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Intramolecular Donor-Site Exchange Processes in Square-Pyramidal Nickel(II) Complexes Containing Five Arsenic Donors

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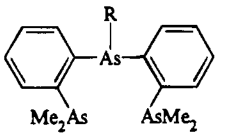
The unusual dynamic solution behavior of two, five-coordinate Ni(II) complexes containing either the tridentate ligand bis(2-(dimethylarsino)phenyl)methylarsine (**1**) or bis(2-(dimethylarsino)phenyl)phenylarsine (**2**) and the bidentate ligand 1,2-phenylenebis(dimethylarsine) (**3**) was investigated by variable-temperature ^{1}H NMR spectroscopy in a variety of solvents. The preparations of **2** and [Ni(**2**)(**3**)]$(ClO_4)_2$ (**5**) are reported. The solid-state structure of [Ni(**1**)(**3**)]$(ClO_4)_2$ (**4**) was reinvestigated. $4\cdot 4C_6H_6$ crystallizes in the monoclinic spacegroup $P2_1/c$ with $a = 22.762$ (6) Å, $b = 12.324$ (2) Å, $c = 20.274$ (5) Å, $\beta = 108.42$ (2)°, $V = 5396$ (2) Å^3, $Z = 4$, and $R/R_w = 0.0587/0.0475$ for 4210 data. Compound **4** adopts an unsymmetrical square-pyramidal geometry; the mean basal Ni−As distance = 2.285 (2) Å and the apical Ni−As distance = 2.400 (2) Å. Spectroscopic evidence suggests **5** has a similar structure. At low temperatures the spectral data for each complex are consistent with a rapid exchange between square-pyramidal enantiomers as one of the $AsMe_2$ groups of **3** oscillates between equivalent sites. At higher temperatures both $AsMe_2$ groups of **3** spin over the three positions of a facial site on the complexes. The bound tridentate ligands appear to be static. In certain solvents small amounts of free ligands are found, but they are not involved in the fluxional processes.

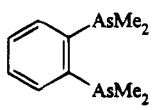
Introduction

Nyholm and co-workers demonstrated the versatility of multidentate arsine ligands in stabilizing a wide range of oxidation states and coordination geometries for nickel.[1] Much of the emphasis of this and later work has been on the preparation, characterization, and structural assignment of arsine containing nickel complexes.[2] Such preoccupations have mistakenly left the impression that these complexes are static in solution. It has already been shown[3−5] that, for complexes containing $[NiAs_4X]^+$ (X = halide) donor sets, there is rapid axial halide exchange. It has also been shown[6] that in $[NiAs_4X]^+$ complexes of the bidentate 1,2-phenylenebis(methylphenylarsine), in addition to rapid axial halide exchange, intermolecular bidentate ligand exchange (redistribution) of chelate rings occurs. In these complexes all of the processes are intermolecular, although intramolecular isomerization of chelate rings occurs in the analogous bidentate phosphine compounds[6] and in the analogous Ni compounds with hybrid arsine−phosphine ligands.[7] The detailed investigation of the dynamic behavior of these $[NiAs_4X]^+$ complexes required the preparation and use of asymmetric ligands in order to lower the symmetry of the $[NiAs_4]^{2+}$ square-planar intermediates. However, Ni complexes with symmetrical arsine ligands exist that are sufficiently unsymmetrical to allow investigation of their dynamic behavior in solution.

We describe here variable-temperature ^{1}H NMR spectral studies, in various solvents, of the five-coordinate complexes [Ni(**1**)(**3**)]$(ClO_4)_2$ (**4**) and [Ni(**2**)(**3**)]$(ClO_4)_2$ (**5**) formed from the symmetric tridentate ligands bis(2-(dimethylarsino)phenyl)methylarsine (**1**) and bis(2-(dimethylarsino)phenyl)phenylarsine (**2**) and the bidentate ligand 1,2-phenylenebis(dimethylarsine) (**3**). The complexes contain only As donor atoms. In order to interpret the ^{1}H NMR spectra, the crystal structure of **4** was redetermined accurately. Compound **4** was found to have a distorted square-pyramidal geometry. Results of the study show that the bidentate ligand undergoes rapid intramolecular exchange of donor sites. At low temperatures electronic and NMR spectral data are consistent with a dynamic process in which one $AsMe_2$ donor group remains stationary while the other group oscillates between two coordination sites. At higher temperatures both donor groups spin over the three positions of a facial site. The tridentate ligands appear to be unaffected by the exchange processes. By these processes the complexes are rapidly racemized. This is the first time such unusual intramolecular exchange processes have been identified for nickel(II)−arsine compounds.



