Inorg. Chem. **2008**, *47*, 1524−1531

Palladium(II) and Platinum(II) Complexes with Heteroditopic 10-(Aryl)phenoxarsine (Aryl = 2-C_6H_4OR, R = H, Me, Pr^i) Ligands: Solvent-Oriented Crystallization of cis Isomers

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Received November 2, 2007

The synthesis and characterization of 10-(*o*-alkoxyphenyl)phenoxarsines 2-$ROC_6H_4As(C_6H_4)_2O$ (R = H, Me, and Pr^i, $As(C_6H_4)_2O$ = phenoxarsine) and their platinum(II) and palladium(II) complexes *cis*-$[PtCl_2\{2\text{-}Pr^iOC_6H_4As(C_6H_4)_2O\text{-}\kappa As\}_2]$ (**1**), *trans*-$[PdCl_2\{2\text{-}Pr^iOC_6H_4As(C_6H_4)_2O\text{-}\kappa As\}_2]$ (**2**), *cis*-$[PtCl_2\{2\text{-}HOC_6H_4As(C_6H_4)_2O\text{-}\kappa As\}_2]$ (**3**), *cis*-$[PdCl_2\{2\text{-}HOC_6H_4As(C_6H_4)_2O\text{-}\kappa As\}_2]$ (**4**), *cis*-$[PtI_2\{2\text{-}MeOC_6H_4As(C_6H_4)_2O\text{-}\kappa As\}_2]$ (**5**), and *trans*-$[PdCl_2\{2\text{-}MeOC_6H_4As(C_6H_4)_2O\text{-}\kappa As\}_2]$ (**6**) are reported. The chelate complex *cis*-$[Pt\{2\text{-}OC_6H_4As(C_6H_4)_2O\text{-}\kappa As,O\}_2]$ (**7**) is also described. The molecular structures of **1**–**4** and **7** were determined. The short As···O intramolecular interaction found in complexes **1**–**4** in the solid state was also verified by calculations at the B3LYP/LANL2DZ level for complex **2** and for 10-(*o*-isopropoxyphenyl)phenoxarsine in the gas phase, and this suggests that the interaction is a characteristic of the ligand rather than a packing effect. Calculations at the B3LYP/LANL2DZ and Oniom(B3LYP/LANL2DZ:uff) levels for complexes **1**–**4** showed that the solvent plays a crucial role in the crystallization (through geometry constraints) of the kinetically stable cis isomers.

Introduction

Organoarsenic compounds are mainly known as ligands in transition metal complexes, some of which are used in catalytic reactions, and as biologically active compounds. Tertiary arsines have been reported as more efficient ligands than their phosphorus analogues in a number of transition-metal-catalyzed reactions, for example, Stille[1–3] and Suzuki−Miyaura coupling reactions,[4] the hydroformylation of terminal alkenes,[5,6] Heck olefination,[7] carbonylation,[8]and the copolymerization of olefins and CO.[9]

Heteroditopic ligands containing oxygen as a potential donor along with arsenic may be good candidates to prepare catalytically active transition metal complexes. So far, only a limited number of 10-(aryl)phenoxarsines have been reported (aryl = RC_6H_4, with R = 2-MeO[10] and 2-, 3-, or 4-PhO[11]), which were obtained from 10-chlorophenoxarsine and the corresponding Grignard reagent. The 10-(phenoxyaryl)phenoxarsines are useful as fungicides, herbicides, and insecticides.[11]

We now report the synthesis and characterization of ligands with the general formula 2-$ROC_6H_5As(C_6H_4)_2O$, where R = H, Me, or Pr^i, and their platinum(II) and

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10.1021/ic7021648 CCC: $40.75
Published on Web 02/07/2008

Table 1. Crystal Data and Refinement Details for *cis*-[$PtCl_2${2-Pr^i$OC_6H_4As(C_6H_4)_2$O-κAs}$_2$] (**1**), *trans*-[$PdCl_2${2-Pr^i$OC_6H_4As(C_6H_4)_2$O-κAs}$_2$] (**2**), *cis*-[$PtCl_2${2-$HOC_6H_4As(C_6H_4)_2$O-κAs}$_2$] (**3**), *cis*-[$PdCl_2${2-$HOC_6H_4As(C_6H_4)_2$O-κAs}$_2$] (**4**), and *cis*-[Pt{2-$OC_6H_4As(C_6H_4)_2$O-$\kappa As,O$}$_2$] (**7**)

	1	**2**	**3**	**4**	**7**
empirical formula	$C_{42}H_{38}As_2Cl_2O_4Pt$	$C_{42}H_{38}As_2Cl_2O_4Pd$	$C_{36}H_{26}As_2Cl_2O_4Pt{\cdot}CH_2Cl_2$	$C_{36}H_{26}As_2Cl_2O_4Pd{\cdot}CH_2Cl_2$	$C_{36}H_{24}As_2O_4Pt$
fw	1022.55	933.86	1023.32	934.63	865.48
temp. (K)	210(2)	210(2)	297(2)	297(2)	213(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$C2/c$	$C2/c$	$P2_1/c$
unit cell					
a (Å)	9.953(6)	10.865(2)	16.388(1)	16.331(1)	10.287(1)
b (Å)	20.800(12)	12.586(3)	14.964(1)	14.988(1)	19.241(1)
c (Å)	18.408(11)	14.840(3)	14.960(1)	14.933(1)	14.867(1)
α (deg)	90	90	90	90	90
β (deg)	97.238(12)	109.956(4)	93.258(1)	93.405(1)	96.458(1)
γ (deg)	90	90	90	90	90
vol (Å^3)	3780(4)	1907.5(7)	3662.8(5)	3648.6(4)	2923.9(3)
density (calcd) (Mg/m^3)	1.797	1.626	1.856	1.701	1.966
abs coeff (mm^{-1})	5.632	2.390	5.954	2.640	7.086
F(000)	2000	936	1976	1848	1664
cryst size (mm^3)	0.30 × 0.10 × 0.10	0.40 × 0.20 × 0.20	0.47 × 0.34 × 0.26	0.40 × 0.20 × 0.19	0.60 × 0.60 × 0.30
θ range (deg)	1.96–28.31	2.18–29.07	1.84–26.37	1.85–26.37	1.99–28.40
index ranges	$-9 \le h \le +13$	$-14 \le h \le +9$	$-20 \le h \le +20$	$-20 \le h \le +20$	$-13 \le h \le +13$
	$-27 \le k \le +25$	$-16 \le k \le +14$	$-18 \le k \le +18$	$-18 \le k \le +18$	$-25 \le k \le +23$
	$-24 \le l \le +10$	$-18 \le l \le +19$	$-18 \le l \le +18$	$-18 \le l \le +18$	$-19 \le l \le +17$
reflns collected	18053	11761	14435	14449	20178
independent (R_{int})	8973 (0.0639)	4684 (0.0247)	3744 (0.0323)	3728 (0.0305)	6740 (0.0438)
data/restraints/parameters	8973/ 0/464	4684/0/234	3744/0/224	3728/0/219	6740/0/388
final R indices	$R_1 = 0.0438$	$R_1 = 0.0317$	$R_1 = 0.0382$	$R_1 = 0.0458$	$R_1 = 0.0392$
	$wR_2 = 0.0717$	$wR_2 = 0.0722$	$wR_2 = 0.0891$	$wR_2 = 0.1007$	$wR_2 = 0.0968$
R indices (all data)	$R_1 = 0.0897$	$R_1 = 0.0483$	$R_1 = 0.0412$	$R_1 = 0.0502$	$R_1 = 0.0470$
	$wR_2 = 0.0852$	$wR_2 = 0.0760$	$wR_2 = 0.0905$	$wR_2 = 0.1029$	$wR_2 = 0.1009$
goodness-of-fit on F^2	0.938	1.051	1.146	1.163	1.063
largest difference peak and hole (e Å^{-3})	2.156 and −1.162	0.656 and −0.550	1.903 and −0.873	0.748 and −0.839	3.097 and −1.515

