Tri(allyl)- and tri(methylallyl)arsine complexes of palladium(II) and platinum(II): synthesis, spectroscopy, photochemistry and structures

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Tri(allyl)- and tri(methylallyl)arsine complexes of palladium(II) and platinum(II) with the formulae $[MX_2L_2]$ (M = Pd, Pt and X = Cl, Br, I): $[Pd_2Cl_2(\mu\text{-}Cl)_2L_2]$, $[PdCl(S_2CNEt_2)L]$ and $[Pd_2Cl_2(\mu\text{-dmpz})_2L_2]$ [L = $As(CH_2CH{=}CH_2)_3$ (L′), $As(CH_2CMe{=}CH_2)_3$ (L″), dmpz = 3,5-dimethylpyrazolate] have been prepared. All the complexes have been characterized by elemental analyses and by IR and NMR (^{1}H, ^{13}C, ^{195}Pt) spectroscopy. The stereochemistry of the complexes has been deduced from the spectroscopic data. The molecular structures of complexes $[MX_2\{As(CH_2CH{=}CH_2)_3\}_2]$ (M = Pd, X = Cl or Br), $[MX_2\{As(CH_2CMe{=}CH_2)_3\}_2]$ (M = Pd, X = Cl or Br; M = Pt, X = Cl) and $[Pd_2Cl_2(\mu\text{-}Cl)_2\{As(CH_2CMe{=}CH_2)_3\}_2]$ have been established by single crystal X-ray diffraction analyses. The mononuclear complexes exclusively adopt the *trans* configuration with the exception of $[PdCl_2L''_2]$, which could be isolated as *cis* and *trans* isomers. In the binuclear derivative the arsine ligands are attached to an envelope-shaped Pd–(μ-Cl)$_2$–Pd rectangle with a *trans* (*anti*) orientation towards each other. The mononuclear complexes are slightly photoreactive upon irradiation in their long-wavelength absorption band.

Introduction

Organoarsenic and -antimony compounds have attracted considerable attention in recent years due to their relevance as molecular precursors in the deposition of III–V semiconductor materials for microelectronic technologies.[1–4] In view to replace the EH_3 source (E = As or Sb; AsH_3 being an extremely toxic gas difficult to purify and SbH_3 unstable at room temperature) and to develop low-decomposition-temperature precursors, several trialkyl derivatives have been evaluated. For instance, triisopropylstibine has been successfully used for the preparation of antimonide materials.[5] The growth temperature for SbR_3 compounds has been reported to decrease with decreasing bond strength of the Sb–R bond, which lies in the following order: Sb–methyl (439.9 kJ mol^{-1}) > Sb–isopropyl (398.1 kJ mol^{-1}) > Sb–allyl (361.2 kJ mol^{-1}).[6] Thus, triallyl derivatives may prove to be precursors of choice.

Although metal complexes containing unsaturated phosphines, such as $Ph_2P(CH{=}CH_2)$, $PhP(CH{=}CH_2)_2$ and $Ph_2P(CH_2CH{=}CH_2)$[7–12] have been investigated, only a few allylarsine complexes have been reported for comparative study.[8,12] The structures of some allylic phosphines and arsines have been studied by *ab initio* quantum chemical methods and photoelectron spectroscopy.[13] The C–E bond (E = P or As) has been shown to be out-of-plane of the allyl system and is stabilized by negative hyperconjugation between the π orbital and the σ* orbital of the C–E bond (β effect). Consequently, the electron pair of E interacts strongly with the π system. This geometrical arrangement of allylphosphines and -arsines may give complexes having structures and chemical reactivities different from their alkyl or aryl counter parts. In light of the above and in pursuance of our work on the design and development of organometallic precursors of group V elements, we have examined the chemistry of $E(CH_2CR{=}CH_2)_3$ (E = As or Sb; R = H or Me) complexes of palladium and platinum. In this paper we will report the preparation and thorough characterization of some tri(allyl)arsine and tri(methylallyl)arsine complexes of Pt or Pd by multiple spectroscopies and single crystal X-ray diffraction. Furthermore, we report the first trials to prepare the corresponding antimony derivatives.

Experimental

Materials and methods

The compounds Na_2PdCl_4, $[PdCl_2(MeCN)_2]$,[14] $As(CH_2CH{=}CH_2)_3$ (L′; b.p. 52–53 °C/2.5 mm),[15,16] $As(CH_2CMe{=}CH_2)_3$ (L″; b.p. 53–55 °C/2.5 mm),[16] $Sb(CH_2CH{=}CH_2)_3$ (b.p. 70–73 °C/2.5 mm)[6,17,18] and $Sb(CH_2CMe{=}CH_2)_3$ (b.p. 73–74 °C/2.5 mm)[17] were prepared according to literature methods. Allylarsines and -stibines were purified by distillation under vacuum. All reactions were carried out under a nitrogen atmosphere in dry and distilled analytical grade solvents. Microanalyses were carried out in the Analytical Chemistry Division, B.A.R.C. The ^{1}H, ^{13}C{^{1}H} and ^{195}Pt{^{1}H} NMR spectra were recorded on a Bruker DPX-300 spectrometer operating at 300 (^{1}H), 75.47 (^{13}C) or 64.52 (^{195}Pt) MHz. Chemical shifts are relative to the internal chloroform peak (δ = 7.26 ppm for ^{1}H and δ = 77.0 ppm for ^{13}C) and external Na_2PtCl_6 in D_2O for ^{195}Pt. IR spectra were recorded as Nujol mulls using CsI plates on a Bomen-102 FT IR spectrometer in the range 200–4000 cm^{-1}. NMR and IR data for all the compounds are given in Tables 1 and 2. UV/Vis absorption spectra were recorded on a Bruins Instruments Omega 10 or a JASCO V-530 spectrophotometer. Emission and excitation spectra were recorded on a Perkin Elmer LS5B spectrophotometer.

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Table 1 ^1H, $^{13}C\{^1H\}$ NMR (in $CDCl_3$) and IR spectral data of triallylarsine complexes of palladium and platinum

