer with the phosphorus and the arsenic atoms *trans* to each other is formed. The ^{31}P NMR spectrum of **27** displays a singlet at δ 30.6 which is shifted *ca.* 8 ppm downfield compared to **25**. In the ^{1}H NMR spectrum of **27**, the signal for the protons of the Pd–CH_3 group appears as a doublet at δ 0.93 with a ^{1}H–^{31}P coupling constant (4.4 Hz) that is somewhat larger than for the mono-nuclear compound **25** (0.9 Hz). The value of the chemical shift for the Pd–CH_3 resonance is similar to that of the related A-frame complexes [$Pd_2(CH_3)_2$(μ-X)(μ-Ph_2PCH_2-$PPh_2)_2$]PF_6 (X = Cl, Br) with dppm as the bridging ligand.[16] With regard to the formation of **27** from **25** and Na[B(Ar_F)$_4$] we note that the platinum derivative [PtCl(CH_3)(κ^2-Ph_2PCH_2-PPh_2)] rearranges in methanol–CH_2Cl_2 at room temperature completely to the thermodynamically more stable compound [$Pt_2(CH_3)_2$(μ-Cl)(μ-$Ph_2PCH_2PPh_2)_2$]Cl.[17]

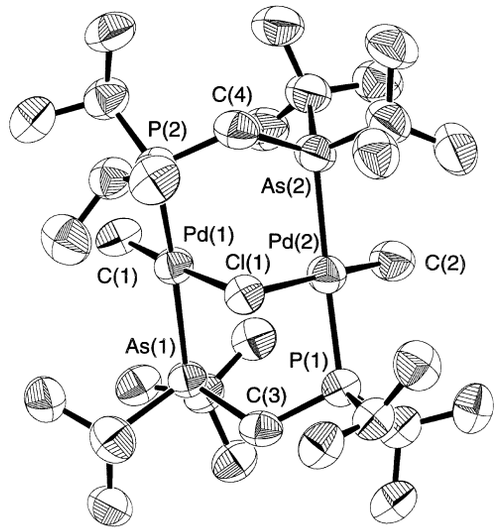
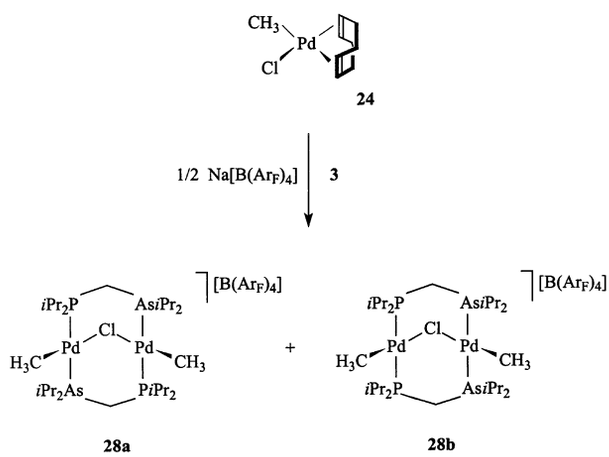


Fig. 4 Molecular structure of compound **27** [B(Ar_F)$_4$ counterion omitted for clarity]. Selected bond distances (Å) and angles (°): Pd(1)–As(1) 2.4823(18), Pd(1)–P(2) 2.306(2), Pd(1)–C(1) 2.052(6), Pd(1)–Cl(1) 2.459(2), Pd(2)–As(2) 2.4678(18), Pd(2)–P(1) 2.301(2), Pd(2)–C(2) 2.064(6), Pd(2)–Cl(1) 2.460(3); As(1)–Pd(1)–P(2) 173.45(4), As(1)–C(3)–P(1) 119.2(3), C(1)–Pd(1)–Cl(1) 176.3(2), Pd(1)–Cl(1)–Pd(2) 77.51(10), As(2)–Pd(2)–P(1) 173.44(4), As(2)–C(4)–P(2) 118.5(3), C(2)–Pd(2)–Cl(1) 176.3(2).

The result of the X-ray crystal structure analysis of **27** is shown in Fig. 4. The di-nuclear cation consists of two $PdCH_3$ fragments which are bridged by two *t*Bu$_2$AsCH$_2$P*i*Pr$_2$ ligands and one chloride. The coordination geometry around the palladium(II) centres is approximately square-planar with As–Pd–P and C(1)–Pd–Cl bond angles of *ca.* 173.4 and 176.3°, respectively. The Pd(1)–C(1) and Pd(2)–C(2) bond lengths of 2.052(6) and 2.064(6) Å are nearly identical to the Pd–CH_3 bond length in the unsymmetrical hydrido(methyl) complex [$Pd_2H(CH_3)$(μ-Cl)(μ-$Ph_2PCH_2PPh_2)_2$]BPh_4 [2.050(11) Å].[18] Moreover, the Pd–Pd distance of 3.079(4) Å is within the range reported for other structurally related palladium compounds of the A-frame type [2.976(6)–3.190(4) Å].[18,19]

To obtain the counterpart of **27** with two molecules of **3** as bridging ligands, the preparative route used for **27** had to be slightly modified. Following the observation that the mono-nuclear chelate complex [PdCl(CH_3)(κ^2-*i*Pr$_2$AsCH$_2$P*i*Pr$_2$)] seems to be rather labile and undergoes subsequent reactions in toluene even at room temperature, this compound was generated *in situ* from **24** and **3** in ether suspension. Treatment of the suspension with a solution of Na[B(Ar_F)$_4$] in ether affords a pale-yellow solid of analytical composition [$Pd_2(CH_3)_2$(μ-Cl)-(μ-*i*Pr$_2$AsCH$_2$P*i*Pr$_2$)$_2$][B(ArF)$_4$] consisting, however, in contrast to **27** of a mixture of two isomers **28a** and **28b** (Scheme 6).



Scheme 6

Since the NMR data of the dominating species **28a** are quite similar to those of **27**, we assume that **28a** is the head-to-tail isomer with the As*i*Pr$_2$ and P*i*Pr$_2$ groups in *trans*-disposition. The most typical features of the minor component **28b** (observed in the ^{1}H- and ^{31}P-decoupled ^{13}C NMR spectrum of the mixture **28a**,**b**) are the two resonances for the metal-bonded CH_3 carbon atoms at δ −5.5 and −11.7, of which only the first one shows in the $^{13}C\{^1H\}$ NMR spectrum a ^{13}C–^{31}P coupling. The signal at δ −5.5 can therefore be assigned to the methyl group *cis* to the P*i*Pr$_2$ and the other at δ −11.7 to the methyl group *cis* to the As*i*Pr$_2$ fragment. We found that in CD_2Cl_2 in the temperature range of 20 to 40 °C no rearrangement of **28a** to **28b** or *vice versa* occurs.

In summary, the work presented in this paper has shown that the arsino(phosphino)methanes **2** and **3** with bulky alkyl instead of phenyl substituents at the donor centres can behave both as chelating and bridging ligands towards palladium(II). Besides neutral and mono- as well as di-cationic compounds, in which **2** and **3** are bonded in a chelating fashion, di-nuclear complexes of the A-frame type with **2** and **3** as bridging units can also be generated. While related compounds with dppm, particularly in a bridging coordination mode, are well known we note that prior to our investigations [3,4] only a few examples of dimeric rhodium or mixed platinum–rhodium compounds with $Ph_2AsCH_2PPh_2$ as the ligand have been described in the literature.[20] We are currently attempting to find out what the catalytic potential of the rhodium(I) and palladium(II) complexes with the new arsino(phosphino)methanes is and will report on the results of these studies in due course.

Experimental

All experiments were carried out under an atmosphere of Argon by Schlenk techniques. The starting materials **1**,[21] **12**,[22] **24**[23] and the ligands **2** and **3**[3] were prepared as described in the literature. NMR spectra were recorded at room temperature on Bruker AC 200, DRX 300, AMX 400 and DMX 600 instruments, IR spectra on a Bruker IFS 25 FT-IR infrared spectrometer, and mass spectra on a Finnigan 90 MAT instrument (70 eV). Conductivity measurements were carried out in nitromethane with a Schott Konduktometer CG 851. Melting points were measured by DTA. Abbreviations used: s, singlet; d, doublet; q, quartet; sept, septet; m, multiplet; br, broadened signal; coupling constants *J* in Hz.