palladium(II) halide complexes *cis*- or *trans*-[MX_2{2-$ROC_6H_4As(C_6H_4)_2$O-κAs}$_2$]. The chelate complex *cis*-[Pt{2-$OC_6H_4As(C_6H_4)_2$O-$\kappa As,O$}$_2$] (**7**) was obtained by the elimination of HCl from *cis*-[$PtCl_2${2-$HOC_6H_4As(C_6H_4)_2$O-κAs}$_2$] (**3**).

Experimental Section

Materials. All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk or vacuum line techniques. The solvents were purified (THF, toluene: refluxed over Na/benzophenone; CH_2Cl_2, *n*-hexane, MeOH: refluxed over powdered CaH_2) and distilled under nitrogen. All chemicals were of reagent grade and were used as received: phenol, anisole, isopropyl bromide, Ph_2O, *n*-BuLi and *t*-BuLi, TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine), THP (tetrahydropyran), and $AsCl_3$ were purchased from Merck; $PdCl_2$ and $H_2[PtCl_6]{\cdot}6H_2O$ were generously donated by Umicore. [$PtCl_2$(COD)],[12] [$PdCl_2$(COD)],[12] isopropyl phenyl ether,[13] and 10-chlorophenoxarsine were prepared according to published procedures (COD = 1,5-cyclo-octadiene).[14]

Instrumentation. The IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer scanning between 400 and 4000 cm^{-1} by using KBr disks, and between 200 and 400 cm^{-1} by using CsI plates. The ^{1}H, ^{13}C, and APT NMR spectra of the ligands were recorded on an AVANCE DRX 400 spectrometer (Bruker) and those of the transition metal complexes **1**−**7** on an AVANCE 300 spectrometer (Bruker) with tetramethylsilane as the standard. The mass spectra were recorded on a Ltd. ZAB-HSQ-VG Analytical Manchester Spectrometer (FAB mass spectra) and on a FT-ICR-MS Bruker-Daltonics ESI mass spectrometer. The elemental analyses were recorded on a VARIO EL (Heraeus).

Data for X-ray structures were collected on a Siemens CCD diffractometer (SMART) using Mo Kα radiation ($\lambda = 0.71073$ Å) and ω-scan rotation. Data reduction was performed using SAINT, including the program SADABS for empirical absorption correction. The structures were solved by direct methods, and the refinement of all non-hydrogen atoms was performed with SHELX97. H atoms were mainly calculated on idealized positions (Table 1). Structure figures were generated with ORTEP and DIAMOND-3.[15] The Cambridge Crystallographic Data Centre, under CCDC 665586 (**1**), 665587 (**2**), 665588 (**3**), 665589 (**4**), and 665590 (**7**), contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via the Internet at www.ccdc.cam.ac.uk/data_request/cif. Also, CIF files for compounds **1**−**4** and **7** are available as Supporting Information.

Preparation of Ligands. (2-Isopropoxyphenyl)phenoxarsine and (2-Methoxyphenyl)phenoxarsine[10]. A round-bottomed three-neck flask was charged with 0.725 mol of phenyl ether (isopropylphenyl ether or anisole) and 0.725 mol of TMEDA. A total of 0.725 mol of *n*-BuLi (1.95 M, in *n*-hexane) was added dropwise under a

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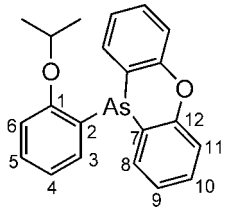
nitrogen stream with continuous stirring. After all of the *n*-BuLi was added, the solution was stirred for 20 h at room temperature. The cloudy reaction mixture was then cooled to 0 °C, and 10-chlorophenoxarsine, dissolved in THF, was added to this solution (1:1 molar ratio). The reaction mixture was refluxed for 2 h, then cooled to 0 °C and neutralized with degassed water. The organic layer was separated.

(2-Isopropoxyphenyl)phenoxarsine. The solvent was evaporated and the residue distilled. The compound was isolated as a pale yellow oil (0.4 mbar, bp 160 °C), which started to crystallize after storage at low temperatures in a refrigerator. Yield: 1.83 g (41%). mp = 91 °C. Anal. calcd (found) for $C_{21}H_{19}O_2As$: C, 66.66 (66.60); H, 5.02 (4.93). EI-MS: *m*/*z* 379 $[M + H]^+$.

The numbering scheme used to assign the NMR spectra is presented below for (2-isopropoxyphenyl)phenoxarsine, and it is valid for the aromatic atoms in all of the compounds reported:



(2-isopropoxyphenyl)phenoxarsine

^{1}H NMR ($CDCl_3$): δ 1.35 (d, 6H, C*H*$_3$, J = 5.86 Hz), 4.57 (m, 1H, C*H*), 6.55 (dd, 1H, H6, $J_{H6\text{-}H5}$ = 7.33 Hz, $J_{H6\text{-}H4}$ = 1.46 Hz), 6.66 (m, 1H, H4), 6.72 (d, 1H, H3, $J_{H3\text{-}H4}$ = 8.31 Hz), 7.11 (m, 3H, H5, H10), 7.19 (dd, 2H, H11, $J_{H11\text{-}H10}$ = 8.31 Hz, $J_{H11\text{-}H9}$ = 1.95 Hz), 7.33 (m, 2H, H9), 7.65 (dd, 2H, H8, $J_{H8\text{-}H9}$ = 7.33 Hz, $J_{H8\text{-}H10}$ = 1.46 Hz). ^{13}C NMR ($CDCl_3$): δ 21.9 (CH_3), 69.7 (CH), 111.7 (C6), 118.2 (C10), 120.3 (C7), 120.5 (C4), 123.3 (C11), 129.5 (C2), 129.6 (C3), 130.4 (C9), 132.2 (C5), 135.7 (C8), 156.0 (C12), 158.9 (C1). IR (cm^{-1}, KBr disks): 461, 753, 1029–1124, 881, 1059, 1262, 1382, 1461, 1580.