Complex	^1H NMR δ	$^{13}C\{^1H\}$ NMR δ	IR data/cm^{-1}
$As(CH_2CH{=}CH_2)_3 = L'$	2.27 (d, 7.9 Hz, $AsCH_2$); 4.95 (t, 1 Hz, CH_2, *cis*-H); 4.99 (d, 7 Hz, CH_2, *trans*-H); 5.78–5.90 (m, CH=)	28.2 (s, $AsCH_2$); 115.2 (s, CH_2=); 134.6 (s, CH=)	
$[PdCl_2L'_2]$	2.79 (d, 7.9 Hz, $AsCH_2$); 5.18 (d, 1 Hz, CH_2, *cis*-H); 5.23 (d, 1 Hz, 7 Hz, CH_2, *trans*-H); 5.89–6.00 (m, CH=)	25.7 (s, $AsCH_2$); 118.9 (s, CH_2=); 131.3 (s, CH=)	1633 νC=C, 354 νPd–Cl
$[PdBr_2L'_2]$	2.90 (d, 7.9 Hz, $AsCH_2$); 5.21 (d, 1 Hz, CH_2, *cis*-H); 5.24 (d, 1 Hz, 7 Hz, CH_2, *trans*-H); 5.90–6.00 (m, CH=)	27.0 (s, $AsCH_2$); 118.9 (s, CH_2=); 131.5 (s, CH=)	1633 νC=C
$[PdI_2L'_2]$	3.11 (d, 7.9 Hz, $AsCH_2$); 5.21 (d, 1 Hz, CH_2, *cis*-H); 5.24 (d, 1 Hz, 7 Hz, CH_2, *trans*-H); 5.88–5.97 (m, CH=)	30.5 (s, $AsCH_2$); 118.9 (s, CH_2=); 131.9 (s, CH=)	1631 νC=C
$[Pd_2Cl_2(\mu\text{-}Cl)_2L'_2]$	2.85 (d, 7.7 Hz, $AsCH_2$); 5.28 (d, 8.0 Hz, CH_2, *trans*-H); 5.36 (s, CH_2, *cis*-H); 5.87–6.04 (m, CH=)	27.8 (s, $AsCH_2$); 120.8 (s, CH_2=); 129.4 (s, CH=)	1633 νC=C, 351 νPd–Cl
$[Pd_2Cl_2(\mu\text{-dmpz})_2L'_2]$	2.20, 2.35 (each s, Me, dmpz); 2.72 (doublet of AB pattern, $AsCH_2$); 5.16 (d, d, 1 Hz, 7 Hz, CH_2, *trans*-H); 5.20 (d, 0.7 Hz, CH_2, *cis*-H); 5.84–5.93 (m, CH=)	13.5, 14.7 (s, Me dmpz); 27.1 (s, $AsCH_2$); 104.7 (s, CH-dmpz); 119.3 (s, CH_2=); 131.1 (s, CH=); 147.4, 149.6 (s, C–Me dmpz)	1632 νC=C, 364 νPd–Cl
$[PdCl(S_2CNEt_2)L']$	1.25 (t, 7 Hz, NCH_2Me); 2.72 (d, 8 Hz, $AsCH_2$); 3.67 (dq, 7 Hz, NCH_2); 5.16–5.22 (m, CH_2=); 5.89–6.00 (m. CH=)		

The photoreactions were performed in 1 cm quarz cuvettes by irradiation of solutions in de-aereated MeCN (dilute solutions for UV/Vis absorption) or MeCN-d^3 (conc. solutions for ^1H NMR spectroscopy) using a Spindler&Hoyer HBO 50 W/AC medium pressure Hg lamp and Schott cut-off filters.

Preparations and reactions

$[PdCl_2\{As(CH_2CH{=}CH_2)_3\}_2]$. To a stirred benzene solution (50 cm^3) of $[PdCl_2(MeCN)_2]$ (510 mg, 1.97 mmol), $As(CH_2CH{=}CH_2)_3$ (800 mg, 4.04 mmol) was added under a nitrogen atmosphere. The reactants were stirred for 3 h. The solvent was evaporated *in vacuo* and the residue was recrystallized from hexane as yellowish-orange crystals (930 mg, 82%). Anal. found: C, 37.3; H, 5.5%; calcd for $C_{18}H_{30}As_2Cl_2Pd$ (573.59): C, 37.7; H 5.3%.

Similarly, $[MCl_2\{As(CH_2CMe{=}CH_2)_3\}_2]$ (M = Pd or Pt) were prepared. For the platinum complex K_2PtCl_4 was employed. Anal. found: C, 38.2; H, 5.8%; calcd for $C_{24}H_{42}As_2Cl_2Pt$ (746.42): C, 38.6; H, 5.7%. The palladium complex, $[PdCl_2\{As(CH_2CMe{=}CH_2)_3\}_2]$, was isolated in orange and yellow forms. Both analyze identically. Anal. found: C, 43.6; H, 6.4%; calcd for $C_{24}H_{42}As_2Cl_2Pd$ (657.77): C, 43.8; H, 6.4%.

$[PdBr_2\{As(CH_2CH{=}CH_2)_3\}_2]$. To a stirred acetone solution (30 cm^3) of $[PdCl_2\{As(CH_2CH{=}CH_2)_3\}_2]$ (97 mg, 0.17 mmol), excess KBr (450 mg, 3.77 mmol) was added. The reactants were stirred at room temperature for 48 h. The solvent was evaporated *in vacuo* and the residue was extracted with CH_2Cl_2 and filtered. The filtrate was concentrated under reduced pressure and the residue was recrystallized from acetone–hexane as orange crystals (73 mg, 65%). Anal. found: C, 32.7; H, 4.8%; calcd for $C_{18}H_{30}As_2Br_2Pd$ (662.49): C, 32.6; H, 4.6%.

Other bromo and iodo complexes were prepared similarly. $[PdI_2L_2]$: anal. found: C, 28.5; H, 4.0%; calcd for $C_{18}H_{30}As_2I_2Pd$ (756.49): C, 28.6; H, 4.0%. $[PdBr_2L''_2]$: Anal. found: C, 38.4; H, 5.7%; calcd for $C_{24}H_{42}As_2Br_2Pd$ (746.67): C, 38.6; H, 5.7%. $[PdI_2L''_2]$: Anal. found: C, 34.0; H, 5.1%; calcd for $C_{24}H_{42}As_2I_2Pd$ (840.67): C, 34.3; H, 5.0%. $[PtBr_2L''_2]$: Anal. found: C, 34.3; H, 5.4%; calcd for $C_{24}H_{42}As_2Br_2Pt$ (835.32): C, 34.5; H, 5.0%. $[PtI_2L''_2]$: Anal. found: C, 30.9; H, 4.8%; calcd for $C_{24}H_{42}As_2I_2Pt$ (929.32): C, 31.0; H, 4.6%.

$[Pd_2Cl_2(\mu\text{-}Cl)_2\{As(CH_2CH{=}CH_2)_3\}_2]$. To a stirred benzene solution (50 cm^3) of $[PdCl_2\{As(CH_2CH{=}CH_2)_3\}_2]$ (975 mg, 1.70 mmol), $[PdCl_2(MeCN)_2]$ (443 mg, 1.71 mmol) was added. The reactants were stirred under reflux for 3 h. The solvent was evaporated *in vacuo* and the residue was recrystallized from CH_2Cl_2–hexane as deep red cubic crystals (925 mg, 72%). Anal. found: C, 28.5; H, 4.3%; calcd for $C_{18}H_{30}As_2Cl_4Pd_2$ (750.91): C, 28.8; H, 4.0%.

Similarly, $[Pd_2Cl_2(\mu\text{-}Cl)_2\{As(CH_2CMe{=}CH_2)_3\}_2]$ was prepared. Anal. found: C, 34.2; H, 5.2%; calcd for $C_{24}H_{42}As_2Cl_4Pd_2$ (835.09): C, 34.5; H, 5.1%.