Preparations

[PdCl$_2$(κ^2-*t*Bu$_2$AsCH$_2$P*i*Pr$_2$)] 4. A solution of compound **1** (277 mg, 0.72 mmol) in CH_2Cl_2 (10 cm^3) was treated dropwise with a solution of **2** (235 mg, 0.73 mmol) in CH_2Cl_2 (5 cm^3) and then stirred for 1 h at room temperature. The solution was filtered and the filtrate was evaporated *in vacuo*. Pentane (20 cm^3) was added to the oily residue and the suspension irradiated in an ultrasound bath for 30 min. A red–brown solid precipitated which was separated from the mother liquor, washed twice with 5 cm^3 portions of pentane and dried. Yield 270 mg (75%); mp 188 °C (decomp.) (Found: C, 36.06; H, 6.61. $C_{15}H_{34}AsCl_2PPd$ requires: C, 36.20; H, 6.89%). NMR (CD_2Cl_2): δ_H (400 MHz) 2.94 [2 H, d, *J*(P,H) = 9.7, PCH_2As], 2.66–2.54 (2 H, m, PC*H*CH$_3$), 1.56 (18 H, s, br, AsCCH$_3$), 1.46–1.40 (12 H, m, br, PCHC*H*$_3$); δ_C (100.6 MHz) 45.4 (s, As*C*CH$_3$), 29.5 (s, AsC*C*H$_3$), 26.5 [d, *J*(P,C) = 19.1, P*C*HCH$_3$], 21.4 [d, *J*(P,C) = 18.1, PCH_2As], 19.2 [d, *J*(P,C) = 1.9, PCH*C*H$_3$], 17.9 [d, *J*(P,C) = 1.9, PCH*C*H$_3$]; δ_P (162.0 MHz) −12.9 (s).

[PdCl$_2$(κ^2-*i*Pr$_2$AsCH$_2$P*i*Pr$_2$)] 5. This compound was prepared as described for **4** from **1** (320 mg, 0.83 mmol) and **3** (245 mg, 0.83 mmol). Red solid: yield 310 mg (83%); mp 232 °C (decomp.) (Found: C, 33.99; H, 6.25. $C_{13}H_{30}AsCl_2PPd$ requires: C, 33.25; H, 6.44%). NMR (CD_2Cl_2): δ_H (400 MHz) 2.88 [2 H, d, *J*(P,H) = 9.7, PCH_2As], 2.69 [2 H, sept, *J*(H,H) = 7.0, AsC*H*CH$_3$], 2.42–2.30 (2 H, m, PC*H*CH$_3$], 1.44–1.38 (18 H, m, br, AsCHC*H*$_3$ and PCHC*H*$_3$), 1.27 [6 H, dd, *J*(P,H) = 17.9, *J*(H,H) = 7.0, PCHC*H*$_3$]; δ_C (100.6 MHz) 30.3 (s, As*C*HCH$_3$), 26.2 [d, *J*(P,C) = 21.9, P*C*HCH$_3$], 21.1 [d, *J*(P,C) = 21.0, PCH_2As], 20.2, 19.6 (both s, AsCH*C*H$_3$), 18.8 (s, PCH*C*H$_3$), 17.4 [d, *J*(P,C) = 1.9, PCH*C*H$_3$]; NMR ($CDCl_3$) δ_P (81.0 MHz) −6.1 (s); NMR (CD_2Cl_2) δ_P (162.0 MHz) −6.9 (s).

[PdBr$_2$(κ^2-*t*Bu$_2$AsCH$_2$P*i*Pr$_2$)] 6. A solution of **4** (90 mg, 0.18 mmol) in acetone (6 cm^3) was treated with KBr (107 mg, 0.90 mmol) and the reaction mixture was stirred for 90 min at 40 °C. After the solvent was evaporated *in vacuo*, the remaining residue was washed twice with 10 cm^3 portions of water. The residue was dissolved in CH_2Cl_2 (10 cm^3), the solution was dried with Na_2SO_4 and then filtered. The filtrate was brought to dryness *in vacuo*, the yellow solid was washed with pentane (5 cm^3) and dried. Yield 66 mg (63%); mp 219 °C (decomp.) (Found: C, 30.75; H, 5.82. $C_{15}H_{34}AsBr_2PPd$ requires: C, 30.72; H, 5.84%). NMR (CD_3NO_2): δ_H (400 MHz) 3.28 [2 H, d, *J*(P,H) = 10.0 Hz, PCH_2As], 2.70–2.61 (2 H, m, PC*H*CH$_3$), 1.56 (18 H, s, br, AsCCH$_3$), 1.48–1.38 (12 H, m, PCHC*H*$_3$); δ_C (100.6 MHz) 47.0 (s, As*C*CH$_3$), 30.0 (s, AsC*C*H$_3$), 28.3 [d, *J*(P,C) = 20.3, P*C*HCH$_3$], 23.1 [d, *J*(P,C) = 19.3, PCH_2As], 19.8, 18.4 [both d, *J*(P,C) = 2.0, PCH*C*H$_3$]; δ_P (162.0 MHz) −12.3 (s).

[PdBr$_2$(κ^2-*i*Pr$_2$AsCH$_2$P*i*Pr$_2$)] 7. A solution of **5** (80 mg, 0.17 mmol) in acetone–CH_2Cl_2 (1 : 1, 12 cm^3) was treated with KBr (230 mg, 1.93 mmol) and the reaction mixture was stirred for 12 h at room temperature. The solvent was evaporated *in vacuo*, the residue was dissolved in CH_2Cl_2 (12 cm^3) and the solution was filtered. The filtrate was brought to dryness *in vacuo*, the residue was washed with pentane (8 cm^3) and then dissolved in warm methanol (6 cm^3, *ca.* 40 °C). The solution was first cooled to room temperature and then stored for 6 h at −78 °C. Small yellow crystals precipitated, which were separated from the mother liquor, washed with pentane (6 cm^3) and dried. Yield 56 mg (59%); mp 204 °C (decomp.) (Found: C, 27.77; H, 5.21. $C_{13}H_{30}AsBr_2PPd$ requires: C, 27.96; H, 5.41%). NMR (CD_2Cl_2): δ_H (400 MHz) 3.03 [2 H, d, *J*(P,H) = 10.0, PCH_2As], 2.78 [2 H, sept, *J*(H,H) = 7.0, AsC*H*CH$_3$), 2.52–2.39 (2 H, m, PC*H*CH$_3$), 1.51–1.45 (18 H, m, br, AsCHC*H*$_3$ and PCHC*H*$_3$), 1.33 [6 H, dd, *J*(P,H) = 17.6, *J*(H,H) = 6.8, PCHC*H*$_3$]; δ_C (100.6 MHz) 30.8 (s, As*C*HCH$_3$), 27.0 [d, *J*(P,C) = 21.0, P*C*HCH$_3$], 22.3 [d, *J*(P,C) = 20.0, PCH_2As], 20.3, 19.7 (both s, AsCH*C*H$_3$), 19.1 (s, br, PCH*C*H$_3$), 17.5 [d, *J*(P,C) = 2.9 Hz, PCH*C*H$_3$]; δ_P (162.0 MHz) −7.6 (s).

[PdI$_2$(κ^2-*t*Bu$_2$AsCH$_2$P*i*Pr$_2$)] 8. This compound was prepared as described for **6** from **4** (80 mg, 0.16 mmol) and KI (133 mg, 0.80 mmol) in acetone (6 cm^3) at room temperature; time of reaction 48 h. Brown solid: yield 93 mg (85%); mp 137 °C (decomp.) (Found: C, 26.48; H, 4.78. $C_{15}H_{34}AsI_2PPd$ requires: C, 26.47; H, 5.04%). NMR (CD_2Cl_2): δ_H (400 MHz) 3.22 [2 H, d, *J*(P,H) = 10.0, PCH_2As], 2.71–2.61 (2 H, m, PC*H*CH$_3$), 1.54 (18 H, s, br, AsCCH$_3$), 1.43 [6 H, dd, *J*(P,H) = 18.2, *J*(H,H) = 7.0, PCHC*H*$_3$], 1.39 [6 H, dd, *J*(P,H) = 19.4, *J*(H,H) = 7.4, PCHC*H*$_3$]; δ_C (100.6 MHz) 45.3 (s, As*C*CH$_3$), 29.4 (s, AsC*C*H$_3$), 27.7 [d, *J*(P,C) = 18.1, P*C*HCH$_3$], 23.5 [d, *J*(P,C) = 16.2, PCH_2As], 19.4 (s, br, PCH*C*H$_3$), 17.8 [d, *J*(P,C) = 3.8, PCH*C*H$_3$]; δ_P (162.0 MHz) −15.0 (s).