(2-Methoxyphenyl)phenoxarsine. After the solvent was removed, the compound was obtained as a pale yellow powder, which was recrystallized from *n*-hexane. Yield: 2.95 g (52%). mp = 115 °C. Anal. calcd (found) for $C_{19}H_{15}O_2As$: C, 65.14 (64.60); H, 4.28 (4.39). EI-MS: *m*/*z* 350 $[M]^+$. ^{1}H NMR ($CDCl_3$): δ 3.82 (s, 3H, CH_3), 6.55 (dd, 1H, H6, $J_{H6\text{-}H5}$ = 7.33 Hz, $J_{H6\text{-}H4}$ = 1.46 Hz), 6.70 (m, 1H, H4), 6.74 (d, 1H, H3, $J_{H3\text{-}H4}$ = 7.82 Hz), 7.12 (m, 3H, H5, H10), 7.20 (dd, 2H, H11, $J_{H11\text{-}H10}$ = 8.31 Hz, $J_{H11\text{-}H9}$ = 1.46 Hz), 7.34 (m, 2H, H9), 7.62 (dd, 2H, H8, $J_{H8\text{-}H9}$ = 7.33 Hz, $J_{H8\text{-}H10}$ = 1.46 Hz). ^{13}C NMR ($CDCl_3$): δ 55.5 (CH_3), 110.2 (C6), 118.3 (C10), 119.8 (C7), 121.2 (C4), 123.4 (C11), 129.2 (C2), 129.8 (C3), 130.6 (C9), 132.1 (C5), 135.6 (C8), 155.9 (C12), 160.8 (C1). IR (cm^{-1}, KBr disks): 460, 753, 1021–1122, 1021–1057, 1241–1261, 1580, 1392, 1428, 2954, 2929, 3059.

(2-Hydroxyphenyl)phenoxarsine. *ortho*-Dilithiated phenol was prepared by adding dropwise 2.8 equiv of *t*-BuLi in *n*-pentane to 1.0 equiv of phenol dissolved in 4.2 equiv of THP at 25 °C (exothermic reaction). The reaction mixture was stirred for 5 h after the addition of *t*-BuLi was completed. The reaction mixture was cooled to 0 °C; 2 equiv of 10-chlorophenoxarsine dissolved in THF was added, and the solution was stirred at room temperature overnight. The reaction mixture was cooled to 0 °C and treated with an aqueous solution of NH_4Cl (3%). Two liquid layers and a precipitate at the interface of these layers were formed. The product was isolated from the organic layer, combined with the precipitate, and purified by column chromatography on silica with MeOH/toluene (1:5) as the eluent. A white crystalline powder was obtained. Yield: 1.85 g (37%). mp = 106 °C. Anal. calcd (found) for $C_{18}H_{13}O_2As$: C, 64.28 (64.60); H, 3.86 (4.22); O, 9.54 (9.46). EI-MS: *m*/*z* 336 $[M]^+$. ^{1}H NMR ($CDCl_3$): δ 6.47 (dd, 1H, H6, $J_{H6\text{-}H5}$ = 7.33 Hz, $J_{H6\text{-}H4}$ = 2 Hz), 6.58 (m, 1H, H4), 6.63 (d, 1H, H3, $J_{H3\text{-}H4}$ = 7.33 Hz), 7.03 (m, 3H, H5, H10), 7.11 (dd, 2H, H11, $J_{H11\text{-}H10}$ = 8.31 Hz, $J_{H11\text{-}H9}$ = 1.46 Hz), 7.25 (m, 2H, H9), 7.57 (dd, 2H, H8, $J_{H8\text{-}H9}$ = 7.33 Hz, $J_{H8\text{-}H10}$ = 1.46 Hz), OH not observed. ^{13}C NMR ($CDCl_3$): δ 114.0 (C6), 117.6 (C10), 119.3 (C4), 119.9 (C7), 123.1 (C11), 126.8 (C2), 129.2 (C3), 130.2 (C9), 131.6 (C5), 135.3 (C8), 155.6 (C12), 158.8 (C1). IR (cm^{-1}, KBr disks): 435, 763, 1018–1074, 1223, 1265, 1597, 3059, 3403 ν(O−H).

Preparation of Complexes. A total of 2 equiv of the arsine ligand dissolved in toluene was added very slowly to a solution of 1 equiv of $[MCl_2(COD)]$ (M = Pt, Pd) dissolved in dichloromethane so as to form two layers. The complexes which contain arsine ligands with a 2-methoxyphenyl moiety were prepared by treating the ligand with $[MX_2(COD)]$ (M = Pt, Pd; X = I, Cl) in dichloromethane at a molar ratio of 2:1.

***cis*-[PtCl$_2${2-Pr^{i}OC$_6$H$_4$As(C$_6$H$_4$)$_2$O-κ*As*}$_2$] (1).** A yellow crystalline product was obtained. Yield: 0.066 g (56%). mp = 294 °C (decomp. without melting). Anal. calcd (found) for $C_{42}H_{38}O_4As_2PtCl_2$: C, 49.33 (49.20); H, 3.75 (3.66); Cl, 6.93 (6.81). ^{1}H NMR ($CDCl_3$): δ 1.33 (d, 12H, CH_3, J = 6.04 Hz), 4.57 (m, 2H, CH), 6.70 (d, 2H, H6, $J_{H6\text{-}H5}$ = 7.74 Hz), 6.85 (d, 2H, H3, $J_{H3\text{-}H4}$ = 8.30 Hz), 6.91 (m, 2H, H4), 7.20–7.37 (m, 14H, H5, H9, H10, H11), 7.72 (m, 4H, H8). IR (cm^{-1}, CsI plates): 311, 324 ν(Pt−Cl). IR (cm^{-1}, KBr disks): 462, 750, 1030–1132, 1263, 882, 1383, 1461, 1580, 2976, 3062.

***trans*-[PdCl$_2${2-Pr^{i}OC$_6$H$_4$As(C$_6$H$_4$)$_2$O-κ*As*}$_2$] (2).** Orange crystals were obtained. Yield: 0.068 g (60%). mp = 222–225 °C (decomp. without melting). Anal. calcd (found) for $C_{42}H_{38}O_4As_2PdCl_2$: C, 54.01 (53.82); H, 4.10 (3.97); Cl, 7.59 (7.43). ^{1}H NMR ($CDCl_3$): δ 1.32 (d, 12H, CH_3, J = 6.04 Hz), 4.57 (m, 2H, CH), 6.74 (d, 2H, H6, $J_{H6\text{-}H5}$ = 8.30 Hz), 6.86 (d, 2H, H3, $J_{H3\text{-}H4}$ = 8.30 Hz), 6.93–7.37 (m, 16H, H4, H5, H9, H10, H11), 8.15 (m, 4H, H8). IR (cm^{-1}, CsI plates): 362 δ(Pd−Cl); 278 ν(Pd−As). IR (cm^{-1}, KBr disks): 459, 751, 1031–1127, 884, 1265, 1384, 1464, 1580, 2971, 3064.

***cis*-[PtCl$_2${2-HOC$_6$H$_4$As(C$_6$H$_4$)$_2$O-κ*As*}$_2$] (3).** Pale yellow crystals were obtained. Yield: 0.022 g (45%). mp = 268–272 °C (decomp. without melting). Anal. calcd (found) for $C_{36}H_{26}O_4As_2PtCl_2$: C, 46.08 (45.50); H, 2.79 (2.52); Cl, 7.56 (7.39). ^{1}H NMR ($CDCl_3$): δ 6.85 (dd, 2H, H6, $J_{H6\text{-}H5}$ = 8.30 Hz, $J_{H6\text{-}H4}$ = 0.94 Hz), 6.91–7.22 (m, 14H, H3, H4, H5, H10, H11), 7.35 (m, 4H, H9), 7.45 (dd, 4H, H8, $J_{H8\text{-}H9}$ = 7.74 Hz, $J_{H8\text{-}H10}$ = 1.70 Hz), OH not observed. IR (cm^{-1}, CsI plates): 311, 325 ν(Pt−Cl). IR (cm^{-1}, KBr disks): 460, 752, 1225, 1267, 1583, 3073, 3374 ν(O−H).

