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Thermochemistry of pyridine and picolines complexes of *p*-chlorophenyldihaloarsines

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Abstract

The complexes $p\text{-ClC}_6\text{H}_4\text{AsX}_2 \cdot n\text{L}$ (L = pyridine, β- or γ-picoline; X = Cl, Br or I; $n = 1$, 1.5 or 2) were synthesized and characterized by melting point, elemental analysis, thermogravimetric studies and IR spectroscopy. From the enthalpies of dissolution (in 25 vol.% ethanolic ethanolamine) of the *p*-chlorophenyldihaloarsines–ligand complexes at 298.15 K, the standard enthalpies ($\Delta_r H^\ominus$) for the Lewis acid–base reactions were determined. From $\Delta_r H^\ominus$ values and thermochemical parameters for the arsines and the ligands, standard enthalpies for the complexes were calculated: enthalpy of formation $\Delta_f H^\ominus$; enthalpy of decomposition $\Delta_D H^\ominus$; lattice enthalpy $\Delta_M H^\ominus$; enthalpy of the Lewis acid–base reaction in the gaseous phase $\Delta_r H^\ominus(\text{g})$. The mean standard enthalpies of arsenic–nitrogen bonds were estimated.

INTRODUCTION

The mean arsenic–nitrogen coordinate bond energies for a series of pyridine (py) and picoline (pico) complexes of phenyldihaloarsines have recently been determined [1]. This paper describes the interaction of *p*-chlorophenyldihaloarsines with the same bases. The mean arsenic–nitrogen bond energies in these complexes range from 113 to 217 kJ mol^{-1} [1]. The substitution of one hydrogen atom by a chloride atom in the phenyl group bonded to the arsine atom leads to the formation of solid complexes by interaction with the same ligands. These were submitted to calorimetric measurements in order to determine the influence of this substitution on the As–N bond energies.

EXPERIMENTAL

All preparations and manipulations were carried out in polyethylene glove bags under a nitrogen atmosphere.

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Chemicals

The *p*-chlorophenyldihaloarsines were prepared from *p*-chlorophenylarsenic acid [2] by methods outlined in the literature [3,4]. Solvents and ligands used in the synthesis of complexes were purified by distillation and stored over Line 4-A molecular sieves.

Analytical section

Carbon, hydrogen and nitrogen contents were determined by microanalytical procedures. Halogen analysis was obtained by potentiometric titration with standard 0.1 N $AgNO_3$ solution [5] after the adducts were disssolved in water. Arsenic content was determined by redox titration of the solutions of complex samples with standard 0.05 N iodine solution until the appearance of the blue color of starch used as an indicator [6].

Complexes synthesis

The complexes were prepared by the reaction of *p*-chlorophenyldihaloarsines and the ligands in solution. A typical procedure is given below.

p-$ClC_6H_4AsCl_2 \cdot 2\gamma$-*pico*

To a solution of 2.1 ml of *p*-$ClC_6H_4AsCl_2$ (13.5 mmol) in 20 ml of petroleum ether–*n*-hexane (1:1 by vol.), 2.7 ml of γ-picoline (27.0 mmol) dissolved in 20 ml of petroleum ether was added slowly and dropwise with stirring under a dry nitrogen current. The stirring was maintained for at least three hours. The white solid formed was filtered, washed with three portions of 10 ml of petroleum ether (always in a dry nitrogen current) and then dried for several hours in vacuo. The compound obtained was stored in a desiccator over calcium chloride. A molar ratio arsine:ligand of 1:2 was used because the 1:1 molar ratio led to an oily non-crystalline product. This was also the case for the *p*-chlorophenyldiiodoarsine complexes. All the other complexes were prepared with a molar ratio of 1:1.

IR spectra

These were obtained with sample mulls in nujol sandwiched between KBr plates for complexes and by using a liquid cell with NaCl windows for the ligands and arsines, on a Perkin-Elmer 180 spectrophotometer.

Thermogravimetric studies

These were made under a nitrogen atomsphere with a Du Pont 1090 thermogravimetric analyzer with samples varying in weight from 2.42 to 8.33 mg and a heating rate of 10 K min^{-1}.

Calorimetric measurements

All the solution calorimetric determinations were carried out in a LKB 8700-1 precision calorimeter as described previously [7].

RESULTS AND DISCUSSION

All the adducts prepared were solids. The yield ranged from 42 to 96%. The melting points, colors, appearance and analytical data are summarized in Table 1.