[PdI$_2$(κ^2-*i*Pr$_2$AsCH$_2$P*i*Pr$_2$)] 9. This compound was prepared as described for **7** from **5** (80 mg, 0.17 mmol) and NaI (300 mg, 2.00 mmol); time of reaction 48 h. Orange solid: yield 55 mg (49%); mp 233 °C (decomp.) (Found: C, 24.22; H, 4.58. $C_{13}H_{30}AsI_2PPd$ requires: C, 23.93; H, 4.63%). NMR (CD_2Cl_2): δ_H (200 MHz) 3.19 [2 H, d, *J*(P,H) = 9.9, PCH_2As], 2.78 [2 H, sept, *J*(H,H) = 6.9, AsC*H*CH$_3$], 2.55–2.32 (2 H, m, PC*H*CH$_3$), 1.54–1.41 (18 H, m, br, AsCHC*H*$_3$ and PCHC*H*$_3$), 1.31 [6 H,

dd, J(P,H) = 17.2, J(H,H) = 6.9, PCHCH_3]; δ_C (50.3 MHz) 30.9 (s, AsCHCH$_3$), 28.1 [d, J(P,C) = 19.4, PCHCH$_3$], 24.5 [d, J(P,C) = 18.5, PCH$_2$As], 20.3, 19.6 (both s, AsCHCH$_3$), 19.3 (s, br, PCHCH$_3$), 17.4 [d, J(P,C) = 1.8, PCHCH$_3$]; δ_P (81.0 MHz) −11.3 (s).

[Pd(CF$_3$CO$_2$)$_2$(κ^2-*t*Bu$_2$AsCH$_2$P*i*Pr$_2$)] 10. A solution of **4** (110 mg, 0.22 mmol) in CH_2Cl_2 (5 cm^3) was treated at −40 °C with a solution of CF_3CO_2Ag (98 mg, 0.44 mmol) in acetone (7 cm^3). After warming to room temperature the reaction mixture was stirred for 4 h. The solvent was evaporated *in vacuo*, the remaining residue was dissolved in CH_2Cl_2 (10 cm^3) and the solution was filtered. The filtrate was brought to dryness *in vacuo*, the residue was washed with pentane (8 cm^3), and then methanol (3 cm^3) was added. The suspension was filtered and the filtrate was stored for 12 h at −78 °C. A pale-yellow solid precipitated, which was separated from the mother liquor, washed with pentane (8 cm^3) and dried. Yield 80 mg (56%); mp 195 °C (decomp.); Λ = 25.3 cm^2 Ω^{-1} mol^{-1} (Found: C, 35.04; H, 5.35. $C_{19}H_{34}AsF_6O_4PPd$ requires: C, 34.96; H, 5.25%). IR (Nujol) ν(OCO)$_{asym}$ 1687, ν(OCO)$_{sym}$ 1413 cm^{-1}; NMR (CD_2Cl_2): δ_H (300 MHz) 2.87 [2 H, d, J(P,H) = 10.0, PCH$_2$As], 2.70–2.53 (2 H, m, PCHCH$_3$), 1.54 (18 H, s, br, AsCCH$_3$), 1.43 [6 H, dd, J(P,H) = 18.5, J(H,H) = 7.4, PCHCH_3], 1.36 [6 H, dd, J(P,H) = 17.9, J(H,H) = 7.2, PCHCH_3]; δ_C (75.5 MHz) 161.3 [q, J(F,C) = 36.0, CF$_3$$CO_2$], 116.4 [q, J(F,C) = 291.5, CF$_3$CO$_2$], 46.3 (s, AsCCH$_3$), 29.4 (s, AsCCH$_3$), 27.5 [d, J(P,C) = 21.4, PCHCH$_3$], 20.1 [d, J(P,C) = 21.1, PCH$_2$As], 19.3 [d, J(P,C) = 1.8, PCHCH$_3$], 18.1 [d, J(P,C) = 1.5, PCHCH$_3$]; δ_F (282.4 MHz) −75.3 (s); δ_P (81.0 MHz) −11.7 (s).

[Pd(CF$_3$CO$_2$)$_2$(κ^2-*i*Pr$_2$AsCH$_2$P*i*Pr$_2$)] 11. This compound was prepared as described for **10** from **5** (80 mg, 0.17 mmol) and CF_3CO_2Ag (75 mg, 0.34 mmol). Pale-yellow solid: yield 96 mg (90%); mp 107 °C (decomp.); Λ = 24.1 cm^2 Ω^{-1} mol^{-1} (Found: C, 32.4; H, 4.76. $C_{17}H_{30}AsF_6O_4PPd$ requires: C, 32.69; H, 4.84%). IR (Nujol) ν(OCO)$_{asym}$ 1686, ν(OCO)$_{sym}$ 1410 cm^{-1}; NMR (CD_2Cl_2): δ_H (400 MHz) 2.95 [2 H, sept, J(H,H) = 7.0, AsCHCH$_3$], 2.75 [2 H, d, J(P,H) = 10.2, PCH$_2$As], 2.54–2.45 (2 H, m, PCHCH$_3$), 1.50–1.26 (24 H, m, AsCHCH_3 and PCHCH_3); δ_C (75.5 MHz) 161.6 [q, br, J(F,C) = 6.7, CF$_3$$CO_2$], 116.2 [q, br, J(F,C) = 290.6, CF$_3$CO$_2$], 33.3 (s, AsCHCH$_3$), 26.8 [d, J(P,C) = 22.5, PCHCH$_3$], 21.4, 19.2 (both s, AsCHCH$_3$), 19.1 (s, br, PCHCH$_3$), 18.0 [d, J(P,C) = 21.0, PCH$_2$As], 17.5 [d, J(P,C) = 2.5, PCHCH$_3$]; δ_F (282.4 MHz) −75.0 (s); δ_P (162.0 MHz) −2.9 (s).

[Pd(η^3-C$_3$H$_5$)(κ^2-*t*Bu$_2$AsCH$_2$P*i*Pr$_2$)]PF$_6$ 13. A solution of **12** (78 mg, 0.21 mmol) in CH_2Cl_2 (4 cm^3) was treated with a solution of **2** (170 mg, 0.53 mmol) in CH_2Cl_2 (6 cm^3) and stirred at room temperature. After 3 h a solution of NH_4PF_6 (340 mg, 2.10 mmol) in methanol (3 cm^3) was added dropwise and the reaction mixture was stirred for 12 h. The solvent was evaporated *in vacuo*, the residue was suspended in CH_2Cl_2 (8 cm^3) and the solution was filtered. The filtrate was brought to dryness *in vacuo*, the oily residue was treated with pentane (8 cm^3) and the mixture was irradiated for 20 min in an ultrasound bath. An off-white solid was formed, which was separated from the mother liquor, dried, and then dissolved in warm (*ca.* 40 °C) ethyl acetate (4 cm^3). Upon storing the solution for 12 h at −78 °C, a white microcrystalline solid precipitated, which was washed twice with pentane (8 cm^3) and dried. Yield 136 mg (53%); mp 142 °C (decomp.); Λ = 72.8 cm^2 Ω^{-1} mol^{-1} (Found: C, 34.52; H, 6.26. $C_{18}H_{39}AsF_6P_2Pd$ requires: C, 35.28; H, 6.42%). NMR ($CDCl_3$): δ_H (400 MHz) 5.25–5.15 (1 H, m, H^2 of C$_3$H$_5$), 4.67–4.63 (1 H, m, H^{1s} of C$_3$H$_5$), 4.58–4.46 (1 H, m, H^{3s} of C$_3$H$_5$), 3.47, 3.41 [1 H each, ABX spin system; in ^{1}H{^{31}P} AB spin system, J(A,B) = 15.9, PCH$_2$As], 2.98–2.88 (2 H, m, H^{1a} and H^{3a} of C$_3$H$_5$), 2.36, 2.24 [1 H each, both m; in ^{1}H{^{31}P} both sept, J(H,H) = 7.6, PCHCH$_3$], 1.37, 1.29 (9 H each, both s, AsCCH$_3$), 1.27–1.14 (12 H, m, PCHCH_3); δ_C (100.6 MHz) 119.1 [d, J(P,C) = 7.6, C^2 of C$_3$H$_5$], 66.4 [d, J(P,C) = 31.5, C^1 of C$_3$H$_5$], 63.7 [d, J(P,C) = 6.7, C^3 of C$_3$H$_5$], 41.3, 41.2 [both d, J(P,C) = 2.9, AsCCH$_3$], 29.3, 29.2 (both s, AsCCH$_3$), 27.6 [d, J(P,C) = 20.0, PCH$_2$As], 25.5–25.3 [m; in ^{13}C{^{1}H, ^{31}P} two s at 25.3, 25.2, PCHCH$_3$)], 20.2–20.0 [m; in ^{13}C{^{1}H, ^{31}P} two s at 20.0, 19.9, PCHCH$_3$)], 18.6, 18.4 (both s, PCHCH$_3$); for assignment of protons and carbon atoms of C$_3$H$_5$ see Chart 1; δ_P (162.0 MHz) 12.5 (s, PCH$_2$As), −144.3 [sept, J(F,P) = 712.8, PF$_6$]; MS (FAB): m/z 467 (M$^+$, 100.0%).