$[Pd_2Cl_2(\mu\text{-dmpz})_2\{As(CH_2CH{=}CH_2)_3\}_2]$ (dmpz = 3,5-dimethylpyrazolate). To a CH_2Cl_2 solution (30 cm^3) of $[Pd_2Cl_2(\mu\text{-}Cl)_2\{As(CH_2CH{=}CH_2)_3\}_2]$ (82 mg, 0.11 mmol), a methanolic solution of dmpzH (23.2 mg, 0.24 mmol) containing aqueous NaOH (0.5 cm^3, 0.49 N, 0.245 mmol) was added under a nitrogen atmosphere. The mixture was stirred for 5 h at room temperature and then filtered. The filtrate was dried *in vacuo* and the residue was recrystallized from CH_2Cl_2–hexane as a pale yellow crystalline compound (46 mg, 48%). Anal. found: C, 38.8; H, 5.3; N, 6.8%; calcd for $C_{28}H_{44}N_4As_2Cl_2Pd_2$ (870.25): C, 38.6; H, 5.1; N, 6.4%.

Table 2 ^{1}H, ^{13}C{^{1}H} NMR (in $CDCl_3$) and IR spectral data of tri(methylallyl)arsine complexes of palladium and platinum

Complex	^{1}H NMR δ	^{13}C{^{1}H} NMR δ	IR data/cm^{-1}
$As(CH_2CMe{=}CH_2)_3{=}L''$	1.78 (s, Me); 2.28 (s, $AsCH_2$); 4.68 (s, $CH_2{=}$)	23.6 (s, Me); 37.0 ($AsCH_2$); 110.5 ($CH_2{=}$); 143.3 (s, C=)	
trans-$[PdCl_2L''_2]$	1.95 (s, Me); 2.82 (s, $AsCH_2$); 4.95 (s, $CH_2{=}$)	24.7 (s, Me); 30.5 ($AsCH_2$); 115.4 ($CH_2{=}$); 139.8 (s, C=)	1643 νC=C, 344 νPd–Cl
cis-$[PdCl_2L''_2]$	1.92 (s, Me); 2.97 (s, $AsCH_2$); 4.95 (s, $CH_2{=}$); 5.02 (m, $CH_2{=}$)	23.8 (s, Me); 40.8 ($AsCH_2$); 117.1 ($CH_2{=}$); 135.3 (s, C=)	1640 νC=C; 354, 316 νPd–Cl
$[PdBr_2L''_2]$	1.93 (s, Me); 2.95 (s, $AsCH_2$); 4.95 (br, s, $CH_2{=}$)	24.9 (s, Me); 31.8 ($AsCH_2$); 115.6 ($CH_2{=}$); 140.0 (s, C=)	
$[PdI_2L''_2]$	1.90 (s, Me); 3.19 (s, $AsCH_2$); 4.95 (s, $CH_2{=}$)	25.2 (s, Me); 35.4 ($AsCH_2$); 115.9 ($CH_2{=}$); 140.4 (s, C=)	1798, 1640 νC=C
$[PtCl_2L''_2]^{a}$	1.96 (s, Me); 2.83 (s, $AsCH_2$; ^{3}J (Pt–H) = 13.5 Hz); 4.93, 4.94 (each s, $CH_2{=}$)	24.6 (s, Me); 29.0 ($AsCH_2$); 115.4 ($CH_2{=}$); 139.7 (s, C=)	1780, 1638 νC=C, 333 νPt–Cl
$[PtBr_2L''_2]$	1.94 (s, Me); 2.94 (s, $AsCH_2$; ^{3}J (Pt–H) = 14 Hz); 4.94, 4.97 (each s, $CH_2{=}$)	24.8 (s, Me); 29.8 ($AsCH_2$); 115.6 ($CH_2{=}$); 139.8 (s, C=)	1898, 1639 νC=C
$[PtI_2L''_2]$	1.92 (s, Me); 3.16 (s, $AsCH_2$; ^{3}J (Pt–H) = 15.5 Hz); 4.95, 4.98 (each s, $CH_2{=}$)	25.0 (s, Me); 33.0 ($AsCH_2$); 115.9 ($CH_2{=}$); 140.0 (s, C=)	
$[Pd_2Cl_2(\mu\text{-}Cl)_2L''_2]$	2.11 (s, Me); 2.88 (s, $AsCH_2$); 5.05, 5.09 (each s, CH=)	24.7 (s, Me); 32.6 ($AsCH_2$); 117.3 ($CH_2{=}$); 138.2 (s, C=)	1798, 1640 νC=C, 352 νPd–Cl
$[Pd_2Cl_2(\mu\text{-dmpz})_2L''_2]$	1.98 (s, Me); 2.21, 2.36 (each s, Me-dmpz); 2.73 (AB pattern, $AsCH_2$); 4.93, 4.94, 4.95, 4.95 (1:2:2:1 CH_2); 5.57 (s, CH-dmpz)		
$[PdCl(S_2CNEt_2)L'']$	1.25 (t, d, 7 Hz, NCH_2Me); 2.03 (s, Me); 2.75 (s, $AsCH_2$); 3.67 (qd, 7 Hz, NCH_2); 4.93 (br, $CH_2{=}$)	12.4 (s, NCH_2Me); 24.7 (s, Me); 31.7 ($AsCH_2$); 43.5, 44.0 (s, NCH_2); 115.3($CH_2{=}$); 139.7 (s, C=); 207.6 (s, S_2C)	1638 νC=C, 304 νPd–Cl

[a] ^{195}Pt{^{1}H} in $CDCl_3$ $\delta = -3732$ ppm

Similarly, $[Pd_2Cl_2(\mu\text{-dmpz})_2\{As(CH_2CMe{=}CH_2)_3\}_2]$ was prepared. Anal. found: C, 42.2; H, 6.1; N, 5.5%; calcd for $C_{34}H_{56}N_4As_2Cl_2Pd_2$ (954.43): C, 42.8; H, 5.9; N, 5.9%.

$[PdCl(S_2CNEt_2)\{As(CH_2CH{=}CH_2)_3\}]$. To a stirred acetone solution (30 cm^{3}) of $[Pd_2Cl_2(\mu\text{-}Cl)_2\{As(CH_2CH{=}CH_2)_3\}_2]$ (94 mg, 0.125 mmol), $NaS_2CNEt_2{\cdot}3H_2O$ (61 mg, 0.272 mmol) was added. The reactants were stirred for 3 h and the solvent was evaporated *in vacuo*. The residue was extracted with CH_2Cl_2 and recrystallized from acetone–hexane as orange cubic crystals (96 mg, 83%). Anal. found: C, 32.9; H, 5.0; N, 2.7%; calcd for $C_{14}H_{25}NS_2AsClPd$ (488.27): C, 34.4; H, 5.1; N, 2.9%.

$[PdCl(S_2CNEt_2)\{As(CH_2CMe{=}CH_2)_3\}]$ was prepared in a similar manner. Anal. found: C, 38.6; H, 5.7; N, 2.5%; calcd for $C_{17}H_{31}NS_2AsClPd$ (530.41): C, 38.5; H, 5.9; N, 2.6%.