IR data

The IR spectra of the pyridine complexes showed dislocations and intensity decreases of some bands when compared with the spectrum of free pyridine. The stretching of the As–C (chlorophenyl) bond is found in the region 1085–1090 cm^{-1} [8]. Qualitatively, the coordinated pyridine is distinguished from free pyridine by the presence of a weak band between 1235 and 1255 cm^{-1}, by a shift in the strong band at 1577 cm^{-1} to 1600 cm^{-1} and by shifts of the 598 and 403 cm^{-1} bands to 620 and 420 cm^{-1} respectively [9]. These facts were observed here.

The IR spectra of the β- and γ-picoline complexes were similar to those of the free ligands except for dislocations, splitting and intensity decreases of several bands. Appreciable dislocations toward higher frequencies are observed after coordination for adsorptions at 1600, 1560 and 1218 cm^{-1}. The IR data can be interpeted in terms of a coordination of ligands to the arsine [10, 11]. The stretching of the As–C (chlorophenyl) bond is found in the region 1086–1090 cm^{-1} [8].

The main IR bands of the ligands and the complexes are presented in Tables 2–4.

Thermogravimetric data

The thermogravimetry of the adducts show similar behavior. Nearly all of the complexes show loss of part of the ligand as a first step. The rest of

TABLE 1

Melting point, appearance, yield and analytical data for each complex

Compound	Melting point (°C) [a]	Appearance	Yield (%)	C (wt.%)		H (wt.%)		N (wt.%)		As (wt.%)		Halogen (wt.%)	
				Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
p-$ClC_6H_4AsCl_2 \cdot$ py	173	wh.cr.	90	39.27	39.10	2.70	2.79	4.16	4.22	22.27	22.37	21.07	21.29
p-$ClC_6H_4AsCl_2 \cdot \beta$-pico	155	wh.cr.	88	41.12	41.31	3.16	3.29	4.00	4.17	21.38	21.58	20.23	20.44
p-$ClC_6H_4AsCl_2 \cdot 2\gamma$-pico	105–6	ye.cr.	61	48.73	48.85	4.09	4.56	6.31	6.30	16.89	16.66	23.97	23.61
$2p$-$ClC_6H_4AsBr_2 \cdot 3$py	137	wh.pw.	83	34.88	34.79	2.49	2.64	4.52	4.41	16.11	15.92	34.37	34.10
p-$ClC_6H_4AsBr_2 \cdot \beta$-pico	101	s.ye.pw.	84	32.80	32.29	2.52	2.63	3.19	3.10	17.05	17.39	36.37	36.74
p-$ClC_6H_4AsBr_2 \cdot \gamma$-pico	92	wh.pw.	96	32.80	32.91	2.52	2.76	3.18	3.29	17.05	16.80	36.37	36.75
p-$ClC_6H_4AsI_2 \cdot$ py	145–6	s.gr.pw	81	25.44	25.68	1.75	1.94	2.70	2.98	14.43	14.34	48.87	49.30
p-$ClC_6H_4AsI_2 \cdot 2\beta$-pico	153–4	ye.pw	92	34.51	34.01	2.90	3.03	4.47	4.36	11.96	12.16	40.51	40.01
p-$ClC_6H_4AsI_2 \cdot \gamma$-pico	122–3	br.ye.pw.	42	27.02	27.42	2.08	2.27	2.63	2.62	14.05	14.21	47.58	47.94

[a] Uncorrected. Key: wh., white; ye., yellow; br., brownish; gr., gray; s., slighly; cr., crystals; pw., powder.