[Pd(η^3-C$_3$H$_5$)(κ^2-*i*Pr$_2$AsCH$_2$P*i*Pr$_2$)]PF$_6$ 14. This compound was prepared as described for **13** from **12** (53 mg, 0.14 mmol) and **3** (106 mg, 0.36 mmol) in CH_2Cl_2 (4 cm^3) plus a solution of NH_4PF_6 (235 mg, 1.44 mmol) in methanol (3 cm^3). White solid: yield 123 mg (72%); mp 190 °C (decomp.) (Found: C, 32.6; H, 5.75; Pd, 19.02. $C_{16}H_{35}AsF_6P_2Pd$ requires: C, 32.87; H, 6.03; Pd, 18.20%). NMR ($CDCl_3$): δ_H (400 MHz) 5.26–5.15 (1 H, m, br, H^2 of C$_3$H$_5$), 4.70–4.67 (1 H, m, br, H^{1s} of C$_3$H$_5$), 4.55–4.54 (1 H, m, br, H^{3s} of C$_3$H$_5$), 3.39, 3.34 [1 H each, m; in ^{1}H{^{31}P} AB-spin system, J(A,B) = 15.6, PCH$_2$As], 3.01–2.95 (1 H, m, H^{1a} of C$_3$H$_5$), 2.90 (1 H, m, br, H^{3a} of C$_3$H$_5$), 2.60–2.42 (2 H, m, br, AsCHCH$_3$), 2.30–2.12 (2 H, m, br, PCHCH$_3$), 1.32–1.09 (24 H, m, br, AsCHCH_3 and PCHCH_3); δ_C (100.6 MHz) 119.3 [d, J(P,C) = 8.1, C^2 of C$_3$H$_5$], 68.1 [d, J(P,C) = 30.5, C^1 of C$_3$H$_5$], 62.8 [d, J(P,C) = 6.1, C^3 of C$_3$H$_5$], 27.8 (s, br, AsCHCH$_3$), 26.0 [d, J(P,C) = 20.3, PCH$_2$As], 25.6 [d, J(P,C) = 23.0, PCHCH$_3$], 25.4 [d, J(P,C) = 22.4, PCHCH$_3$], 20.2, 20.1, 18.8, 18.7, 18.6 (all s, AsCHCH$_3$ and PCHCH$_3$); for assignment of protons and carbon atoms of C$_3$H$_5$ see Chart 1; δ_P (162.0 MHz) 16.6 (s, PCH$_2$As), −144.3 [sept, J(F,P) = 712.8, PF$_6$].

[Pd(NCCH$_3$)$_2$(κ^2-*t*Bu$_2$AsCH$_2$P*i*Pr$_2$)](PF$_6$)$_2$ 15. A solution of **4** (100 mg, 0.20 mmol) in CH_2Cl_2 (5 cm^3) was treated at −30 °C with a solution of $AgPF_6$ (100 mg, 0.40 mmol) in CH_3CN (5 cm^3). After the reaction mixture was warmed to room temperature, it was stirred for 1 h. The solvent was evaporated *in vacuo*, the residue was suspended in CH_2Cl_2 (8 cm^3) and the solution was filtered. The filtrate was concentrated *in vacuo* to *ca.* 1.5 cm^3 and diethyl ether (15 cm^3) was added dropwise. An oily solid precipitated, which was separated from the mother liquor and washed three times with diethyl ether (8 cm^3). After it was stored for 12 h at 0 °C, a yellow solid was formed. Yield 133 mg (83%); mp 98 °C (decomp.); Λ = 157 cm^2 Ω^{-1} mol^{-1} (Found: C, 28.48; H, 4.75; N, 3.42; Pd, 13.03. $C_{19}H_{40}AsF_{12}N_2P_3Pd$ requires: C, 28.57; H, 5.05; N, 3.51; Pd, 13.32%). NMR (CD_3NO_2): δ_H (400 MHz) 3.41 [2 H, d, J(P,H) = 10.6, PCH$_2$As], 2.80–2.68 (2 H, m, PCHCH$_3$), 2.43 (6 H, s, br, CH$_3$CN), 1.62 (18 H, s, br, AsCCH$_3$), 1.50–1.42 (12 H, m, PCHCH_3); δ_C (100.6 MHz) 125.3 (m, CH$_3$$C$N), 50.4 (s, As$CCH_3$), 29.4 (s, AsC$CH_3$), 28.1 [d, J(P,C) = 21.4, PCHCH$_3$], 19.5 [d, J(P,C) = 25.4, PCH$_2$As], 18.7 [d, J(P,C) = 2.0, PCHCH$_3$], 18.5 (s, PCHCH$_3$), 2.4 (s, br, CH$_3$CN); δ_P (162.0 MHz) −16.1 (s, PCH$_2$As), −144.6 [sept, J(F,P) = 706.3, PF$_6$].

[Pd(NCCH$_3$)$_2$(κ^2-*i*Pr$_2$AsCH$_2$P*i*Pr$_2$)](PF$_6$)$_2$ 16. This compound was prepared as described for **15** from **5** (100 mg, 0.22 mmol) and $AgPF_6$ (104 mg, 0.41 mmol). Yellow solid: yield 79 mg (47%); mp 64 °C (decomp.) (Found: C, 26.21; H, 4.48; N, 3.45. $C_{17}H_{36}AsF_{12}N_2P_3Pd$ requires: C, 26.49; H, 4.71; N, 3.63%). NMR (CD_3NO_2): δ_H (400 MHz) 3.40 [2 H, d, J(P,H) = 10.6, PCH$_2$As], 3.12 [2 H, sept, J(H,H) = 7.0, AsCHCH$_3$], 2.67–2.56 (2 H, m, PCHCH$_3$), 2.41 (6 H, s, br, CH$_3$CN), 1.52 [12 H, d, J(H,H) = 7.0, AsCHCH_3], 1.47 [6 H, dd, J(P,H) = 20.5, J(H,H) = 7.0, PCHCH_3], 1.41 [6 H, dd, J(P,H) = 19.9, J(H,H) = 6.7, PCHCH_3]; δ_C (100.6 MHz) 125.4 (m, br, CH$_3$$C$N), 33.8 (s, As$CHCH_3$), 27.5 [d, J(P,C) = 22.9, PCHCH$_3$], 20.2, 19.9 (both s, AsCHCH$_3$), 18.7 (s, PCHCH$_3$), 18.4 [d, J(P,C) = 25.8, PCH$_2$As], 17.7 [d, J(P,C) = 1.9, PCHCH$_3$], 2.5 (s, br, CH$_3$CN);

δ_P (162.0 MHz) −8.6 (s, PCH_2As), −144.6 [sept, J(F,P) = 708.4, PF_6].

[Pd(κ²-acac)(κ²-*t*Bu₂AsCH₂P*i*Pr₂)]PF₆ 17. A solution of **15** (45 mg, 0.06 mmol) in methanol (5 cm³) was treated at −60 °C with Na(acac) (10 mg, 0.08 mmol). After the reaction mixture was warmed to room temperature, it was stirred for 30 min and then the solvent was evaporated *in vacuo*. The residue was suspended in CH_2Cl_2 (7 cm³) and the solution was filtered. The filtrate was brought to dryness *in vacuo*, the white solid was washed twice with pentane (5 cm³) and dried. Yield 30 mg (79%); mp 183 C (decomp.) (Found: C, 36.10; H, 5.90. $C_{20}H_{41}AsF_6O_2P_2Pd$ requires: C, 35.81; H, 6.16%). IR (KBr) ν(CO) 1570, 1521 cm⁻¹; NMR (CD_2Cl_2): δ_H (400 MHz) 5.46 (1 H, s, CH of acac), 3.08 [2 H, d, J(P,H) = 10.0, PCH_2As], 2.52–2.42 (2 H, m, PC*H*CH_3), 2.00, 1.98 (3 H each, both s, CH_3 of acac), 1.56 (18 H, s, $AsCCH_3$), 1.45 [6 H, dd, J(P,H) = 18.5, J(H,H) = 7.3, $PCHCH_3$], 1.39 [6 H, dd, J(P,H) = 17.6, J(H,H) = 7.3, $PCHCH_3$]; δ_C (50.3 MHz) 186.8 [d, J(P,C) = 1.9, CH_3C^2O of acac], 186.4 (br s, CH_3C^4O of acac), 99.3 (s, C^3 of acac), 45.6 (s, As*C*CH_3), 29.4 (s, $AsCCH_3$) 27.2 (m, C^1 and C^5 of acac), 26.5 [d, J(P,C) = 20.3, P*C*HCH_3], 21.1 [d, J(P,C) = 23.1, PCH_2As], 18.7 (s, $PCHCH_3$), 18.3 [d, J(P,C) = 2.8, $PCHCH_3$], for assignment of carbon atoms of acac see Chart 1; δ_P (162.0 MHz) −14.0 (s, PCH_2As), −144.4 [sept J(F,P) = 712.3, PF_6]; MS (FAB): *m*/*z* 525 (M^+, 7.9%).