Reaction between $[Pd_2Cl_2(\mu\text{-}Cl)_2\{As(CH_2CMe{=}CH_2)_3\}_2]$ and $Pb(SePh)_2$. To a stirred CH_2Cl_2 solution (25 cm^{3}) of $[Pd_2Cl_2(\mu\text{-}Cl)_2\{As(CH_2CMe{=}CH_2)_3\}_2]$ (98 mg, 0.12 mmol), $Pb(SePh)_2$ (67 mg, 0.13 mmol) was added and the mixture stirred for 3 h, then filtered and the solvent evaporated *in vacuo*. The reaction yields an insoluble compound (41 mg, 58%). $[PdCl(SePh)]_n$: Anal. found: C, 24.5; H, 2.2%; calcd for $C_6H_5SeClPd$ (297.92): C, 24.2; H, 1.7%.

Similar reactions of $[Pd_2Cl_2(\mu\text{-}Cl)_2\{As(CH_2CH{=}CH_2)_3\}_2]$ with $Pb(SPh)_2$ or $Pb(SePh)_2$ gave $[PdCl(EPh)]_n$ (E = S or Se). Anal. found for E = S: C, 29.5; H, 2.1%; calcd for C_6H_5SClPd (251.02): C, 28.7; H, 2.0%. Anal. found for E = Se: C, 25.5; H, 2.4%.

Reaction between $[PdCl_2(PhCN)_2]$ and $Sb(CH_2CMe{=}CH_2)_3$. To a stirred benzene solution (30 cm^{3}) of $PdCl_2(PhCN)_2$(103 mg, 0.267 mmol), $Sb(CH_2CMe{=}CH_2)_3$(160 mg, 0.56 mmol) was added under a nitrogen atmosphere. The mixture was stirred for 3 h and filtered. Along with an insoluble residue, a CH_2Cl_2-soluble compound was obtained (m.p. 153 °C decomp.). Anal. found: C, 24.9; H, 4.0%; calcd for $[Pd_2(\mu\text{-}Cl)_2(\eta^{3}\text{-}C_3H_4Me)_2]$ ($C_8H_{14}Cl_2Pd_2$): C, 24.4; H, 3.6%. ^{1}H NMR ($CDCl_3$): δ 2.14 (s, Me); 2.88 (s, CH_2); 3.85 (s, CH_2).

A similar reaction of $[PdCl_2(PhCN)_2]$ with $Sb(CH_2CH{=}CH_2)_3$ gave $[Pd_2(\mu\text{-}Cl)_2(\eta^{3}\text{-}C_3H_5)_2]$. Anal. found: C, 18.9; H, 2.8%; calcd for $[Pd_2(\mu\text{-}Cl)_2(\eta^{3}\text{-}C_3H_5)_2]$ ($C_6H_{10}Cl_2Pd_2$): C, 19.7; H, 2.7%. IR (Nujol mull) 252 νPd–Cl, 401 νPd–allyl/cm^{-1}.[19] ^{1}H NMR ($CDCl_3$): δ 3.03 (d, 12.2 Hz, CH_2); 4.10 (d, 6.7 Hz, CH_2); 5.41–5.50 (m, CH).

Crystallography

For the complexes $[PdCl_2L_2]$, $[PdCl_2L'_2]$, $[PdBr_2L''_2]$, $[PtCl_2L''_2]$, and $[Pd_2Cl_2(\mu\text{-}Cl)_2L''_2]$ data collection was performed at $T = 173(2)$ K on a Siemens P4 diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) employing the ω–2θ scan technique. The data for $[PdBr_2L'_2]$ were collected at $T = 293(2)$ K on a KappaCCD device (Mo-Kα: $\lambda = 0.71073$ Å; horizontally mounted graphite crystal; 95 mm CCD camera on a κ-goniostat) using Collect (Nonius BV, 1997-2000) software. All structures were solved using the SHELXTL package[20] and refinement was carried out with SHELXL97[21] employing full-matrix least-squares methods on F^2 with $F_0^{\,2} \geq 2\sigma(F_0^{\,2})$ with the results shown in Table 3. All non-hydrogen atoms were treated anisotropically except for the disordered allyl C atoms in $[PdBr_2L'_2]$. Hydrogen atoms were included by using appropriate riding models.†

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† CCDC reference numbers 214025–214030. See http://www.rsc.org/suppdata/nj/b3/b303990k/ for crystallographic data in .cif or other electronic format.

Table 3 Crystal data and structure refinement for six of the complexes

Compound	[$PdCl_2L'_2$]	[$PdBr_2L'_2$]	[$PdCl_2L''_2$]	[$PdBr_2L''_2$]	[$PtCl_2L''_2$]	[$Pd_2Cl_2(\mu\text{-}Cl)_2L''_2$]
Chemical formula	$C_{18}H_{30}As_2Cl_2Pd$	$C_{18}H_{30}As_2Br_2Pd$	$C_{24}H_{42}As_2Cl_2Pd$	$C_{24}H_{42}As_2Br_2Pd$	$C_{24}H_{42}As_2Cl_2Pt$	$C_{24}H_{42}As_2Cl_4Pd_2$
M_W/g mol^{-1}	573.59	662.49	657.72	746.64	746.41	835.09
T/K	173(2)	293(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$Pbca$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.0698(19)	8.21980(10)	7.9820(9)	8.8295(17)	8.6461(16)	7.7802(15)
b/Å	8.102(2)	18.41340(10)	9.366(2)	9.4059(14)	9.4107(17)	10.0937(16)
c/Å	18.278(3)	49.8803(5)	10.1692(9)	9.5258(19)	9.532(3)	20.620(3)
α/°	90	90	68.166(12)	108.471(13)	108.190(17)	94.326(12)
β/°	98.426(14)	90	82.138(9)	103.331(14)	102.878(18)	98.760(13)
γ/°	90	90	77.166(11)	96.937(12)	97.604(14)	100.107(14)
U/Å^3	1182.1(5)	7549.6(1)	686.81(18)	713.9(2)	701.0(3)	1566.9(5)
Z	2	12	1	1	1	2
Abs.coeff./mm^{-1}	3.787	6.521	3.270	5.758	7.546	3.596
Total reflect.	2749	33 313	3471	3581	3522	7514
Indep. reflect.	2568	5797	3237	3366	3307	7514
R_{int}	0.0381	0.0633	0.0221	0.0332	0.0317	0.0381
Obs. reflect.	1744	4184	2675	2744	3013	5602
Abs. correction	Psi scans	Numerical	XABS2[34]	XABS2[34]	Psi scans	Psi scans
Final R_1 [$I > 2\sigma(I)$]	0.0465	0.0539	0.0365	0.0360	0.0293	0.0490
Final wR [$I > 2\sigma(I)$]	0.0980	0.1183	0.0937	0.0835	0.0700	0.1162
R_1 (all data)	0.0902	0.0841	0.0485	0.0520	0.0349	0.0747
wR_2 (all data)	0.1142	0.1270	0.0992	0.0895	0.0728	0.1270