***cis*-[PdCl$_2${2-HOC$_6$H$_4$As(C$_6$H$_4$)$_2$O-κ*As*}$_2$] (4).** Reddish-orange crystals were obtained. Yield: 0.017 g (58%). mp = 190–200 °C (decomp. without melting). Anal. calcd (found) for $C_{36}H_{26}O_4As_2PdCl_2$: C, 50.88 (49.94); H, 3.08 (2.95); Cl, 8.34 (8.02). ^{1}H NMR ($CDCl_3$): δ 6.84–7.21 (m, 16H), 7.35–7.46 (m, 8H), OH not observed. IR (cm^{-1}, CsI plates): 300, 326 ν(Pd−Cl). IR (cm^{-1}, KBr disks): 459, 751, 1225, 1267, 1582, 3070, 3347 ν(O−H).

***cis*-[PtI$_2${2-MeOC$_6$H$_4$As(C$_6$H$_4$)$_2$O-κ*As*}$_2$] (5).** An orange powder was obtained. Yield: 0.103 g (45%). mp = 266–272 °C (decomp. without melting). Anal. calcd (found) for $C_{38}H_{30}O_4As_2PtI_2$: C, 39.71 (39.58); H, 2.63 (2.41); I, 22.08 (21.89). ^{1}H NMR ($CDCl_3$): δ 3.93 (s, 6H, CH_3), 6.64 (dd, 2H, H6, $J_{H6\text{-}H5}$ = 7.36 Hz, $J_{H6\text{-}H4}$ = 1.32 Hz), 6.71–6.83 (m, 10H, H3, H4, H5, H10), 7.24 (dd, 4H, H11, $J_{H11\text{-}H10}$ = 7.17 Hz, $J_{H11\text{-}H9}$ = 1.32 Hz), 7.46 (m, 4H, H9), 8.12

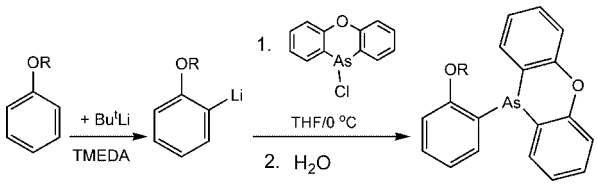
(dd, 4H, H8, J_{H8-H9} = 7.55 Hz, J_{H8-H10} = 1.70 Hz). IR (cm^{-1}, CsI plates): 310, 322 ν(Pt−I). IR (cm^{-1}, KBr disks): 459, 799, 1262, 1580, 2963, 3060.

***trans*-[PdCl$_2${2-MeOC$_6$H$_4$As(C$_6$H$_4$)$_2$O-κAs}$_2$] (6).** An orange powder was obtained. Yield: 0.130 g (60%). mp = 167–175 °C (decomp. without melting). Anal. calcd (found) for $C_{38}H_{30}O_4As_2PdCl_2$: C, 51.99 (50.97); H, 3.44 (3.12); Cl, 8.08 (7.93). ^{1}H NMR ($CDCl_3$): δ 3.95 (s, 6H, CH_3), 6.57 (dd, 2H, H6, J_{H6-H5} = 7.55 Hz, J_{H6-H4} = 1.70 Hz), 6.79–6.86 (m, 10H, H3, H4, H5, H10), 7.22 (dd, 4H, H11, $J_{H11-H10}$ = 7.36 Hz, J_{H11-H9} = 1.32 Hz), 7.39 (m, 4H, H9), 8.22 (dd, 4H, H8, J_{H8-H9} = 7.54 Hz, J_{H8-H10} = 1.51 Hz). IR (cm^{-1}, CsI plates): 368 ν(Pd−Cl). IR (cm^{-1}, KBr disks): 459, 798, 1262, 1579, 2963, 3061.

***cis*-[Pt{2-OC$_6$H$_4$As(C$_6$H$_4$)$_2$O-$\kappa As,O$}$_2$] (7).** A mixture of *cis*-[PtCl$_2${2-HOC$_6$H$_4$As(C$_6$H$_4$)$_2$O-κAs}$_2$] (**3**) (0.02 g, 0.026 mmol) and sodium acetate (0.008 g, 0.104 mmol) in ethanol (5 mL) was refluxed for several minutes until a white suspension formed. The white precipitate was filtered off and washed with water to give the product as a white powder. Yield: 0.01 g (47%). The complex was recrystallized from dichloromethane and *n*-hexane to give colorless crystals. mp = 262 °C (decomp. without melting). Anal. calcd (found) for $C_{36}H_{24}O_4As_2Pt$: C, 49.96 (49.54); H, 2.79 (2.32). ^{1}H NMR ($CDCl_3$): δ 6.46 (m, 2H, H4), 6.81–6.95 (m, 12H), 7.13–7.27 (m, 10H). IR (cm^{-1}, KBr disks): 613 ν(Pt−O); 467, 1224, 1263, 1578, 751, 3070.

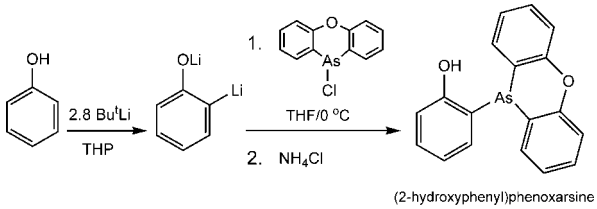
Discussion

Heteroditopic ligands 2-ROC$_6$H$_5$As(C$_6$H$_4$)$_2$O, where R = Me and Pr^i, were prepared by ortho-lithiation of the corresponding alkyl aryl ethers, followed by transmetalation with 10-chlorophenoxarsine according to the methods presented in the literature for phosphorus and arsenic analogues (eq 1).[16,17]



(1)

The free hydroxyphenyl ligand was prepared via dilithiated phenol[18] followed by transmetalation with 10-chlorophenoxarsine (eq 2).



(2)

Platinum(II) and palladium(II) complexes containing the arylphenoxarsine ligands were synthesized by reaction of the organoarsenic ligands with [MCl$_2$(COD)] (M = Pt, Pd; COD = 1,5-cyclo-octadiene) in a molar ratio of 2:1 (eq 3).

$$2 \times \underset{R = Pr^i, Me, H}{2\text{-}ROC_6H_4AsC_{12}H_8O} + \underset{\substack{M = Pt, Pd; X = Cl, I \\ COD = 1,5\text{-cyclo-octadiene}}}{[MX_2(COD)]} \rightarrow \underset{(1-6)}{[MX_2\{2\text{-}ROC_6H_4As(C_6H_4)_2O\text{-}\kappa As\}_2]} \quad (3)$$

The complex *cis*-[Pt{2-OC$_6$H$_4$As(C$_6$H$_4$)$_2$O-$\kappa As,O$}$_2$] (**7**) was obtained upon heating **3** with sodium acetate in ethanol for several minutes (eq 4).