[{Pd(μ-Cl)(κ²-*t*Bu₂AsCH₂P*i*Pr₂)}₂](PF₆)₂ 18. A solution of **4** (150 mg, 0.30 mmol) in CH_2Cl_2 (5 cm³) was treated at −40 °C with a solution of $AgPF_6$ (76 mg, 0.30 mmol) in acetone (5 cm³). After the reaction mixture was warmed to room temperature, it was stirred for 1 h. The solvent was evaporated *in vacuo*, the residue was dissolved in CH_2Cl_2 (10 cm³) and the solution was filtered. The filtrate was brought to dryness *in vacuo*, the pale-yellow solid was washed twice with pentane (10 cm³) and dried. Yield 145 mg (80%); mp 159 °C (decomp.); Λ = 132.7 cm² Ω⁻¹ mol⁻¹ (Found: C, 29.68; H, 5.40. $C_{30}H_{68}As_2Cl_2F_{12}P_4Pd_2$ requires: C, 29.67; H, 5.64%). NMR (CD_2Cl_2): δ_H (400 MHz) 3.31 [4 H, d, J(P,H) = 10.6, PCH_2As], 2.65–2.52 (4 H, m, PC*H*CH_3), 1.59 (36 H, s, $AsCCH_3$), 1.49–1.41 (24 H, m, $PCHCH_3$); δ_C (100.6 MHz) 49.8 (s, br, As*C*CH_3), 29.7 (s, $AsCCH_3$), 28.1 [d, J(P,C) = 20.0, P*C*HCH_3], 21.2 [d, J(P,C) = 24.8, PCH_2As], 18.9 [d, J(P,C) = 2.9, $PCHCH_3$], 18.7 (br s, $PCHCH_3$); δ_P (162.0 MHz) −12.1 (s, PCH_2As), −144.3 [sept, J(F,P) = 712.8, PF_6].

[{Pd(μ-Cl)(κ²-*i*Pr₂AsCH₂P*i*Pr₂)}₂](PF₆)₂ 19. This compound was prepared as described for **18** from **5** (315 mg, 0.67 mmol) and $AgPF_6$ (169 mg, 0.67 mmol) in CH_2Cl_2–acetone (16 cm³, 1 : 1). Yellow solid: yield 268 mg (69%); mp 118 °C (decomp.) (Found C, 27.14; H, 4.94; Pd, 18.27. $C_{26}H_{60}As_2Cl_2F_{12}P_4Pd_2$ requires: C, 26.96; H, 5.22; Pd, 18.38%). NMR (CD_2Cl_2): δ_H (400 MHz) 3.35 [4 H, d, J(P,H) = 10.2, PCH_2As], 2.96 [4 H, sept, J(H,H) = 7.0, $AsCHCH_3$], 2.50–2.40 (4 H, m, PC*H*CH_3), 1.52–1.39 (48 H, m, $AsCHCH_3$ and $PCHCH_3$); δ_C (100.6 MHz) 33.2 (s, As*C*HCH_3), 27.0 [d, J(P,C) = 22.4, P*C*HCH_3], 20.2 (m, PCH_2As), 20.1, 20.0 (both s, br, $AsCHCH_3$), 18.5 (s, $PCHCH_3$), 17.7 (s, br, $PCHCH_3$); δ_P (162.0 MHz) −4.7 (s, PCH_2As), −144.4 [sept, J(F,P) = 710.6, PF_6].

[PdCl(Sb*i*Pr₃)(κ²-*t*Bu₂AsCH₂P*i*Pr₂)]PF₆ 20a. A solution of **18** (70 mg, 0.06 mmol) in CH_2Cl_2 (3 cm³) was treated at −50 °C with Sb*i*Pr_3 (0.03 cm³, 0.14 mmol). After the reaction mixture was warmed to room temperature, it was stirred for 45 min. A change of color from yellow to deep red occurred. The solvent was evaporated *in vacuo*, the oily residue was layered with pentane (5 cm³) and the suspension was irradiated for 15 min in an ultrasound bath. A pale-yellow solid was formed, which was separated from the mother liquor, washed twice with pentane (5 cm³) and dried. Yield 76 mg (74%); mp 68 °C (decomp.); Λ = 69.2 cm² Ω⁻¹ mol⁻¹ (Found: C, 33.34; H, 6.18; Pd, 13.01. $C_{24}H_{55}AsClF_6P_2PdSb$ requires: C, 33.59; H, 6.46; Pd, 12.40%). NMR (CD_2Cl_2): δ_H (400 MHz) 3.26 [2 H, d, J(P,H) = 10.3, PCH_2As], 2.71 [3 H, sept, J(H,H) = 7.3, $SbCHCH_3$], 2.39–2.26 (2 H, m, PC*H*CH_3), 1.59 (18 H, s, br, $AsCCH_3$), 1.53 [18 H, d, J(H,H) = 7.3, $SbCHCH_3$], 1.48 [6 H, dd, J(P,H) = 19.0, J(H,H) = 7.3, $PCHCH_3$], 1.36 [6 H, dd, J(P,H) = 17.0, J(H,H) = 7.0, $PCHCH_3$]; δ_H (100.6 MHz) 47.6 (s, As*C*CH_3), 30.0 (s, $AsCCH_3$), 29.2 [d, J(P,C) = 20.0, P*C*HCH_3], 23.4 (s, Sb*C*HCH_3), 22.4 (s, $SbCHCH_3$), 21.1 (s, $PCHCH_3$), 20.5 [d, J(P,C) = 21.0, PCH_2As], 18.3 [d, J(P,C) = 2.9, $PCHCH_3$]; δ_P (162.0 MHz) 2.3 (s, PCH_2As), −144.4 [sept, J(F,P) = 710.6, PF_6]; MS (FAB): *m*/*z* 713 (M^+, 10.6%).

[PdCl(Sb*i*Pr₃)(κ²-*i*Pr₂AsCH₂P*i*Pr₂)]PF₆ 21a,b. This mixture of two isomers was prepared as described for **20a** from **19** (80 mg, 0.07 mmol) and Sb*i*Pr_3 (0.03 cm³, 0.16 mmol) in CH_2Cl_2 (4 cm³). After recrystallization from methanol (2 cm³) red crystals were obtained. Yield 69 mg (60%); mp 106 °C (decomp.) (Found: C, 31.70; H, 5.82. $C_{22}H_{51}AsClF_6P_2PdSb$ requires: C, 31.83; H, 6.19%). NMR (CD_2Cl_2): δ_H (600 MHz) 3.39 [d, J(P,H) = 10.0, PCH_2As of isomer B], 3.24 [d, J(P,C) = 10.2, PCH_2As of isomer A], 2.92–2.85, 2.74–2.65, 2.63–2.53, 2.28–2.20 (all m, br, $AsCHCH_3$, PC*H*CH_3, $SbCHCH_3$ of isomers A and B), 1.54–1.31 (m, br, $AsCHCH_3$, $PCHCH_3$, $SbCHCH_3$ of isomers A und B); δ_C (150.9 MHz) 32.1 (s, As*C*HCH_3 of isomer B), 31.8 (s, As*C*HCH_3 of isomer A), 28.5 [d, J(P,C) = 21.3, P*C*HCH_3 of isomer A], 27.2 [d, J(P,C) = 15.8, P*C*HCH_3 of isomer B], 23.6 (s, br, Sb*C*HCH_3 of isomer A), 22.45 (s, br, $SbCHCH_3$ of isomer A), 22.4 (s, br, $SbCHCH_3$ of isomer A), 22.0 [d, J(P,C) = 6.9, Sb*C*HCH_3 of isomer B], 21.4 [d, J(P,C) = 19.9, PCH_2As of isomer B], 21.2 (s, $AsCHCH_3$ or $PCHCH_3$ of isomer B), 21.0 [d, J(P,C) = 24.0, PCH_2As of isomer A], 20.4 (s, $AsCHCH_3$ of isomer A), 20.2 [d, J(P,C) = 3.0, $PCHCH_3$ of isomer A], 20.1 (s, $AsCHCH_3$ of isomer A), 19.4, 19.0 (both s, $AsCHCH_3$ and $PCHCH_3$ of isomer B), 17.8 [d, J(P,C) = 1.8, $PCHCH_3$ of isomer B], 17.6 [d, J(P,C) = 2.9, $PCHCH_3$ of isomer A]; δ_P (162.0 MHz) 5.3 (s, PCH_2As of isomer A), −14.2 (s, PCH_2As of isomer B), −144.4 [sept, J(F,P) = 710.6, PF_6].