Results and discussion

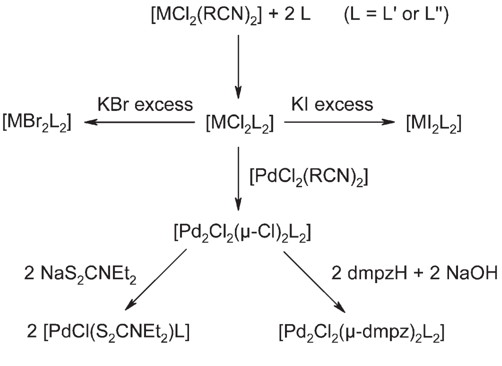
Synthesis and spectroscopic analyses

The syntheses of palladium(II) and platinum(II) complexes with triallylarsine and trimethylallylarsine are depicted in Scheme 1; their spectroscopic data for characterization are given in Tables 1 and 2. The reactions of [$MCl_2(RCN)_2$] with 2 equivalents of AsR_3 (R = $CH_2CH{=}CH_2$, $CH_2CMe{=}CH_2$) readily gave [MCl_2L_2]. For [$PdCl_2L''_2$] yellow microcrystals were obtained from careful recrystallization in the cold. Upon heating the recrystallization procedure gave orange crystals. For all the other compounds we had no evidence for more than one form. The chloride in the latter was substituted with Br or I by treating it with an excess of KBr or KI in acetone.

The allyl- and methylallylarsine proton resonances in the ^1H NMR spectra (Tables 1 and 2) are shifted downfield in the palladium and platinum complexes with respect to the corresponding signals in the free ligands. This is in accordance with the coordination of arsenic to the metal centers. Deshielding is more pronounced for the $AsCH_2$ protons (Δ = 0.5–0.9 ppm) than those of the allyl group [(CH/CMe: $\Delta \sim 0.1$ ppm; CH_2: $\Delta \sim 0.25$ ppm). Furthermore, we found that the degree of deshielding of the $AsCH_2$ proton resonance in MX_2L_2 complexes depends on the halogen ligands. It increases with increasing size of the halogen atom, which can be explained by an increasing degree of $M \rightarrow L$ charge transfer (see later, absorption spectra). For [$PtX_2L''_2$] and [$Pd_2Cl_2(\mu\text{-}Cl)_2L''_2$] two closely spaced signals for the CH_2 protons were observed as expected; however, spectra of [$PdX_2L''_2$] display only one singlet with one exception. The orange form of [$PdCl_2L''_2$] exhibits the same singlet as the other derivatives; however, the yellow form shows two signals: a singlet at 4.95 ppm and a multiplet at 5.02 ppm. Additionally, the shift of the $AsCH_2$ signal is not the same in the two forms (see Table 2) and we therefore conclude that the orange and yellow forms are the *trans* and *cis* isomers. The ^{13}C NMR spectra of free arsine and their complexes show single resonances each for chemically equivalent carbon atoms. The $AsCH_2$ carbon resonances for [MX_2L_2], except for [$MI_2\{As(CH_2CH{=}CH_2)_3\}_2$], appear at higher field than those of the corresponding free allylarsines. The $AsCH_2$ signal moves to higher frequency with increasing mass of the halogen atom in the series [MX_2L_2] (M = Pd or Pt). Upon coordination of the allylarsines, the ^{13}C NMR chemical shifts of the allyl carbons are also affected by shielding for CH/C(Me) and deshielding for CH_2 carbons relative to the corresponding signals for the free arsines. The $^{195}Pt\{^1H\}$ NMR spectrum of [$PtCl_2\{As(CH_2CMe{=}CH_2)_3\}_2$] displays a singlet at −3732 ppm, indicating the formation of only one isomeric form.

The IR spectra of these complexes exhibit an absorption at around 1630 cm^{-1} attributable to $\nu C{=}C$. This indicates that the allylic double bonds are not coordinated to the metal atoms.[10,11] The spectra of [MX_2L_2] display a band at around 345 cm^{-1} due to M–Cl stretches.[14] The presence of only one band for M–Cl suggests that these complexes have a *trans* configuration. However, the yellow form of [$PdCl_2\{As(CH_2CMe{=}CH_2)_3\}_2$] shows two such bands at 316 and 354 cm^{-1}, indicative of a *cis* geometry. The IR spectrum of [$Pd_2Cl_2(\mu\text{-}Cl)_2(L_2)$] displays four νPd–Cl attributable to terminal and bridging Pd–Cl stretches as is usually observed for [$M_2Cl_2(\mu\text{-}Cl)_2L_2$] complexes.[22,23]

The allylarsine complexes described here are stable in solution for several days in the dark. They did not undergo olefin isomerization as has been reported for the corresponding rhodium complexes derived from $Ph_2PCH_2CH{=}CH_2$, which



Scheme 1 Preparation of the compounds [M = Pd, Pt; R = Me, Ph; L′ = $As(CH_2CH{=}CH_2)_3$, L″ = $As(CH_2CMe{=}CH_2)_3$].

undergo isomerization to the *Z*-propenyl isomers, $Ph_2PCH{=}CHMe$.[11] Nor did they show any sign of a cyclometallation reaction as reported for $R_2P(allyl)$ ($R = Bu^t$, c-Hx) with $[IrCl(COT)]_2$ (COT = cyclooctene) in the presence of γ-picoline, yielding $[IrHCl(R_2PCH_2CH{=}CH)(R_2PCH_2CH{=}CH_2)(\gamma\text{-picoline})]$.[9] When a methanolic solution of $[PdCl_2L''_2]$ was refluxed for 3 h, unchanged parent complex was recovered. Assuming that agostic M–H interactions are a pre-requisite for such metallation reactions we can conclude that in the present complexes such interactions do not occur. This will be further substantiated in the crystal structure section.

Treatment of $[Pd_2Cl_2(\mu\text{-}Cl)_2(L_2)]$ with 2 equiv. of dmpzH in the presence of NaOH yields the bis-pyrazolato bridged complexes $[Pd_2Cl_2(\mu\text{-dmpz})_2(L_2)]$. The presence of only one singlet for the CH-4 proton of the dmpz group in the ^1H NMR spectra indicates a *trans* configuration for these complexes. The $AsCH_2$ resonances appear as an AB pattern, which in the case of $As(CH_2CH{=}CH_2)_3$ further shows coupling with the =CH proton. Reaction of $[Pd_2Cl_2(\mu\text{-}Cl)_2(L_2)]$ with $NaS_2CNEt_2 \cdot 3H_2O$ gave $[PdCl(S_2CNEt_2)(L)]$. The NMR spectra show characteristic resonances for the arsine and dithio ligands.