$$\underset{(3)}{cis\text{-}[PtCl_2\{2\text{-}HOC_6H_4As(C_6H_4)_2O\text{-}\kappa As\}_2]} \xrightarrow{NaOAc,\ \Delta} \underset{(7)}{cis\text{-}[Pt\{2\text{-}OC_6H_4As(C_6H_4)_2O\text{-}\kappa^2 As,O\}_2]} \quad (4)$$

The new platinum(II) and palladium(II) complexes *cis*-[PtCl$_2${2-Pr^{i}OC$_6$H$_4$As(C$_6$H$_4$)$_2$O-κAs}$_2$] (**1**), *trans*-[PdCl$_2${2-Pr^{i}OC$_6$H$_4$As(C$_6$H$_4$)$_2$O-κAs}$_2$](**2**), *cis*-[PtCl$_2${2-HOC$_6$H$_4$As(C$_6$H$_4$)$_2$O-κAs}$_2$] (**3**), *cis*-[PdCl$_2${2-HOC$_6$H$_4$As(C$_6$H$_4$)$_2$O-κAs}$_2$] (**4**), *cis*-[PtI$_2${2-MeOC$_6$H$_4$As(C$_6$H$_4$)$_2$O-κAs}$_2$] (**5**), *trans*-[PdCl$_2${2-MeOC$_6$H$_4$As(C$_6$H$_4$)$_2$O-κAs}$_2$] (**6**), and **7** were characterized by IR and ^{1}H NMR spectroscopy and **1**–**4**, **7** also by single-crystal X-ray diffraction. The stereochemistry around the central atom (cis or trans geometry) was assigned on the basis of the IR spectra.

The IR spectra of compounds **1**, **3**, and **4** exhibit two bands which can be assigned to symmetric and antisymmetric Pt−Cl vibrations: 311 and 324 cm^{-1} (**1**), 311 and 325 cm^{-1} (**3**), and 300 and 326 cm^{-1} (**4**), supporting a cis arrangement of the ligands, while in the spectra of compounds **2** and **6**, the presence of only one band [362 cm^{-1} (**2**) and 368 cm^{-1} (**6**)] can be attributed to a trans orientation of the two chlorine atoms.[19] In the case of the chelate complex, **7**, only one absorption band at 613 cm^{-1} due to ν(Pt−O) is observed. No O−H vibrational bands are present in the spectrum due to deprotonation of the ligand. The ^{1}H NMR spectra of complexes **1**–**7** show the characteristic signals of the organoarsenic ligands with the appropriate coupling constants (see the Experimental Section).

X-ray structure determinations were carried out on compounds **1**−**4** and **7**. The molecular structures of the platinum(II) and palladium(II) complexes with (2-isopropoxyphenyl)phenoxarsine (**1** and **2**) are presented in Figure 1, those with (2-hydoxyphenyl)phenoxarsine (**3** and **4**) in Figure 2, and the structure of the chelate complex *cis*-[Pt{2-OC$_6$H$_4$As(C$_6$H$_4$)$_2$O-$\kappa As,O$}$_2$] (**7**) is shown in Figure 3. Selected structural parameters for complexes **1**−**4** and **7** are summarized in Table 2.

Although all complexes have a square-planar geometry, **1**, **3**, and **4** have the two arsine ligands in a cis orientation, while the ligands are coordinated in trans positions in the palladium complex **2** (Figures 1 and 2). In **3** and **4**, the metal atom is located on a crystallographic C_2 axis, and in **2**, it is on an inversion center.

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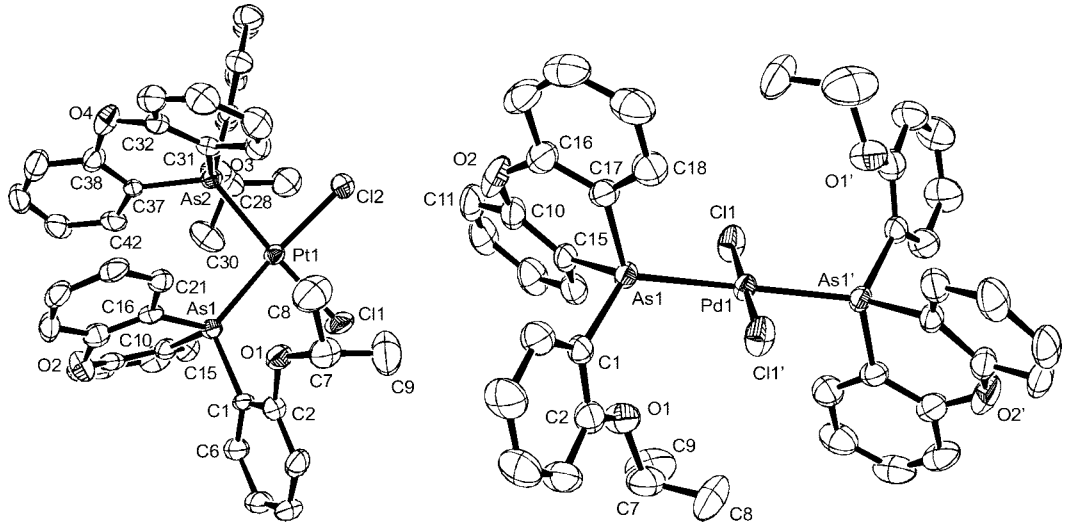

Figure 1. ORTEP drawings of *cis*-[$PtCl_2$\{2-$Pr^iOC_6H_4As(C_6H_4)_2O$-κAs\}$_2$] (**1**) (left) and *trans*-[$PdCl_2$\{2-$Pr^iOC_6H_4As(C_6H_4)_2O$-κAs\}$_2$] (**2**) (right). 50% ellipsoids are shown. Hydrogen atoms are omitted for clarity.

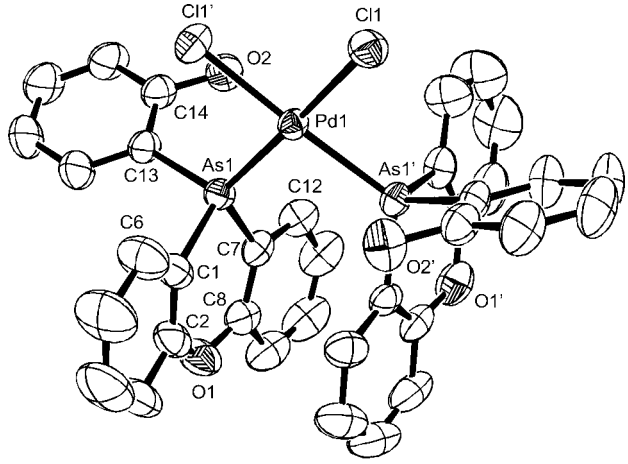

Figure 2. ORTEP drawing of *cis*-[$PdCl_2$\{2-$HOC_6H_4As(C_6H_4)_2O$-κAs\}$_2$] (**4**). 50% ellipsoids are shown (disordered solvent molecules and hydrogen atoms other than OH are omitted for clarity). *cis*-[$PtCl_2$\{2-$HOC_6H_4As(C_6H_4)_2O$-κAs\}$_2$] (**3**) is isostructural and isotypical.