TABLE 2

Assignment of IR frequencies (cm^{-1}) of py and its complexes

py	p-$ClC_6H_4AsCl_2 \cdot py$	$2p$-$ClC_6H_4AsBr_2 \cdot 3py$	p-$ClC_6H_4AsI_2 \cdot py$	Assignment
1590sh	1597m	1598w	1600s	$\nu(CC)$
1577vs	1573m	n.o.	n.o.	$\nu(CC)$
1480s	1475s	n.o.	n.o.	$\nu(CC)$, $\nu(CN)$
1435vs	n.o.	n.o.	1435sh	$\nu(CC)$, $\nu(CN)$
1355sh	1382s	n.o.	n.o.	$\nu(CC)$, $\nu(CN)$
n.o.	1230w	1255w	1250w	ring
1213s	1195w	n.o.	1227m	$\beta(CH)$
1142s	1156w	1142w	1152m	$\nu(CC)$, $\nu(CN)$
	1086m	1090w	1085w	$\nu(As{-}C)$
1063s	1067m	1065w	1070w	$\beta(CH)$
n.o.	n.o.	n.o.	1050m	$\beta(CH)$
1027s	1012s	1010m	1025m	ring
990s	n.o.	n.o.	995m	ring
940w	908w	968w	n.o.	$\gamma(CH)$
	812s	810m	810vs	sust. para
747vs	n.o.	748m	745s	$\phi(CC)$
	731s	720m	723s	$\gamma(CH)_{(C_6H_4)}$
677sh	670m	663s	675sh	$\phi(CC)$
	n.o.	n.o.	665s	$\phi(CC)_{(C_6H_4)}$
598s	609w	620s	n.o.	$\alpha(CCC)$

Key: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; b, broad; n.o., not observed, ν, stretching; β, bending in plane; γ, bending out of plane; α, ring deformation in plane; ϕ, ring deformation out of plane; ring, ring breathing; R, rocking; a, antisymmetric; s, symmetric.

TABLE 3

Assignment of IR frequencies (cm^{-1}) of β-pico and its complexes [a]

β-pico	p-$ClC_6H_4AsCl_2 \cdot \beta$-pico	p-$ClC_6H_4AsBr_2 \cdot \beta$-pico	p-$ClC_6H_4AsI_2 \cdot 2\beta$-pico	Assignment
1578sh	1630m	1610w	1612w	$\nu(CC)$
1570vs	1555m	1550m	1555m	$\nu(CC)$
1473vs	n.o.	n.o.	n.o.	$\nu(CC)$, $\nu(CN)$
1448vs	n.o.	n.o.	n.o.	$\nu_a(CH_3)$
1408vs	n.o.	n.o.	n.o.	$\nu(CC)$, $\nu(CN)$
1378s	n.o.	1350w	1348w	$\nu_s(CH_3)$
1331m	n.o.	n.o.	1310m	$\nu(CC)$, $\nu(CN)$
1223m	1265w	n.o.	1267m	ring
1185s	n.o.	1178w	1110w	$\beta(CH)$
n.o.	1119w	n.o.	n.o.	$\nu(CC)$, $\nu(CN)$
	1086w	1087m	1090 m	$\nu(As{-}C)$
n.o.	1071m	n.o.	1075m	$\beta(CH)$
1036sh	n.o.	1020m	1043m	$R(CH_3)$
n.o.	1012m	n.o.	1023w	ring
983m	n.o.	1005m	1015m	ring
	812s	808s	818vs	subs. para
	783s	725m	785s	$\gamma(CH)_{(C_6H_4)}$
706vs	729w	720s	733s	$\phi(CC)$
n.o.	680m	n.o.	680s	$\phi(CC)$
658w	n.o.	670s	670s	$\alpha(CCC)$
n.o.	627vs	625s	628s	$\alpha(CCC)$

[a] See footnote to Table 2.

TABLE 4

Assignment of IR frequencies (cm^{-1}) of γ-pico and its complexes[a]

γ-pico	p-$ClC_6H_4AsCl_2 \cdot 2\gamma$-pico	p-$ClC_6H_4AsBr_2 \cdot \gamma$-pico	p-$ClC_6H_4AsI_2 \cdot \gamma$-pico	Assignment
1600vs	1610m	1660vs	n.o.	$\nu(CC)$
1560s	1573w	1585w	n.o.	$\nu(CC)$
1445vs	n.o.	1490m	n.o.	$\nu(CC)$, $\nu(CN)$
1410vs	n.o.	n.o.	n.o.	$\nu_a(CH_3)$
1378s	1373m	n.o.	1380sh	$\nu(CC)$, $\nu(CN)$
1350sh	1350w	n.o.	1350w	$\nu_s(CH_3)$
1292w	1260m	1300m	1275m	$\nu(CC)$. $\nu(CN)$
1218s	1223w	1230w	1205m	ring
	1090m	1087w	1090w	$\nu(As–C)$
1087m	n.o.	1080w	1080w	$\beta(CH)$
1067m	1075m	1060w	1068w	$\beta(CH)$
1038s	1037m	n.o.	1048m	$R(CH_3)$
n.o.	n.o.	n.o.	1020m	ring
995s	1010m	1000w	992w	ring
798vs	783s	805m	795s	$\gamma(CH)$
	805vs	808m	n.o.	subs. para
	730m	720m	n.o.	$\gamma(CH)_{(C_6H_4)}$
665w	670m	660s	678m	$\phi(CC)$
n.o.	n.o.	620s	n.o.	$\phi(CCC)$

[a] See footnote to Table 2.