[PdCl(py)(κ²-*t*Bu₂AsCH₂P*i*Pr₂)]PF₆ 22a,b. A solution of **18** (50 mg, 0.04 mmol) in CH_2Cl_2 (3 cm³) was treated at −50 °C with pyridine (0.01 cm³, 0.12 mmol). After the reaction mixture was warmed to room temperature, it was stirred for 2 h. The solvent was evaporated *in vacuo*, the oily residue was layered with pentane (6 cm³) and the suspension was irradiated for 20 min in an ultrasound bath. A brownish solid was formed, which was separated from the mother liquor, washed twice with pentane (5 cm³) and dried. Yield 55 mg (93%); mp 72 °C (decomp.) (Found: C, 34.66; H, 5.30; N, 2.17. $C_{20}H_{39}AsClF_6NP_2Pd$ requires C, 35.00; H, 5.73; N, 2.04%). NMR (CD_2Cl_2, 295 K): δ_H (400 MHz) 8.67 (m, *ortho*-H of C_5H_5N), 7.96 (m, *para*-H of C_5H_5N), 7.58 (m, *meta*-H of C_5H_5N), 3.20 [d, br, J(P,H) = 10.3, PCH_2As], 2.75 (m, PC*H*CH_3 of isomer A), 2.57 (m, PC*H*CH_3 of isomer B), 1.63–1.20 (m, br, $AsCCH_3$ and $PCHCH_3$); δ_C (100.6 MHz) 151.2 (m, *ortho*-C of C_5H_5N), 139.8 (m, *para*-C of C_5H_5N), 126.4 (m, *meta*-C of C_5H_5N), 47.2 (m, As*C*CH_3 of isomer B), 46.0 (m, As*C*CH_3 of isomer A), 29.6 (s, $AsCCH_3$), 26.7 (m, br, P*C*HCH_3), 20.4 (m, br, PCH_2As), 19.2, 17.6 (both s, br, $PCHCH_3$ of isomer A), 18.8, 17.9 (both s, br, $PCHCH_3$ of isomer B); δ_P (162.0 MHz) −6.5 (s, br, PCH_2As of isomer A), −18.4 (s, br, PCH_2As of isomer B), −144.3 [sept, J(F,P) = 710.6, PF_6]; NMR (CD_3NO_2, 353 K): δ_H (200 MHz) 8.75 (2 H, m, *ortho*-H of C_5H_5N), 8.07 (1 H, m, *para*-H of C_5H_5N), 7.65 (2 H, m, *meta*-H of C_5H_5N), 3.37 [2 H, d, J(P,H) = 10.6, PCH_2As], 2.90–2.65 (2 H, m, br, PC*H*CH_3), 1.63 (18 H, s, $AsCCH_3$), 1.61–1.32 (12 H, m, br, $PCHCH_3$).

[PdCl(py)(κ²-*i*Pr₂AsCH₂P*i*Pr₂)]PF₆ 23a,b. This mixtures of two isomers was prepared as described for **22a**,**b** from **19**

(90 mg, 0.08 mmol) and pyridine (0.02 cm^3, 0.20 mmol) in CH_2Cl_2 (4 cm_3). Light red solid: yield 55 mg (54%); mp 88 °C (decomp.) (Found: C, 33.10; H, 5.08; N, 2.19. $C_{18}H_{35}AsClF_6NP_2Pd$ requires: C, 32.85; H, 5.36; N. 2.13%). NMR (CD_2Cl_2, 295 K): δ_H (300 MHz) 8.63 (2 H, m, *ortho*-H of C_5H_5N), 7.96 (1 H, m, *para*-H of C_5H_5N), 7.57 (2 H, m, *meta*-H of C_5H_5N), 3.19 [2 H, d, *J*(P,H) = 10.2, PCH_2As], 3.00–2.75, 2.65–2.35 (2 H each, both m, br, As*C*HCH_3 and PC*H*CH_3), 1.65–1.15 (24 H, m, br, AsCHC*H*$_3$ and PCHC*H*$_3$); δ_C (75.5 MHz) 151.4 (s, *ortho*-C of C_5H_5N), 140.0 (s, *para*-C of C_5H_5N), 126.5 (s, *meta*-C of C_5H_5N), 31.5 (s, br, As*C*HCH_3 of isomer B), 30.5 (s, br, As*C*HCH_3 of isomer A), 26.5 [d, br, *J*(P,C) = 21.8, P*C*HCH_3 of isomer A], 25.4 (m, br, P*C*HCH_3 of isomer B), 20.3, 19.8 (both s, AsCH*C*H$_3$), 19.4 (m, br, PCH_2As), 19.0, 17.4 (both s, br, PCH*C*H$_3$); δ_P (81.0 MHz) −0.5 (s, PCH_2As of isomer A), −11.1 (s, PCH_2As of isomer B), −143.9 [sept, *J*(F,P) = 711.9, PF_6]; NMR (CD_2Cl_2, 213 K) δ_H (300 MHz) 8.55 (m, *ortho*-H of C_5H_5N), 7.94 (m, *para*-H of C_5H_5N), 7.56 (m, *meta*-H of C_5H_5N), 3.13 (m, br, PCH_2As of isomers A and B), 2.94–2.77, 2.60–2.40, 2.30–2.25 (all m, br, As*C*HCH_3 and PC*H*CH_3 of isomers A and B), 1.50–1.00 (m, br, AsCHC*H*$_3$ and PCHC*H*$_3$ of isomers A and B); δ_C (75.5 MHz) 150.5 (s, *ortho*-C of C_5H_5N of isomer A), 150.4 (s, *ortho*-C of C_5H_5N of isomer B), 139.5 (s, *para*-C of C_5H_5N of isomer B), 139.4 (s, *para*-C of C_5H_5N of isomer A), 126.2 (s, *meta*-C of C_5H_5N of isomer B), 125.8 [d, *J*(P,C) = 2.5, *meta*-C of C_5H_5N of isomer A], 30.1 (s, br, As*C*HCH_3 of isomer B), 29.2 (s, br, As*C*HCH_3 of isomer A), 25.3 [d, *J*(P,C) = 24.0, P*C*HCH_3 of isomer A], 23.7 [d, *J*(P,C) = 21.1, P*C*HCH_3 of isomer B], 19.4 (s, br, AsCH*C*H$_3$ or PCH*C*H$_3$ of isomers A and B), 19.0 (s, AsCH*C*H$_3$ or PCH*C*H$_3$ of isomer B), 18.9 (s, AsCH*C*H$_3$ or PCH*C*H$_3$ of isomer A), 18.2 (m, PCH_2As of isomer B), 18.0 (s, AsCH*C*H$_3$ or PCH*C*H$_3$ of isomer A), 17.6 [d, *J*(P,C) = 23.3, PCH_2As of isomer A], 17.3 (s, br, AsCH*C*H$_3$ or PCH*C*H$_3$ of isomer B), 16.6 [d, *J*(P,C) = 1.8, PCH*C*H$_3$ of isomer A], 16.3 (s, br, PCH*C*H$_3$ of isomer B); δ_P (81.0 MHz) −2.1 (s, PCH_2As of isomer A), −10.1 (s, PCH_2As of isomer B), −144.2 [sept *J*(F,P) = 711.9, PF_6].