R = Me; **1**
= Ph; **2**



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Experimental Section

Ligands **1**[8] and **3**[9] and complex **4**[10] were prepared by literature methods, as were the ligand precursors (2-bromophenyl)dimethylarsine[11] and dichlorophenylarsine.[12]

⊗ Abstract published in *Advance ACS Abstracts,* August 15, 1995.

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CAUTION! Metal perchlorate complexes are often unpredictably explosive and due precautions should be taken. No explosions were experienced in this study. Deuterated solvents were purchased from Aldrich. Standard NMR spectra were recorded on a Varian 300- or 200-MHz spectrometer locked to the deuterated solvent. The variable temperature ^1H NMR experiments were performed on a Varian 300-MHz spectrometer using 5-mm-od tubes, fitted with a coaxial 1.2-mm-od tube containing the deuterated solvent and TMS to provide a reference. Temperature was maintained by an Oxford Instruments VT controller VTC4 unit calibrated with ethylene glycol and methanol solutions using standard procedures. Temperatures are considered accurate to ±2 K. Electronic spectra were recorded on a Perkin Elmer Lambda 9 UV/vis/near-IR spectrometer fitted with a 60 mm integrating sphere attachment. Analyses were performed by the Campbell Microanalytical Laboratory at the University of Otago. All preparations were carried out under an atmosphere of dry nitrogen.

Bis(2-(dimethylarsino)phenyl)methylarsine (1).[8] NMR data have not previously been reported for this compound. NMR (300 MHz, δ, ppm): ^1H (CD_3CN) 1.04 (s, 6 H), 1.24 (s, 6 H), 1.47 (s, 3 H), 7.24 (dd, 2 H, J = 1.2, 7.5 Hz), 7.31 (dt, 2 H, J = 1.4, 7.2, 7.5 Hz), 7.39 (dt, 2 H, J = 1.6, 7.3, 7.4 Hz), 7.60 (dd, 2 H, J = 1.1, 7.5 Hz). $^{13}C\{^1H\}$ 10.00, 10.11, 10.20, 128.50, 128.60, 130.13, 131.46.

Bis(2-(dimethylarsino)phenyl)phenylarsine (2). To a three-necked flask flushed with nitrogen and fitted with a pressure-equalizing dropping funnel, Subaseal septum cap, and reflux condenser was added dry nitrogen-purged diethyl ether (125 cm^3) and (2-bromophenyl)dimethylarsine (19.1 g, 73 mmol). n-BuLi (50 cm^3 of a 1.6 M solution) was added dropwise over 30 min. The yellow solution was refluxed for 30 min. The reaction mixture was allowed to cool to room temperature, and dichlorophenylarsine (8.2 g 37 mmol) in dry nitrogen-purged benzene (75 cm^3) was added dropwise over 30 min. The solution was stirred under nitrogen for 16 h and then hydrolyzed with cold water (90 cm^3). The pale yellow organic layer was separated and dried ($MgSO_4$). Solvents were removed *in vacuo* to yield a crude waxy solid which was recrystallized from hot ethanol to yield an off-white microcrystalline solid. Yield = 8.66 g (46%), mp 126.2 °C. NMR (200 MHz, δ, ppm): ^1H ($CDCl_3$) 1.08 (s, 6 H), 1.10 (s, 6 H), 6.87 (dd, 2 H, J = 1.3, 7.5 Hz), 7.16 (dt, 2 H, J = 1.4, 7.4, 7.4 Hz), 7.31 (m, 5 H), 7.33 (dt, 2 H, J = 1.4, 7.4, 7.4 Hz), 7.55 (dd, 2 H, J = 1.3, 7.5 Hz); $^{13}C\{^1H\}$ 11.20, 128.33, 128.50, 128.70, 128.76, 130.35, 133.64, 134.43. Anal. Calcd for $C_{22}H_{25}As_3$: C, 51.39; H, 4.90. Found: C, 50.72; H, 4.70.