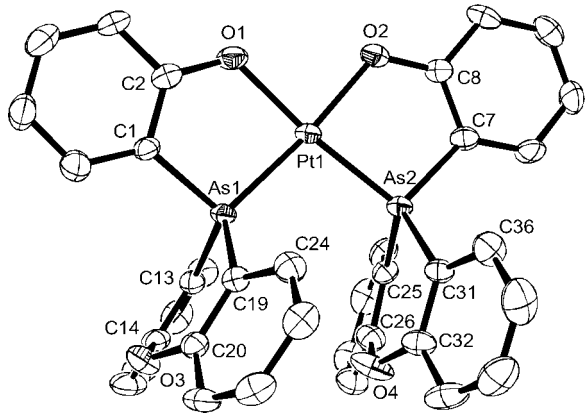

Figure 3. Molecular structure of *cis*-[Pt\{2-$OC_6H_4As(C_6H_4)_2O$-$\kappa^2 As,O$\}$_2$] (**7**). 50% ellipsoids are shown (hydrogen atoms are omitted for clarity).

The arsine ligands are coordinated to the metal center only through the arsenic atom. The Pt−As bond lengths of 2.346(1) and 2.351(1) Å in **1** and 2.3425(5) Å in **3**, and the Pt−Cl bond lengths of 2.308(2) and 2.329(2) Å in **1** and 2.338(2) Å in **3**, are close to the values reported in the literature for related compounds; that is, for *cis*-[$PtCl_2(AsBzMe_2)_2$], the values are 2.337(1) and 2.334(1) Å (Pt−As) and 2.340(3) and 3.355(3) Å (Pt−Cl),[20] and in *cis*-dichloro[(*S*)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)-oxazoline-$\kappa As,N$]platinum(II), they are 2.3048(9) Å (Pt−As) and 2.350(3) and 2.285(3) Å (Pt−Cl).[21]

The Pd−As bond length of 2.4042(5) Å in **2** is slightly longer than the values reported for *trans*-[$PdCl_2(AsBzMe_2)_2$] (2.3524(9) and 2.3586(9) Å),[20] while in **4**, the distance is similar (2.3558(5) Å). The Pd−Cl bond lengths are 2.2904(7) Å in **2** and 2.334(1) Å in **4**, and the former is significantly shorter than those in *trans*-[$PdCl_2(AsBzMe_2)_2$] (2.370(2) and 2.359(2) Å)[20] but close to the values reported for [$PdCl_2(PEt_3)$\{$AsMe(Nap)_2$\}] (Nap = 1-naphthyl).[22]

The molecular structure of *cis*-[Pt\{2-$OC_6H_4As(C_6H_4)_2O$-$\kappa As,O$\}$_2$] (**7**) (Figure 3) has the chelate ligands in a cis arrangement. The Pt−As bond lengths of 2.2962(5) and 2.3024(6) Å are shorter than those in **1**−**4** (Table 2).

The As−M−As angles in the cis complexes **1**, **3**, and **4** range from 95.28(2)° in **4** to 97.77(4)° in **1**, and the Cl−M−Cl angles range from 88.82(8)° to 91.78(6)° (cf. As−M−As = 100.74(5)° and Cl−M−Cl = 90.1(1)° in *cis*-[$PtCl_2(AsBzMe_2)_2$]).[20] The trans complex **2** is located on a crystallographic inversion center with both As−Pd−As and Cl−Pd−Cl angles being 180.00°. The arsenic atoms are in a distorted tetrahedral environment in all of the complexes, with angles in the range of 97.1(3)−116.8(5)° (As1) and 97.1(3)−121.9(2)° (As2) in **1**, 97.2(1)−122.03(9)° in **2**, 97.8(3)−121.0(2)° in **3**, 98.1(2)−121.7(1)° in **4**, and 96.8(2)−122.6(2)° (As1) and 96.3(2)−121.2(2)° (As2) in chelate complex **7**. Arsenic−carbon bonds in the phenoxarsine units in **1**−**4** (range 1.902(6)−1.919(4) Å) are slightly shorter than the arsenic−carbon$_{\text{substituted-phenyl}}$ bonds (As(1)−C(1) = 1.928(5) and As(2)−C(22) = 1.924(6) Å in **1**, As(1)−C(1)

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Table 2. Selected Bond Lengths (Å) and Angles (deg) in *cis*-[$PtCl_2${2-$Pr^iOC_6H_4As(C_6H_4)_2O$-κAs}$_2$] (**1**), *trans*-[$PdCl_2${2-$Pr^iOC_6H_4As(C_6H_4)_2O$-κAs}$_2$] (**2**), *cis*-[$PtCl_2${2-$HOC_6H_4As(C_6H_4)_2O$-κAs}$_2$] (**3**), *cis*-[$PdCl_2${2-$HOC_6H_4As(C_6H_4)_2O$-κAs}$_2$] (**4**), and *cis*-[Pt{2-$OC_6H_4As(C_6H_4)_2O$-κ^2As,O}$_2$] (**7**)

	1	**2**	**3**	**4**	**7**
M(1)−As(1)	2.346(1)	2.4042(5)	2.3425(5)	2.3558(5)	2.2962(5)
M(1)−As(2)	2.351(1)				2.3024(6)
M(1)−Cl(1)	2.308(2)	2.2904(7)	2.338(2)	2.334(1)	
M(1)−Cl(2)	2.329(2)				
M(1)−O(1)					2.043(4)
M(1)−O(2)					2.035(4)
As(1)−M(1)−As(2)	97.77(4)	180.00[a]	96.29(3)[a]	95.28(2)[a]	
As(1)−M(1)−Cl(2)	173.20(5)	87.81(3)	87.48(4)	86.50(3)	
As(1)−M(1)−Cl(1)	86.87(6)	92.19(3)	175.81(4)	117.52(3)	
As(2)−M(1)−Cl(2)	85.85(5)				
As(2)−M(1)−Cl(1)	174.43(5)	87.81(3)	87.48(4)	86.50(3)	
Cl(2)−M(1)−Cl(1)	89.86(7)	180.00[b]	88.82(8)[b]	91.78(6)[b]	
O(1)−M(1)−O(2)					88.2(2)
O(1)−M(1)−As(1)					85.5(1)
O(2)−M(1)−As(1)					173.3(1)
O(2)−M(1)−As(2)					85.3(1)
O(1)−M(1)−As(2)					173.3(1)
As(1)−M(1)−As(2)					101.06(2)

[a] As1−M(1)−As(1′). [b] Cl(1)−M(1)−Cl(1′).

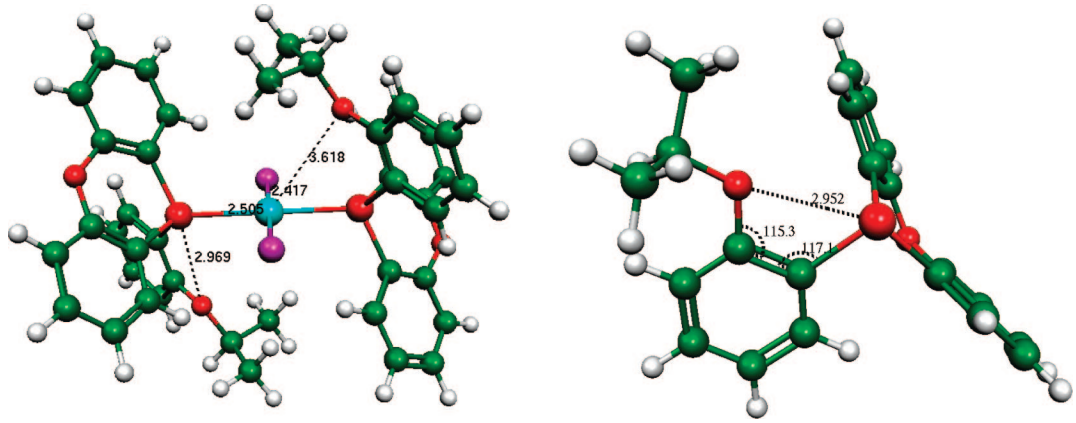

Figure 4. Calculated molecular structures of **2** and 10-(*o*-isopropoxyphenyl)phenoxarsine 2-$Pr^iOC_6H_4As(C_6H_4)_2O$.