Reaction of $[Pd_2Cl_2(\mu\text{-}Cl)_2(L_2)]$ with $Pb(SPh)_2$and $Pb(SePh)_2$ yields a disproportionation product $[PdCl(EPh)]_n$ characterized by elemental analysis.[24] $[PdCl(EPh)]_n$ appears to be formed by disproportionation of $[Pd_2Cl_2(\mu\text{-}EPh)_2(L_2)]$. The instability of the latter indicates a poorer ligation of the allylarsines as compared to alkyl-/arylarsines (AsR_3 : R = Ph, ^{i}Pr, ^{n}Pr).[22]

The reaction of $[PdCl_2(PhCN)_2]$ or $[PdCl_2(MeCN)_2]$ with triallyl- or trimethylallylstibine afforded $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-allyl})_2]$ (allyl = C_3H_5 or C_4H_7) together with white insoluble and uncharacterized products [eqn. (1)].

$$[PdCl_2(PhCN)_2] + 2Sb(CH_2CR{=}CH_2)_3 \rightarrow \tfrac{1}{2}\,[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_4R)_2]\ (R = H \text{ or } Me) + \text{other products} \quad (1)$$

It is noteworthy that reactions with trialkylstibines yield $[PdX_2(SbR_3)_2]$ (R = Me, Et, ^{i}Pr, ^{n}Pr).[4,25] Although transmetallation reactions to prepare allylpalladium complexes have been reported,[26] transfer of an allyl group from stibine to a metal center is unprecedented. The cleavage of the allyl–Sb bond of $RR'SbCH_2CH{=}CH_2$ with $FeCpCl(CO)_2$ has been reported to result in the formation of unstable $[\{FeCp(CO)_2\}_2SbPh_2]Cl$, allyl chloride and *trans* 1-chloro-1-propene.[8] However, similar reactions with $Ph_2E(CH_2CH{=}CH_2)$ (E = P or As) yield $[CpFe(CO)_2(Ph_2E(CH_2CH{=}CH_2)]^+$.[8] The facile cleavage of the Sb–allyl bond can be exploited in organic synthesis involving allyl groups.

Absorption spectroscopy and photochemistry

The compounds exhibit colours that range from pale yellow to deep red in the solid state as well as in solution.

An investigation of the absorption spectra (Table 4) revealed that the long-wavelength absorption maxima are lower in energy for the palladium derivatives when compared to the platinum analogues. Furthermore, the energy decreases along the series Cl > Br > I. Fig. 1 reveals that the different colour of the two forms of $[PdCl_2L''_2]$ is not caused by different long-wavelength absorption maxima but by a dramatically enhanced intensity of the long-wavelength band at around 360 nm for the *trans* derivative. We assume that in both derivatives the same type of transitions occur with different probabilities. The same has been observed for related benzyldimethylarsine complexes $[MX_2(BzAsMe_2)_2]$ (M = Pt or Pd, X = Cl, Br or I).[28] Without detailed quantum chemical calculations we cannot provide any reasonable explanation for this behaviour. Such calculations are ongoing at the moment. The long-wavelength absorptions of the binuclear complex $[Pd_2Cl_2(\mu\text{-}Cl)_2L''_2]$ are also shown in Fig. 1. The maxima and relative intensities follow the pattern of the mononuclear *cis* derivative; however, the bands are generally much stronger. Probably it is the steric strain of the central Pd–(μ-Cl)$_2$–Pd unit that leads to the altered transition probabilities.

Table 4 Long-wavelength absorption maxima for some of the tri(allyl)- and tri(methylallyl)arsine complexes of Pd(II) and Pt(II) measured in CH_2Cl_2 solution.

Complex	λ_{max}/nm (ε/M^{-1} cm^{-1})
$[PdCl_2L'_2]$	353 (24 935)
$[PdBr_2L'_2]$	376 (16 385), 258 (15 791)
$[PdI_2L'_2]$	432 (7253), 357 (5293), 312 (13 977), 256 (23 667)
$[Pd_2Cl_2(\mu\text{-}Cl)_2L'_2]$	396 (4125), 304 (19 593)
trans-$[PdCl_2L''_2]$	357 (19 070), 320sh (2950), 282 (2030)
cis-$[PdCl_2L''_2]$	362 (1230), 314 (920), 298sh (1860), 280 (3050)[27]
$[PdBr_2L''_2]$	382 (12 117), 256 (10 445)
$[PdI_2L''_2]$	436 (8930), 319 (17 130), 279 (17 753), 253 (19 312)
$[PtCl_2L''_2]$	287 (21 609), 248 (12 249)
$[PtBr_2L''_2]$	309 (13 113), 248sh (10 040)
$[PtI_2L''_2]$	354 (6619), 314sh (3327)
$[Pd_2Cl_2(\mu\text{-}Cl)_2L''_2]$	403 (4780), 310 (20 360), 239 (30 250)

Furthermore, we found that the *cis* derivative is the only compound among those listed in Table 4 that shows emission at room temperature in fluid solution. Irradiation into the long-wavelength band at 330–380 nm led to a very weak broad emission with a maximum at 411 nm (Stokes shift: 3290 cm^{-1}). The excitation spectrum shows several maxima (main at 330 nm), which do not fully coincide with the absorption bands. This calls for further investigation of the emission properties (quantum yield, lifetimes) but also for a detailed look at the character of the excited states by quantum chemical calculations. So far we can tentatively assign the long-wavelength absorptions to mixed metal(d_M)-to-ligand(s/p^*_{As})/ligand(p_X)-to-ligand(s/p^*_{As}) (MLCT/L′LCT) charge transfer transitions. This is in line with the assignment for a series of related benzyldimethylarsine complexes $[MX_2(BzAsMe_2)_2]$ (M = Pt or Pd, X = Cl, Br or I)[28] and is further supported by recent investigations on related complexes of the type $[MCl(TeCH_2CH_2NMe_2)(PR_3)]$ (M = Pt or Pd; R = alkyl or aryl) where the long-wavelength absorptions were assigned to ligand(Te)-to-ligand(P) charge transfer (L′LCT) transitions.[29] This detailed study has shown that the acceptor orbitals are composed by metal d orbitals and the anti-bonding component

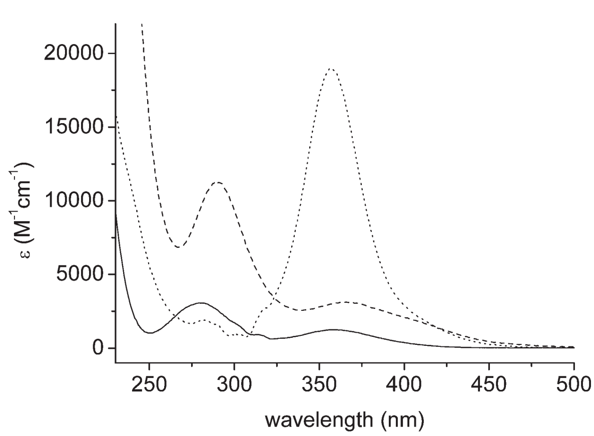


Fig. 1 Absorption spectra of *cis*-$[PdCl_2L''_2]$ (solid line),[27] *trans*-$[PdCl_2L''_2]$ (dotted line) and $[Pd_2Cl_2(\mu\text{-}Cl)_2L''_2]$ (dashed line) in MeCN.