[Ni(1)(3)](ClO$_4$)$_2$ (4).[10] ^{13}C NMR data have not previously been reported for this compound. NMR (300 MHz, δ, ppm): $^{13}C\{^1H\}$(DMF-d_7), 248 K, 14.85, 15.37, 15.52, 15.74, 16.97, 130.67, 130.83, 131.47, 131.95, 133.24, 133.52, 133.87, 139.88, 140.24, 140.35, 141.09; 298 K, 15.04, 15.47, 15.56, 15.7 (br), 17.0 (br), 130.54, 130.7 (br), 131.1 (br), 131.72, 133.10, 133.5 (br), 133.76, 139.65, 140.13, 140.91.

[Ni(2)(3)](ClO$_4$)$_2$ (5). A mixture of **2** (0.092 g, 0.178 mmol) and **3** (0.050 g, 0.178 mmol) in CH_2Cl_2 (40 cm^3) was added to a solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (0.065 g, 0.178 mmol) in CH_2Cl_2 (30 cm^3). The deep red solution was stirred for 30 min, and the volume was reduced under vacuum. Addition of diethyl ether gave a red-brown precipitate. Recrystallization from CH_3CN/1-butanol gave a dark red microcrystalline solid which was filtered and dried *in vacuo*, yield = 0.125 g (68%). Anal. Calcd for $C_{32}H_{41}As_5NiCl_2O_8$: C, 36.33; H, 3.91; Cl, 6.70. Found: C, 36.70; H, 3.97; Cl, 7.26. The complex is a 2:1 electrolyte in CH_3CN: $\Lambda = 294\ \Omega^{-1}\ cm^2\ mol^{-1}$. Electronic spectrum, $10^3\ cm^{-1}$: [diffuse reflectance (relative intensity)] 37.04 (1.8), 31.25 sh, 21.55 (1.1), 18.14 (1.0); [CH_3CN (ϵ_{mol}, $dm^3\ cm^{-1}\ mol^{-1}$)] 21.88 (1183), 18.65 sh. NMR (300 MHz, δ, ppm): $^{13}C\{^1H\}$(DMF-d_7), 248 K, 14.31, 16.02, 16.41, 17.15, 130.81, 131.36, 131.64, 131.74, 132.35, 132.36, 133.54, 133.96, 134.39, 135.06, 138.43, 142.89; 298 K, 14.6 (br), 16.30, 16.52, 17.4 (br), 131.97, 132.1 (br), 132.8 (br), 132.91, 134.20, 134.40, 134.6 (br), 135.06, 138.95, 141.03, 143.40.

Table 1. Crystallographic Data for **4**·4C_6H_6

chem formula	$C_{51}H_{63}As_5Cl_2NiO_8$	space group	$P2_1/c$ (No. 14)
a, Å	22.762(6)	λ, Å	0.710 69
b, Å	12.324(2)	ρ_{measd}, g cm^{-3}	1.60(2)
c, Å	20.274(5)	ρ_{calcd}, g cm^{-3}	1.61
β, deg	108.42(2)	μ, cm^{-1}	34.70
V, Å^3	5396(2)	transm coeff	0.658−0.969
Z	4	R[a]	0.0587
T, K	135	R_w[b]	0.0475
fw	1308.3		

[a] $R = \sum\Delta F/\sum|F_o|$. [b] $R_w = \sum w^{1/2}\Delta F/\sum w^{1/2} F_o$; $w = 1.598/[\sigma^2(F_o) + 0.00015(F_o)^2]$.