[PdCl(CH$_3$)(κ^2-*t*Bu$_2$AsCH$_2$P*i*Pr$_2$)] 25. A solution of **24** (130 mg, 0.49 mmol) in toluene (6 cm^3) was treated with a solution of **2** (185 mg, 0.58 mmol) in toluene (6 cm^3) and stirred for 30 min at room temperature. The solvent was evaporated *in vacuo*, the residue was suspended in pentane (5 cm^3) and the suspension was irradiated for 20 min in an ultrasound bath. A pale-yellow solid precipitated, which was separated from the mother liquor, washed twice with pentane (5 cm^3) and dried. Yield 194 mg (83%); mp 64 °C (decomp.) (Found: C, 40.56; H, 7.82; Pd, 23.25. $C_{16}H_{37}AsClPPd$ requires: C, 40.27; H, 7.81; Pd, 22.30%). NMR ($CDCl_3$): δ_H (400 MHz) 2.58 [2 H, d, *J*(P,H) = 10.0, PCH_2As], 2.56–2.39 (2 H, m, br, PC*H*CH_3), 1.38 (18 H, s, AsC*C*H$_3$), 1.30 [6 H, dd, *J*(P,H) = 16.4, *J*(H,H) = 7.3, PCHC*H*$_3$], 1.28 [6 H, dd, *J*(P,H) = 15.3, *J*(H,H) = 7.3, PCHC*H*$_3$], 0.73 [3 H, d, *J*(P,H) = 0.9, $PdCH_3$]; δ_C (100.6 MHz) 39.4 [d, *J*(P,C) = 2.9, As*C*CH$_3$], 29.8 (s, AsC*C*H$_3$), 26.3 [d, *J*(P,C) = 19.1, P*C*HCH_3], 21.2 [d, *J*(P,C) = 18.1, PCH_2As], 19.7, 18.6 (both s, PCH*C*H$_3$), 0.9 [d, *J*(P,C) = 5.7, $PdCH_3$]; δ_P (162.0 MHz) 22.1 (s).

Reaction of 25 with $AgBF_4$. A solution of **25** (90 mg, 0.19 mmol) in acetonitrile (5 cm^3) was treated under continuous stirring at −30 °C with a solution of $AgBF_4$ (37 mg, 0.19 mmol) in acetonitrile (5 cm^3). An off-white solid precipitated. After the solution was slowly warmed to room temperature, it was stirred for 25 min. The solvent was then evaporated *in vacuo*, the residue was suspended in dichloromethane (10 cm^3) and the suspension was filtered. The filtrate was brought to dryness *in vacuo*, the remaining pale-yellow residue was washed three times with pentane (8 cm^3) and dried. The ^1H and ^{31}P NMR spectra revealed that besides **26** as the major species several by-products were formed. Attempts to separate the by-products by fractional crystallization failed. Data for **26**: NMR (CD_2Cl_2): δ_H (300 MHz) 2.80 [2 H, d, *J*(P,H) = 10.1, PCH_2As], 2.50–2.36 (2 H, m, br, PC*H*CH_3), 2.35 (3 H, s, br, CH_3CN), 1.48–1.25 (12 H, m, PCHC*H*$_3$), 1.41 (18 H, s, AsCCH_3), 0.62 (3 H, s, br, $PdCH_3$); δ_C (75.5 MHz) 122.7 (m, CH_3CN), 40.6 [d, *J*(P,C) = 1.8, As*C*CH$_3$], 29.7 (s, AsC*C*H$_3$), 26.6 [d, *J*(P,C) = 22.2, P*C*HCH$_3$], 21.3 [d, *J*(P,C) = 21.8, PCH_2As], 19.7 (s, PCH*C*H$_3$), 18.4 [d, *J*(P,C) = 1.1, PCH*C*H$_3$], 3.0 (s, br, *C*H$_3$CN), −0.4 [d, *J*(P,C) = 5.5, $PdCH_3$]; δ_P (81.0 MHz) 24.3 (s).

[Pd$_2$(CH$_3$)$_2$(μ-Cl)(μ-*t*Bu$_2$AsCH$_2$P*i*Pr$_2$)$_2$][B(Ar$_F$)$_4$] 27. A solution of **25** (100 mg, 0.21 mmol) (**55**) in diethyl ether (5 cm^3) was treated with a solution of Na[B(Ar_F)$_4$] (92 mg, 0.10 mmol) in diethyl ether (6 cm^3) and stirred for 1 h at room temperature. An off-white solid precipitated. The solution was filtered, the filtrate was concentrated *in vacuo* to *ca.* 3 cm^3 and then stored for 3 d at −78 °C. A pale-red microcrystalline solid was formed, which was separated from the mother liquor, washed twice with pentane (5 cm^3) and dried. Yield 139 mg (74%); mp 70 °C (decomp.) (Found: C, 42.71; H, 4.53. $C_{64}H_{86}As_2BClF_{24}P_2Pd_2$ requires: C, 43.13; H, 4.86). NMR (CD_2Cl_2): δ_H (400 MHz) 7.74 [8 H, s, br, *ortho*-H of B(Ar_F)$_4$], 7.58 [4 H, s, br, *para*-H of B(Ar_F)$_4$], 2.75 [2 H, m, in $^1H\{^{31}P\}$ d, *J*(H,H) = 14.0, PCH_2As], 2.61, 2.44 [2 H each, m, in $^1H\{^{31}P\}$ sept, *J*(H,H) = 7.0, PC*H*CH_3], 2.19 [2 H, m, in $^1H\{^{31}P\}$ d, *J*(H,H) = 12.5, PCH_2As], 1.49 (12 H, m, PCHC*H*$_3$), 1.47, 1.44 (18 H each, both s, br, AsCCH_3), 1.36 [6 H, dd, *J*(P,H) = 11.2, *J*(H,H) = 7.0, PCHC*H*$_3$], 1.28 [6 H, dd, *J*(P,H) = 16.1, *J*(H,H) = 7.3, PCHC*H*$_3$], 0.93 [6 H, d, *J*(P,H) = 4.4, $PdCH_3$]; δ_C (100.6 MHz) 162.1 [q, *J*(B,C) = 49.6, *ipso*-C of B(Ar_F)$_4$], 135.1 [s, br, *ortho*-C of B(Ar_F)$_4$], 129.2 [qq, *J*(F,C) = 31.5, *J*(B,C) = 2.9, *meta*-C of B(Ar_F)$_4$], 124.9 [q, *J*(F,C) = 272.8, CF_3], 117.8 [m, br, *para*-C of B(Ar_F)$_4$], 41.9 [m, X-part of ABX spin system, in $^{13}C\{^1H,^{31}P\}$ s, As*C*CH$_3$], 40.3 [m, br, X-part of ABX spin system, in $^{13}C\{^1H,^{31}P\}$ s, As*C*CH$_3$], 31.4, 30.0 (both s, AsC*C*H$_3$), 28.6 [d, *J*(P,C) = 21.0, P*C*HCH$_3$], 23.2 [d, *J*(P,C) = 19.1, P*C*HCH$_3$], 23.1 [d, *J*(P,C) = 3.8, PCH*C*H$_3$], 21.2, 18.9 [both d, *J*(P,C) = 1.9, PCH*C*H$_3$], 17.6 [d, *J*(P,C) = 7.6, PCH*C*H$_3$], 13.0 [m, X-part of ABX spin system, in $^{13}C\{^1H,^{31}P\}$ s, PCH_2As], −6.4 (s, br, $PdCH_3$); δ_F (376.4 MHz) −62.7 (s, CF_3); δ_P (162.0 MHz) = 30.6 (s); MS (FAB): *m*/*z* 919 (M^+, 6.3%).