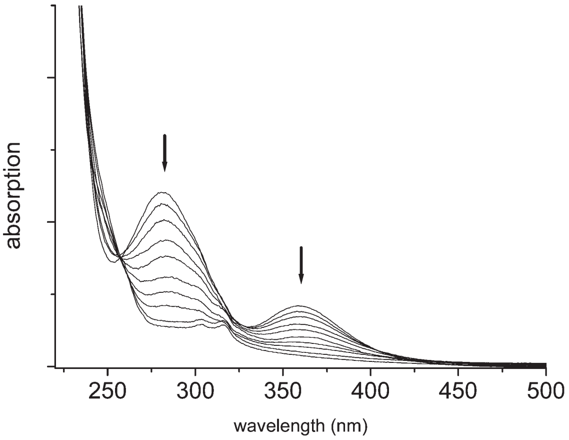


Fig. 2 Absorption spectra during photolysis of *cis*-$[PdCl_2L'''_2]$ in MeCN. The traces are taken after every 40 min of irradiation using a 390 nm cut-off filter.

of the lone pair (s/p*$_P$).[30] Further support comes from the comparison with related palladium complexes where in the series of ER_3 ligands (E = P, As, or Sb) the lowest absorption maxima show a red-shift when going along the series P < As < Sb.[31] Ligand-to-metal charge transfer (LMCT) transitions have been recently assigned for the lowest transitions occurring in arsine ruthenium complexes $[(\eta^6\text{-tol})\text{Ru(PAs)Cl}]^{2+}$ (PAs = 2-arsino-7-phosphanorbornene) from spectroelectrochemical experiments.[11*b*]. Since this system contains a formal Ru(III) (d^5) we expect that in our Pd(II) (d^8) complexes such LMCT transitions are shifted to much higher energy.

We also explored the photochemistry of these compounds. Irradiation into the long-wavelength absorption bands led, for *cis* and *trans* $[PdCl_2L'']$, $[PdI_2L''_2]$ and $[Pd_2Cl_2(\mu\text{-}Cl)_2L''_2]$, to bleaching of nearly all long-wavelength bands as depicted in Fig. 2. Parallel studies using ^{1}H NMR spectroscopy showed that the photoreaction comprises ligand-exchange reactions yielding species like $[PdCl_2(MeCN)L'']$. However, at high concentrations, as necessary for the NMR measurements, the decomposition rates are dramatically decreased, which allowed us to observe only very small quantities of such species and thus prevented unequivocal assignments. We assign this effect to the equilibrium character of $[PdCl_2(MeCN)L'']$.

$$\begin{aligned}[PdCl_2L''_2]^* &\xrightleftharpoons{\text{MeCN}} [PdCl_2(MeCN)L''] + L'' \\ &\xrightleftharpoons{\text{MeCN}} [PdCl_2(MeCN)_2] + 2L'' \end{aligned} \tag{2}$$

The labilization of the arsine ligand in the excited state supports our assignment for an MLCT/L′LCT transition [big contribution from the anti-bonding component of the lone pair (s/p*$_{As}$) to the accepting orbital]. The *trans*-$[PdCl_2L''_2]$ complex additionally undergoes partial isomerization to the *cis* derivative, which has been monitored by absorption and ^{1}H NMR spectroscopy. The quantum yields are, however, very low (estimated lower than 10^{-6}), even in diluted solutions, which prevents application of these reactions.

Crystal structures

The crystal and molecular structures of selected complexes have been obtained by single crystal X-ray diffraction; selected parameters are given in Tables 3, 5 and 6. All complexes of the methylallylarsine ligand L″ are found to crystallize in the triclinic $P\bar{1}$ space group whereas the allylarsine complexes $[PdCl_2L'_2]$ (monoclinic, $P2_1/n$) and $[PdBr_2L'_2]$ (orthorhombic, *Pbca*) adopt higher symmetric structures. There are only two structures that exhibit *inter*molecular interactions. The crystal structure of $[PdBr_2L'_2]$ shows H···Br contacts of 2.848(8) Å [C···Br: 3.727(4) Å, C–H–Br: 151.5(2)°] between As–CH$_2$– groups and bromine, which lead to the formation of layers along the *ab* plane. In the $[Pd_2Cl_2(\mu\text{-}Cl)_2L''_2]$ dimer such contacts were also found [H···Cl: 2.850(9) Å; C···Cl: 3.659(7) Å; C–H–Cl: 169.9(3)°] for both bridging and terminal Cl ligands. Additionally, this structure shows H···Cl contacts between peripheral CH_3 groups and terminal Cl ligands [H···Cl: 2.884(9) Å; C···Cl: 3.842(7) Å; C–H–Cl: 165.7(3)°]. The H···X interaction can be qualified as weak H bridges from their distances and angles.[32]

Table 5 Selected bond lengths (Å) and angles (°) in the mononuclear complexes

	M–As(1)	M–As(2)	M–X(1)	M–X(2)
$[PdCl_2L'_2]$	2.4020(7)	2.4020(7)	2.2993(15)	2.2993(15)
$[PdBr_2L'_2]$	2.3962(9)	2.3970(9)	2.4140(8)	2.4177(8)
$[PdCl_2L''_2]$	2.4012(5)	2.4012(5)	2.2968(10)	2.2968(10)
$[PdBr_2L''_2]$	2.4143(5)	2.4143(5)	2.4397(6)	2.4397(6)
$[PtCl_2L''_2]$	2.3895(5)	2.3895(5)	2.3063(11)	2.3063(11)
	X(1)–M–As(1)	X(2)–M–As(2)	X(1)–M–As(2)	X(2)–M–As(1)
$[PdCl_2L'_2]$	87.51(5)	92.49(5)	92.49(5)	87.51(5)
$[PdBr_2L'_2]$	87.38(3)	92.69(3)	92.86(3)	87.06(3)
$[PdCl_2L''_2]$	87.65(3)	92.35(3)	92.35(3)	87.65(3)
$[PdBr_2L''_2]$	87.98(2)	92.02(2)	92.02(2)	87.98(2)
$[PtCl_2L''_2]$	87.94(3)	92.06(3)	92.06(3)	87.94(3)

$L' = As(CH_2CH{=}CH_2)_3$, $L'' = As(CH_2CMe{=}CH_2)_3$

Regardless of the differences in the crystal structures the metal in all solved structures adopts a square planar environment having the two arsine ligands mutually *trans* (Fig. 3). The yellow form of $[PdCl_2L''_2]$ gave only crystals of very poor quality. The structure solution, which was best in the $P2(1)/n$ space group, could not be refined sufficiently but clearly showed a *cis* configuration.