TABLE 5

Thermoanalytical data of the compounds p-$ClC_6H_4AsX_2 \cdot nL$

Compound	Weight loss (%)		Temperature range (K)	Attribution	Melting point (K)
	Calc.	Obs.			
p-$Cl_6H_4AsCl_2 \cdot$ py	100	98.0	384–435	−py − (p-$ClC_6H_4AsCl_2$)	446
	0	1.5	435–1198		
p-$ClC_6H_4AsCl_2 \cdot \beta$-pico	100	99.9	388–441	−β-pico − (p-$ClC_6H_4AsCl_2$)	428
	0	0	441–1198		
p-$ClC_6H_4AsCl_2 \cdot 2\gamma$-pico	4.2	4.0	302–328	−1/5γ-pico	379
	95.8	91.0	328–438	−9/5γ-pico − (p-$ClC_6H_4AsCl_2$)	
	0	2.0	438–1198		
2p-$ClC_6H_4AsBr_2 \cdot$ 3py	17.0	17.3	360–380	−2py	410
	83.0	77.7	380–449	−py − 2(p-$ClC_6H_4AsBr_2$)	
	0	2.7	449–1198		
p-$ClC_6H_4AsBr_2 \cdot \beta$-pico	100	97.0	456–482	−β-pico − (p-$ClC_6H_4AsBr_2$)	374
	0	1.7	482–1198		
p-$ClC_6H_4AsBr_2 \cdot \gamma$-pico	100	99.5	437–493	−γ-pico − (p-$ClC_6H_4AsBr_2$)	365
	0	0.5	493–1198		
p-$ClC_6H_4AsI_2 \cdot$ py	7.1	5.6	375–381	−1/2py	419
	92.9	92.2	482–537	−1/2py − (p-$ClC_6H_4AsI_2$)	
	0	2.4	537–1198		
p-$ClC_6H_4AsI_2 \cdot 2\beta$-pico	22.3	23.4	328–388	−1.5β-pico	427
	77.7	75.6	388–504	−0.5β-pico − (p-$ClC_6H_4AsI_2$)	
	0	0	504–1198		

the ligand and the arsine are lost in a second step. Only for the β- and γ-pico complexes of p-$ClC_6H_4AsBr_2$ and the py and β-pico complexes of p-$ClC_6H_4AsCl_2$ are ligand and arsine lost in a single step. The thermoanalytical data of the adducts indicate that the complexes are unstable in the liquid phase.

Table 5 presents the thermoanalytical data of the adducts.

Calorimetric measurements

The standard enthalpies of dissolution of p-chlorophenyldihaloarsines, ligands and complexes ($\Delta_i H^{\ominus}$) were obtained as previously reported [7]. Table 6 gives these standard thermochemical values. From the standard