[Pd$_2$(CH$_3$)$_2$(μ-Cl)(μ-*i*Pr$_2$AsCH$_2$P*i*Pr$_2$)$_2$]B(Ar$_F$)$_4$ 28a,b. A solution of **24** (60 mg, 0.23 mmol) in diethyl ether (5 cm^3) was treated at −50 °C with a solution of **3** (80 mg, 0.27 mmol) in diethyl ether (5 cm^3) and under continuous stirring slowly warmed to room temperature (1 h). To this solution, a solution of Na[B(Ar_F)$_4$] (102 mg, 0.12 mmol) in diethyl ether (10 cm^3) was added dropwise and the reaction mixture stirred for 45 min. The solution was filtered, and the filtrate was brought to dryness *in vacuo*. The residue was dissolved in CH_2Cl_2 (2 cm^3) and the solution was stored at −78 °C for 3 d. A pale-yellow microcrystalline solid precipitated, which was separated from the mother liquor, washed twice with pentane (5 cm^3) and dried. Yield 135 mg (68%); mp 145 °C (decomp.); Λ = 45.6 $cm^2\ \Omega^{-1}\ mol^{-1}$ (Found: C, 41.48; H, 4.26. $C_{60}H_{78}As_2BClF_{24}P_2Pd_2$ requires: C, 41.75; H, 4.55%). NMR (CD_2Cl_2): δ_H (400 MHz) 7.75 [8 H, s, br, *ortho*-H of B(Ar_F)$_4$], 7.59 [4 H, s, br, *para*-H of B(Ar_F)$_4$], 2.70–2.58 (4 H, m, AsC*H*CH$_3$ or PC*H*CH$_3$), 2.55–2.40, 2.07–1.87 (4 H each, both m, PCH_2As and AsC*H*CH$_3$ or PC*H*CH$_3$), 1.51–1.12 (48 H, m, AsCHC*H*$_3$ and PCHC*H*$_3$), 0.73 [6 H, d, *J*(P,H) = 4.7, in $^1H\{^{31}P\}$ s, $PdCH_3$]; δ_C (100.6 MHz) 162.1 [q, *J*(B,C) = 49.6, *ipso*-C of B(Ar_F)$_4$], 135.1 [s, br, *ortho*-C of B(Ar_F)$_4$], 129.4 [qq, *J*(F,C) = 31.5, *J*(B,C) = 2.9, *meta*-C of B(Ar_F)$_4$], 124.9 [q, *J*(F,C) = 272.8, CF_3], 117.8 [m, br, *para*-C of B(Ar_F)$_4$], 29.2 [d, *J*(P,C) = 21.0, P*C*HCH$_3$], 28.9 (m, X-part of ABX spin system, As*C*HCH$_3$), 24.8 (m, br, X part of ABX spin system, As*C*HCH$_3$), 23.0, 21.1 (both s, AsCH*C*H$_3$ or PCH*C*H$_3$), 20.6 [d, *J*(P,C) = 21.9, P*C*HCH$_3$], 19.9, 19.6 [both d, *J*(P,C) = 3.8, AsCH*C*H$_3$ or PCH*C*H$_3$], 19.7 (s, AsCH*C*H$_3$ or

Table 1 Crystallographic data for **4**, **13** and **27**

	4	**13**	**27**
Formula	$C_{15}H_{34}AsCl_2PPd$	$C_{18}H_{39}AsF_6P_2Pd$	$C_{64}H_{86}As_2BClF_{24}P_2Pd_2$
M	497.61	612.75	1782.24
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1$ (no. 4)	$P\bar{1}$ (no. 2)
a/Å	18.408(3)	9.0217(18)	14.487(9)
b/Å	8.1421(9)	17.072(3)	17.323(11)
c/Å	14.335(2)	9.0882(18)	17.554(12)
α/°	90	90	112.46(8)
β/°	109.071(18)	113.81(3)	96.69(8)
γ/°	90	90	101.79(8)
V/Å^3	2030.6(5)	1280.6(4)	3892(4)
T/K	173(2)	173(2)	173(2)
Z	2	2	2
D_c/g cm^{-3}	0.814	1.589	1.593
λ(Mo-Kα)/Å	0.71073	0.71073	0.71073
μ/mm^{-1}	1.432	2.177	1.545
No. of reflections measured	19820	17768	38138
No. of unique reflections	3442 [R(int) = 0.0520]	6094 [R(int) = 0.0414]	12934 [R(int) = 0.0654]
$R1$ [a]	0.0378	0.0251	0.0404
$wR2$ [b]	0.1001	0.0620	0.0928
Residual electron density/e Å^{-3}	0.904/−0.915	1.014/−0.567	0.063/−0.064

[a] $R = \Sigma|F_o - F_c|/\Sigma F_o$ [for $F_o > 2\sigma(F_o)$] for the number of observed reflections [$I > 2\sigma(I)$], respectively. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.0691P)^2 + 0.0000P]$ **4**, $[\sigma^2(F_o^2) + (0.0373P)^2 + 0.1233P]$ **13**, $[\sigma^2(F_o^2) + (0.0409P)^2 + 0.0000P]$ **27**, where $P = (F_o^2 + 2F_c^2)/3$; for all data reflections, respectively.

PCHCH_3), 19.0 [d, J(P,C) = 1.9, AsCHCH_3 or PCHCH_3], 18.6 [d, J(P,C) = 3.8, AsCHCH_3 or PCHCH_3], 16.4 [d, J(P,C) = 5.7, AsCHCH_3 or PCHCH_3], 10.4 (m, X part of ABX spin system, PCH_2As), −8.4 [d, J(P,C) = 3.8, PdCH_3]; $\delta_{C\{H,P\}}$ (100.6 MHz) 162.1 [q, J(B,C) = 49.6, *ipso*-C of $B(Ar_F)_4$], 135.1 [s, br, *ortho*-C of $B(Ar_F)_4$], 129.4 [q, br, J(F,C) = 31.5, *meta*-C of $B(Ar_F)_4$], 124.9 [q, J(F,C) = 272.8, CF_3], 117.8 [m, br, *para*-C of $B(Ar_F)_4$], 29.5 (s, AsCHCH_3 of minor isomer), 29.2 (s, PCHCH_3 of major isomer), 29.1 (s, PCHCH_3 of minor isomer), 28.8, 24.8 (both s, AsCHCH_3 of major isomer), 24.7 (s, AsCHCH_3 of minor isomer), 23.1 (s, AsCHCH_3 or PCHCH_3 of major isomer), 21.9, 21.3 (both s, PCHCH_3 of minor isomer), 21.1 (s, AsCHCH_3 or PCHCH_3 of major isomer), 20.8, 20.1 (both s, AsCHCH_3 or PCHCH_3 of minor isomer), 20.6 (s, PCHCH_3 of major isomer), 19.9, 19.65, 19.6 (all s, AsCHCH_3 or PCHCH_3 of major isomer), 19.5, 19.45, 19.4, 19.25 (all s, AsCHCH_3 or PCHCH_3 of minor isomer), 18.9, 18.6 (both s, AsCHCH_3 or PCHCH_3 of major isomer), 17.3 (s, AsCHCH_3 or PCHCH_3 of minor isomer), 16.3 (s, AsCHCH_3 or PCHCH_3 of major isomer), 10.7 [s, in $^{13}C\{^1H\}$ m, X part of ABX spin system, PCH_2As of minor isomer], 10.4 (s, PCH_2As of major isomer), −5.5 [s, in $^{13}C\{^1H\}$ m, PdCH_3 *cis* to P*i*Pr$_2$ of minor isomer], −8.4 (s, PdCH_3 of major isomer), −11.7 [s, in $^{13}C\{^1H\}$ also s, PdCH_3 *cis* to As*i*Pr$_2$ of minor isomer]; δ_F (376.4 MHz) −62.7 (s, CF_3); δ_P (162.0 MHz) 38.5 (s, major isomer), 30.6 (s, minor isomer).

Crystallography

Single crystals of **4** were grown from methanol (50 to −15 °C), those of **13** by diffusion of pentane into a solution of CH_2Cl_2 (20 °C), and those of **27** from CH_2Cl_2 (25 to −20 °C). Crystal data collection parameters are summarized in Table 1. Intensity data were corrected for Lorentz and polarization effects. Data reduction was performed with Stoe IPDS software. The structures were solved by direct methods (SHELXS-97).[24] Atomic coordinates and anisotropic thermal displacement parameters of the non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2 (SHELXL-97).[25] The hydrogen atoms were assigned ideal positions and refined isotropically using a riding model. One of the *tert*-butyl groups in compound **13** is rotationally disordered and was refined anisotropically with an occupancy ratio of 50 : 50. Also, the PF_6 anion is disordered and was refined to a split occupancy ratio of 60 : 40. Four of the CF_3-groups of the $B(Ar_F)_4$ counterion in compound **27** were found disordered and refined anisotropically with restraints on U_{ij}. One molecule of CH_2Cl_2 per unit formula of **27** was located in the lattice.

CCDC reference number 182355 (**13**). The crystal structures of **4** (143399) and **27** (143400) were reported previously.[5]

See http://www.rsc.org/suppdata/dt/b2/b202879b/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (SFB 347) and the Fonds der Chemischen Industrie for financial support, the latter in particular for a Ph.D. grant (to K. I.). Moreover, we are very grateful to Mrs M.-L. Schäfer and Dr R. Bertermann (NMR measurements), Dr G. Lange and Mr F. Dadrich (mass spectra), and to Mrs R. Schedl and Mr C. P. Kneis (elemental analyses and DTA measurements).

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