The M–As distances in the complexes lie in the expected range around 2.4 Å,[28,31] as shown in Table 5, and do not vary greatly in the series of mononuclear compounds. In the binuclear compound $[Pd_2Cl_2(\mu\text{-}Cl)_2L''_2]$ the Pd–As distances are significantly smaller (*ca.* 2.34 Å; Table 6), which is expected since the arsine ligands are located trans to the bridging chlorine atoms. The M–X distances in this compound exhibit shorter values for the terminal ligands than for the bridging chlorine atoms, which is also in line with the argumentation that the arsine ligands have a stonger *trans* influence than chlorine ligands. Comparing the bond lengths in the palladium and platinum derivatives it can be stated that the platinum atom appears to be smaller compared to palladium. This has also been found in related studies[28,29,33] and is attributed to the lanthanide contraction and relativistic effects.[33] Other bond

Table 6 Selected bond lengths (Å) and angles (°) in $[Pd_2Cl_2(\mu\text{-}Cl)_2L''_2]$

Terminal bonds		*Bridging bonds*	
Pd(1)–As(1)	2.3439(8)	Pd(1)–Cl(3)	2.3236(15)
Pd(2)–As(2)	2.3341(8)	Pd(1)–Cl(4)	2.4329(16)
Pd(1)–Cl(1)	2.2686(16)	Pd(2)–Cl(3)	2.4498(16)
Pd(2)–Cl(2)	2.2835(16)	Pd(2)–Cl(4)	2.3218(15)
Angles			
Cl(1)–Pd(1)–Cl(3)	178.13(6)	Cl(1)–Pd(1)–As(1)	91.50(5)
Cl(1)–Pd(1)–Cl(4)	91.55(6)		
Cl(2)–Pd(2)–Cl(4)	176.82(6)	Cl(2)–Pd(2)–As(2)	91.38(5)
Cl(2)–Pd(2)–Cl(3)	94.03(6)		
Cl(3)–Pd(1)–Cl(4)	86.60(5)	Cl(3)–Pd(1)–As(1)	90..35(4)
Cl(4)–Pd(2)–Cl(3)	86.24(5)	Cl(4)–Pd(2)–As(2)	88.31(4)
Pd(1)–Cl(3)–Pd(2)	88.54(5)	As(1)–Pd(1)–Cl(4)	176.93(4)
Pd(2)–Cl(4)–Pd(1)	88.99(5)	As(2)–Pd(2)–Cl(3)	174.53(4)

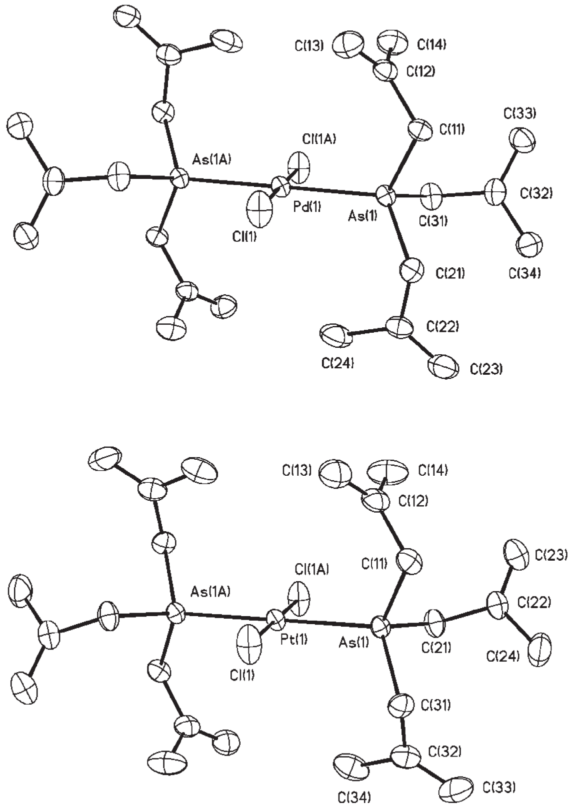


Fig. 3 Molecular structures of *trans*-[$MCl_2L''_2$] [M = Pd (top) or Pt (bottom)]. Atoms are represented by 30% ellipsoids. Hydrogen atoms were omitted for clarity.

lengths in the compounds are in the expected range, that is 1.95–1.97 Å for As–C(1) bonds, 1.49–1.51 Å for C(1)–C(2), 1.30–1.37 Å for the olefinic C(2)=C(3) bond and 1.47–1.51 Å for the terminal C(2)–CH_3 bond. The binuclear compound [$Pd_2Cl_2(\mu\text{-}Cl)_2L''_2$] does not deviate in that sense although the allylarsine ligands are *trans* to Cl. As stated above the palladium or platinum atoms all lie in an almost perfect square planar surrounding; the X–M–As angles (Tables 5 and 6) deviate only by ±2.5° from the ideal 90°. The binuclear [$Pd_2Cl_2(\mu\text{-}Cl)_2L''_2$] adopts an envelope shape for the Pd–(μ-Cl)$_2$–Pd central unit with the terminal arsine ligands (and the terminal Cl ligands) in *anti* positions as shown in Fig. 4.

Conclusions

To summarize our spectroscopic and structural results it is first of all noteworthy that the here-reported allyl- or methylallylarsine complexes present a contrast to the recently reported benzyldimethylarsine complexes [$MX_2(BzAsMe_2)_2$] of the same type[28] where the chlorine derivatives are exclusively found in the *cis* configuration whereas bromine and iodine adopt the *trans* conformation in the solid state (single crystals) as well as in fluid solution. The latter findings implicate a sterically driven selection enabling the thermodynamically favoured *cis* conformation only for the smallest ligands. We therefore suppose that the allyl- and methylallyl substituents on the arsine ligands are more sterically demanding than two methyl and one benzyl group, thus energetically labilizing the *cis* conformers. Having both conformers for [$PdCl_2L''_2$] in hand we could establish some remarkable spectroscopic differences (NMR, UV/Vis). Although olefinic and agostic M–H interactions are frequent in the organometallic chemistry of platinum(II) and palladium(II), such interactions, either through the olefinic group of the allyl moiety or with $AsCH_2$(agostic), are absent in the present case, which supports the above discussion based on the reactivity and spectroscopy of the compounds. The preliminary assignments for the long-wavelength absorption bands as mixed MLCT/L′LCT transitions were supported by the observed photoreactivity. Further detailed investigations focusing on the character of the excited states is warranted.

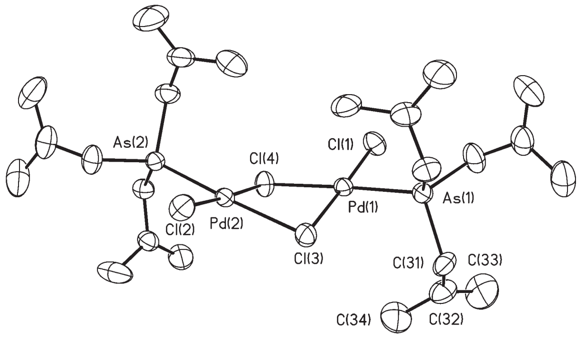


Fig. 4 Molecular structure of [$Pd_2Cl_2(\mu\text{-}Cl)_2L''_2$]. Atoms are represented by 30% ellipsoids. Hydrogen atoms were omitted for clarity.

Acknowledgements

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