TABLE 6

Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent [a]	Number of experiments	i	$\Delta_i H^{\ominus}$ (kJ mol^{-1})
p-$ClC_6H_4AsCl_2$(l)	25% EA–EtOH	5	1	-176.90 ± 0.66
py(l)	1:1 p-$ClC_6H_4AsCl_2$: 25% EA–EtOH	5	2	-1.06 ± 0.09
p-$ClC_6H_4AsCl_2 \cdot$ py(s)	25% EA–EtOH	5	3	-142.94 ± 0.94
β-pico(l)	1:1 p-$ClC_6H_4AsCl_2$: 25% EA–EtOH	5	2	-0.28 ± 0.02
p-$ClC_6H_4AsCl_2 \cdot \beta$-pico(s)	25% EA–EtOH	5	3	-63.96 ± 2.07
γ-pico(l)	2:1 p-$ClC_6H_4AsCl_2$: 25% EA–EtOH	5	2	-1.52 ± 0.17
p-$ClC_6H_4AsCl_2 \cdot 2\gamma$-pico(s)	25% EA–EtOH	5	3	-113.88 ± 0.79
p-$ClC_6H_4AsBr_2$(l)	25% EA–EtOH	5	1	-212.26 ± 0.95
py(l)	3:2 p-$ClC_6H_4AsBr_2$: 25% EA–EtOH	5	2	-0.55 ± 0.07
$2p$-$ClC_6H_4AsBr_2 \cdot 3$py(s)	25% EA–EtOH	5	3	-70.56 ± 1.17
β-pico(l)	1:1 p-$ClC_6H_4AsBr_2$: 25% EA–EtOH	5	2	-0.43 ± 0.04
p-$ClC_6H_4AsBr_2 \cdot \beta$-pico(s)	25% EA–EtOH	5	3	-96.28 ± 0.37
γ-pico(l)	1:1 p-$ClC_6H_4AsBr_2$: 25% EA–EtOH	5	2	-0.29 ± 0.00
p-$ClC_6H_4AsBr_2 \cdot \gamma$-pico(s)	25% EA–EtOH	5	3	-59.92 ± 1.70
p-$ClC_6H_4AsI_2$(l)	25% EA–EtOH	5	1	-164.19 ± 0.69
py(l)	1:1 p-$ClC_6H_4AsI_2$: 25% EA–EtOH	5	2	-0.58 ± 0.03
p-$ClC_6H_4AsI_2 \cdot$ py(s)	25% EA–EtOH	5	3	-77.23 ± 1.40
β-pico(l)	2:1 p-$ClC_6H_4AsI_2$: 25% EA–EtOH	5	2	-0.65 ± 0.03
p-$ClC_6H_4AsI_2 \cdot 2\beta$-pico(s)	25% EA–EtOH	5	3	-52.91 ± 1.26
γ-pico(l)	1:1 p-$ClC_6H_4AsI_2$: 25% EA–EtOH	5	2	-0.86 ± 0.01
p-$ClC_6H_4AsI_2 \cdot \gamma$-pico(s)	25% EA–EtOH	5	3	-51.88 ± 0.40

[a] 25% EA–EtOH = ethanolic ethanolamine (25 vol.%).

enthalpies of dissolution, the standard enthalpies of the acid–base reaction ($\Delta_r H^{\ominus}$) can be determined [1]. Using appropriate thermochemical cycles and applying Hess's law, the standard enthalpies of decomposition ($\Delta_D H^{\ominus}$), the lattice standard enthalpies ($\Delta_M H^{\ominus}$) and the standard enthalpies of the Lewis acid–base reactions in the gaseous phase ($\Delta_r H^{\ominus}(g)$) were obtained [1]. The $\Delta_r H^{\ominus}(g)$ values can be used to calculate the standard enthalpy of the arsenic–nitrogen bond $\bar{D}$(As–N) (equal to $-\Delta_r H^{\ominus}(g)/n$).

Table 7 lists the values for all these parameters.

For the determination of $\Delta_r H^{\ominus}(g)$, it was necessary to assume that the molar standard enthalpy of sublimation of each complex ($\Delta_s^g H^{\ominus}$) is equal to the enthalpy of vaporization of 1 mol of ligand [13]. The melting points and TG studies of the complexes showed that these complexes decompose on heating and are not stable in the liquid phase, nor probably in the gaseous phase.

To determine the standard enthalpy of formation of the complexes it was necessary to estimate the standard enthalpies of formation of the arsines in the gaseous phase. These values are not cited in the literature. They were calculated by a group contribution method [14] from the enthalpies of formation of $PhAsX_2$ [1]. The standard enthalpies of vaporization of the arsines were also calculated by a group contribution method [15, 16] from the enthalpies of vaporization of $PhAsX_2$ [1], adding the difference between the enthalpies of vaporization of halobenzene and benzene [12].

Based on the $\Delta_r H^{\ominus}$ values for a series of complexes with the same stoichiometry and the same ligand, the acidity order $p\text{-}ClC_6H_4AsBr_2 > p\text{-}ClC_6H_4AsI_2 > p\text{-}ClC_6H_4AsCl_2$ is obtained. The substitution of one hydrogen atom by a chlorine atom in the phenyl group leads to the inversion of the first two members in the acidity order observed for the phenyldihaloarsines complexes [1]. When the arsine is fixed and the ligands changed for complexes with the same stoichiometry, the basicity order γ-pico > β-pico > py is obtained, as expected for substitution of one hydrogen atom by a methyl group in the pyridine ring [1].