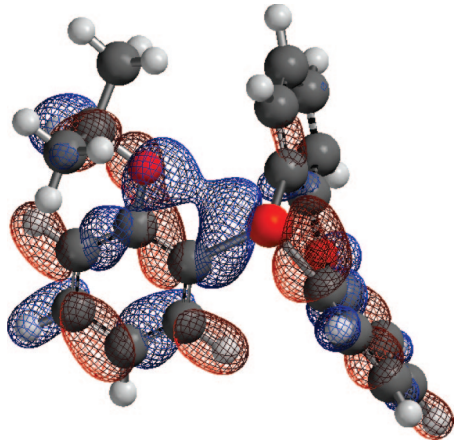

Figure 5. HOMO-8 of 10-(*o*-isopropoxyphenyl)phenoxarsine.

= 1.940(3) Å in **2**, As(1)−C(13) = 1.931(5) Å in **3**, and As(1)−C(13) = 1.931(5) Å in **4**). No significant differences are observed for arsenic−carbon bonds in **7**. Unusually large $C-O_{ether}-C$ angles were found: 119.4(5) and 118.1(5)° in **1** and 120.0(2)° in **2**. Short As···O contacts found in **1**−**4** (2.940 and 2.952 Å in **1**, 2.895 Å in **2**, 3.005 Å in **3**, and 2.986 Å in **4**; sum of the van der Waals radii: 3.37 Å) are related to the $C-O_{ether}-C$ angles.

The phenoxarsine group is very flexible and can adopt either a planar or a folded geometry; the dihedral angles reported so far lie in the range of 150−180°. In $O(C_6H_4)_2AsS(S)PR_2$ (R = Me, Et), this angle is 176.1 and 173.1°,[23] and the known bis(phenoxarsine) compounds $O(C_6H_4)_2As-E-As(C_6H_4)_2O$ (E = S,[24] Se[25]) also contain two nearly planar phenoxarsine moieties (dihedral angles: 175.2 and 175.8° for E = S, and 173.9 and 176.0° for E = Se). In contrast, the phenoxarsine moieties in **1**–**4** exhibit a folded (butterfly) arrangement with dihedral angles of 151.20 and 150.07° in **1**, 153.70° in **2**, 162.96° in **3**, and 163.40° in **4**, close to the values reported for $O(C_6H_4)_2AsCl$ (156.3°),[26] $O(C_6H_4)_2AsS_2CN(CH_2CH_2)_2$ (155.2°),[27] the phenoxarsin-10-yl derivative of 2-aminocyclopent-1-ene-1-carbodithioic acid $O(C_6H_4)_2AsS(S)CC_5H_6NH_2$-2 (150.3°),[28] $O(C_6H_4)_2AsS_2PPh_2$

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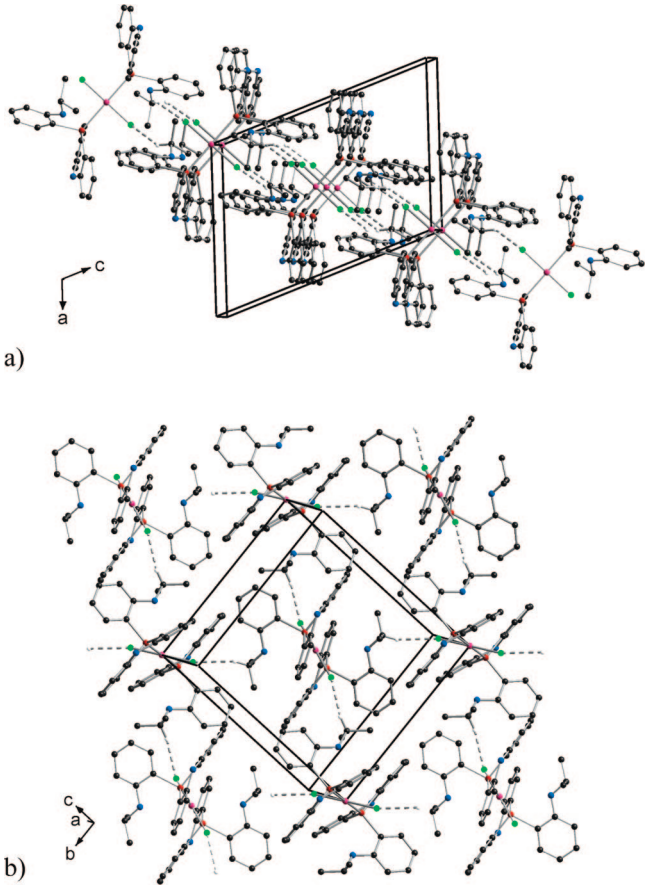

Figure 6. (a) View perpendicular to the two-dimensional sheets in *trans*-[$PdCl_2${2-Pr^i$OC_6H_4As(C_6H_4)_2O$-κAs}$_2$] (**2**). (b) View along a two-dimensional sheet.

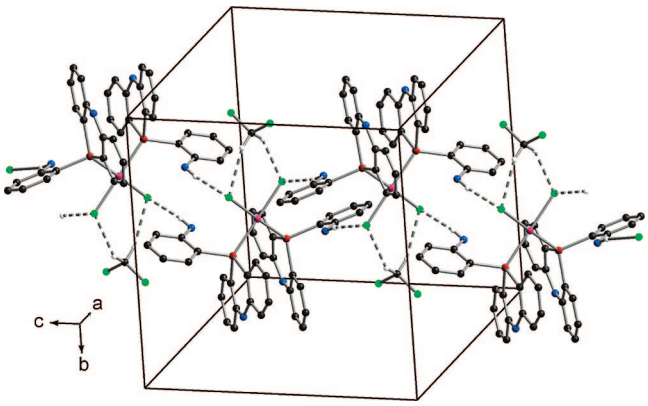

Figure 7. (Pt)Cl···H(O) and (Pt)Cl···H(C) interactions in *cis*-[$PtCl_2${2-$HOC_6H_4As(C_6H_4)_2O$-κAs}$_2$] (**3**).

(154.4°),[29] and $O(C_6H_4)_2AsOAs(C_6H_4)_2O$ (157.6 and 176.0°),[25] or in the adduct of $SbCl_5$ with 10-chlorophenoxarsine oxide {$O(C_6H_4)_2AsClOSbCl_5$} (167.7°).[26] Smaller values (145.24 and 146.64°) are observed in *cis*-[Pt{2-$OC_6H_4As(C_6H_4)_2O$-$\kappa^2 As,O$}$_2$] (**7**).