Based on $\bar{D}$(As–N) values of complexes, the same sequences for basicity and acidity are obtained. The substitution of one hydrogen atom by a chlorine atom in the phenyl group bonded to the arsenic atom in $PhAsX_2$ is expected to withdraw the electronic density from the aromatic ring. By an inductive effect the p-chlorophenyl group formed retires more electronic density from the arsenic atom and improves the reception of electronic density from the Lewis base. This is observed for $p\text{-}ClC_6H_4AsBr_2$ and $p\text{-}ClC_6H_4AsI_2$ complexes, but not for $p\text{-}ClC_6H_4AsCl_2 \cdot py$, in which the As–N bond is weaker than it is in $PhAsCl_2 \cdot py$ [1]. The mean standard enthalpy of the As–N bond of the former is lower than the latter. However, these enthalpy values are higher for $p\text{-}ClC_6H_4AsBr_2$ and $p\text{-}ClC_6H_4AsI_2$ complexes than for the respective phenyldihaloarsine complexes. The mean

TABLE 7

Summary of the thermochemical results (kJ mol^{-1})

Compound	$\Delta_r H^{\ominus}$	$\Delta_f H^{\ominus}$	$\Delta_{s,l}^{g} H^{\ominus}$	$\Delta_M H^{\ominus}$	$\Delta_D H^{\ominus}$	$\Delta_r H^{\ominus}(g)$	$\bar{D}$(As–N)
p-$ClC_6H_4AsCl_2$(l)		−135.4 [a]	67.5 [b]				
p-$ClC_6H_4AsBr_2$(l)		−16.7 [a]	87.6 [b]				
p-$ClC_6H_4AsI_2$(l)		130.0 [a]	109.9 [b]				
py(l)		101.2 ± 0.7 [c]	40.2 ± 0.0 [c]				
β-pico(l)		61.9 ± 0.5 [c]	44.4 ± 0.0 [c]				
γ-pico(l)		58.5 ± 1.1 [c]	45.3 ± 0.4 [c]				
C_6H_6(l)			33.9 ± 0.3 [c]				
ClC_6H_5(l)			40.3 ± 0.7 [c]				
BrC_6H_5(l)			43.8 ± 3.1 [c]				
IC_6H_5(l)			47.7 ± 5.02 [c]				
$C_6H_5AsCl_2$(g)		−36.3 [d]	59.9 [d]				
$C_6H_5AsBr_2$(g)		−49.5 [d]	77.7 [d]				
$C_6H_5AsI_2$(g)		160.6 [d]	96.1 [d]				
p-$ClC_6H_4AsCl_2 \cdot$ py(s)	−35.02 ± 1.15	−169.2		−142.7	75.2 ± 1.2	−102.5	102.5
p-$ClC_6H_4AsCl_2 \cdot \beta$-pico(s)	−113.22 ± 2.17	−186.7		−225.1	157.6 ± 2.2	−180.7	180.7
p-$ClC_6H_4AsCl_2 \cdot 2\gamma$-pico(s)	−64.54 ± 1.04	−82.9		−222.6	155.1 ± 1.1	−177.3	177.3
2p-$ClC_6H_4AsBr_2 \cdot$ 3py(s)	−142.25 ± 1.51	−7.2		−290.2	202.6 ± 1.5	−250.0	166.7
p-$ClC_6H_4AsBr_2 \cdot \beta$-pico(s)	−116.41 ± 1.02	−71.2		−248.4	160.8 ± 1.0	−204.0	204.0
p-$ClC_6H_4AsBr_2 \cdot \gamma$-pico(s)	−152.63 ± 1.95	−110.8		−285.5	197.9 ± 2.0	−240.2	240.2
p-$ClC_6H_4AsI_2 \cdot$ py(s)	−87.54 ± 1.56	143.7		−237.6	127.7 ± 1.6	−197.4	197.4
p-$ClC_6H_4AsI_2 \cdot 2\beta$-pico(s)	−111.93 ± 1.44	141.9		−310.6	200.7 ± 1.4	−266.2	133.1
p-$ClC_6H_4AsI_2 \cdot \gamma$-pico(s)	−113.17 ± 0.80	75.6		−268.4	158.5 ± 0.9	−223.1	223.1

[a,b] See text. [c,d] Refs. 1,12.

energies of the As–N coordinate bond in *p*-chlorophenyldihaloarsine complexes range from 103 to 210 kJ mol^{-1}.

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