Calculations were performed at the B3LYP/LANL2DZ level[30–33] for complex **2** to check for arsenic−oxygen contacts in the gas phase and, in case the interaction is present, to gain insight into the molecular orbitals involved (see Figure 4). Short arsenic−oxygen contacts and O−C−C and C−C−As angles smaller than 120° were calculated both for **2** and for the respective ligand; that is, these values are determined neither by solid-state packing nor by the presence of the metal and are thus rather a characteristic of the ligand.

Table 3. DFT Total (au)/Relative (kcal/mol) Energies for the Optimized Structures of **1**−**4**

	B3LYP/LANL2DZ	Oniom(B3LYP/lnl2dz:uff)
1	−2805.3747389	−164.666774
	+2.29	**+10.60**
1_trans	−2805.3783977	−164.683671
	0.0	**0.0**
2_cis	−2092.9514997	−172.2470994
	+4.81	**+5.66**
2	−2092.9591704	−172.2561179
	0.0	**0.0**
3	−1849.5432723	−164.7033719
	+2.36	**+2.15**
3_trans	−1849.5470302	−164.7068015
	0.0	**0.0**
4	−1857.1185657	−172.2744279
	0.0	**+10.18**
4_trans	−1857.1181863	−172.2906444
	+0.24	**0.0**

The HOMO-8 of 10-(*o*-isopropoxyphenyl)phenoxarsine, drawn at the isodensity value of 0.032 e/Å^3 as calculated at the B3LYP/6-31G(d) level within Spartan'04,[34] shows that direct p−p interaction between arsenic and oxygen is responsible for the shortening of the As···O distance (Figure 5). This As···O interaction explains the stability of both the ligand and the complexes reported here toward dealkylation.

Noteworthy for **2** is the steric effect of the two isopropyl groups of the ligand, located below and above the $PdAs_2Cl_2$plane. B3LYP/LANL2DZ calculations reproduce this arrangement.

Weak intermolecular interactions (C···H and H···H) due to packing effects can be observed in **1**−**4** and **7**. Short intermolecular Cl···H(C) interactions of 2.762 Å in the crystal structure of *trans*-[$PdCl_2${2-Pr^i$OC_6H_4As(C_6H_4)_2O$-κAs }$_2$] (**2**) result in the formation of sheets (Figure 6a). These sheets consist of a polar part with the nonpolar aryl groups located above and below this plane (Figure 6b).

In contrast, the crystal structures of the isotypical compounds *cis*-[$PtCl_2${2-$HOC_6H_4As(C_6H_4)_2O$-κAs}$_2$] (**3**) and *cis*-[$PdCl_2${2-$HOC_6H_4As(C_6H_4)_2O$-κAs}$_2$] (**4**) consist of chains parallel to the *c* axis connected in a 3D structure through short intermolecular (Pt)Cl···H(O) interactions of 2.500 and 2.577 Å in **3** and 2.489 Å in **4** (sum of the van der Waals radii: 2.95 Å). Weak H···Cl interactions of the solvent molecules (CH_2Cl_2) with the $PtCl_2$ unit are also observed (Figure 7).

The formation of the different isomers of PdX_2 and PtX_2 arsine complexes seems to be determined by several factors, as supported by recently reported examples. The benzyldi-

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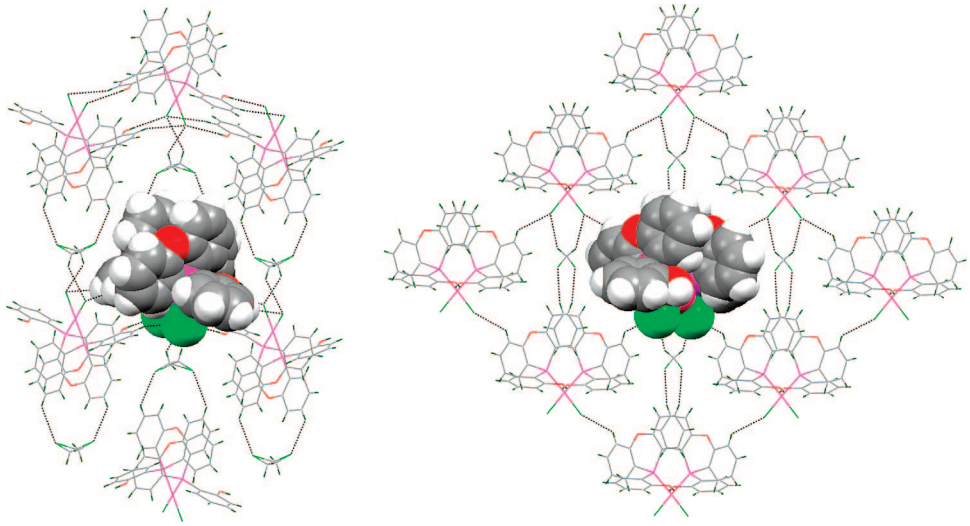

Figure 8. Hydrogen bonds formed by the solvent favor the cis isomer of **3** (left) and **4** (right).

methylarsine complexes $[MX_2(AsBzMe_2)_2]$ (M = Pd or Pt; X = Cl, Br, or I)[20] have been found exclusively in the cis conformation for X = Cl and in the trans conformation for both Pd^{II} and Pt^{II} with X = Br or I. For the triallylarsine complexes $[MX_2\{As(allyl)_3\}_2]$ (M = Pd or Pt),[35] both trans and cis conformers were obtained after preparation for M = Pd and X = Cl, while only the trans conformation is adopted in the solid state by mononuclear complexes of platinum and palladium in which X = Cl or Br. For the complexes $[MX_2\{AsMe(Nap)_2\}_2]$, it was shown by spectroscopic methods[22] that both cis and trans isomers were observed in solution, even when only the trans isomer was obtained in the solid state. The high lability of the bis(1-naphthyl)-methylarsine ligand was considered by these authors to be a prerequisite for isomerization, as this was found to be much more important for the $AsMe(Nap)_2$ ligand than for related $AsBzMe_2$ or $As(allyl)_3$ ligands.

To rationalize the observed experimental geometries, B3LYP/LANL2DZ full-geometry optimizations were performed on **1**−**4** with the aid of the Gaussian 98 package.[36] Since dispersive forces between remote parts of the same molecule might be important in the preference for one or the other of the isomers, combined quantum mechanics/molecular mechanics Oniom(B3LYP/LANL2DZ:uff)[37–39] optimizations were performed on the same compounds, with the expectation that the molecular mechanics treatment would better describe the possible intramolecular dispersion interactions.[40] The calculated data (Table 3) show that in each case the trans isomer is lower in energy and is the thermodynamically favored product. The formation of the cis isomers of **1**, **3**, and **4** is thus kinetically controlled. In the cases of **3** and **4**, crystallization is driven by the presence of the solvent (dichloromethane), which forms H···Cl hydrogen bonds with the two cis-positioned chlorine atoms, and Cl···H hydrogen bonds with two of the cis phenoxarsine ligands (Figure 8).

Thus, the role of the solvent here is more than just to occupy the empty volume in the solid network, but also to orient (through geometry constraints) crystallization of the kinetically stable cis isomers.

Acknowledgment. We thank Umicore for a generous donation of $PdCl_2$ and $H_2[PtCl_6]\cdot 6H_2O$.

Supporting Information Available: Provided are cif files of compounds **1**–**4** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC7021648

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