X-ray Structure Determination. Crystals were grown initially from ethanol, as reported,[10] but preliminary photographic examination[13] revealed that these crystals either were twinned or gave powderlike diffraction patterns. The previously reported crystal structure of **4**[10] has a very high R-factor (0.18), possibly due to poor crystal quality. Suitable red plates were finally obtained by slow diffusion of an acetone solution of the complex into benzene. The crystals obtained from the latter solvent mixture belong to the same space group but contain four benzene molecules of crystallization and have different cell parameters to that found by the original workers. Crystallographic data are given Table 1. A Nicolet P3 diffractometer with graphite-monochromated Mo Kα radiation was used. Accurate unit-cell dimensions were obtained from 25 machine-centered reflections (6° < 2θ < 34°). The intensities of three check reflections (400), (060), and (009) measured after every 100 reflections showed isotropic decay < 2%, which was corrected for during processing. The data were processed[14] and corrected for Lorentz and polarization effects and absorption (empirical ψ-scan absorption corrections[14] based on eight reflections for a lamina plate). The structure was solved with direct methods and difference Fourier synthesis maps and was refined with blocked-full-matrix least squares techniques using SHELX76.[14] All nonhydrogen atoms were assigned anisotropic thermal parameters in the final cycles of refinement. ClO_4^- and the four benzene molecules of solvation were well behaved and showed only slightly elevated thermal parameters. H atoms were placed in fixed calculated positions. Neutral atom scattering factors and anomalous dispersion corrections were inlaid[14] or taken from ref 15. Final atomic coordinates are given in Table 2, and selected bond lengths and angles, in Table 3.

Results and Discussion

Syntheses. Ligand **2** was made in a manner similar to **1**,[8] by replacement of the Br in (2-bromophenyl)dimethylarsine by treatment with n-BuLi and subsequent addition, in a 2:1 mole ratio, to dichlorophenylarsine. Ligand **2** is an off-white crystalline solid that is not particularly air sensitive in the solid state. The two nickel complexes were prepared in a straightforward manner in reasonable yields. The reaction of equimolar solutions of a nickel(II) salt of a noncoordinating anion with **1** and **3** or **2** and **3** gave the heteroleptic complexes [Ni(**1**)(**3**)]X_2 and [Ni(**2**)(**3**)]X_2 (X = ClO_4^-, BF_4^-, PF_6^-). It is necessary to use a reasonable volume of solvent and to add the ligands slowly to prevent formation of homoleptic complexes of **1** and **3**. While ethanol may be used for the preparation of **4**, it is necessary to use CH_2Cl_2 for **5**, as the use of ethanol leads to significant amounts of the homoleptic complexes being formed. Despite the possibility of isomeric forms of the compounds existing, in each case only one compound was ever isolated in the solid state.

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(13) Our X-ray photographic examination of **4** reveals that the reported cell dimensions in ref 10 have been transposed and should read a = 12.61 Å, b = 18.41 Å, c = 20.21 Å.

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Table 2. Fractional Atomic Coordinates and Isotropic Thermal (Å^2)^a Parameters for **4**·4C_6H_6

atom	*x*	*y*	*z*	*U*(eq)
Ni(1)	0.2111(1)	0.1063(1)	0.2103(1)	0.0255(9)
As(1)	0.3047(1)	0.1905(1)	0.2362(1)	0.0395(9)
As(2)	0.2424(1)	0.0544(1)	0.3253(1)	0.0304(8)
As(3)	0.1153(1)	0.0411(1)	0.1987(1)	0.0255(7)
As(4)	0.2322(1)	−0.0607(1)	0.1611(1)	0.0291(7)
As(5)	0.1648(1)	0.2191(1)	0.1185(1)	0.0322(8)
Cl(1)	−0.1191(2)	−0.1031(3)	0.1657(2)	0.045(2)
Cl(2)	0.3133(2)	0.5423(3)	0.0909(2)	0.040(2)
O(11)	0.0823(4)	0.1875(8)	−0.1510(5)	0.086(8)
O(12)	0.1493(6)	0.057(1)	−0.1018(5)	0.14(2)
O(13)	0.0817(5)	0.0248(8)	−0.2083(5)	0.100(8)
O(14)	0.1606(6)	0.143(1)	−0.1959(6)	0.13(1)
O(21)	0.3061(8)	0.580(1)	0.1479(6)	0.18(1)
O(22)	0.3739(5)	0.544(1)	0.0935(8)	0.15(1)
O(23)	0.2831(6)	0.609(1)	0.0399(7)	0.18(1)
O(24)	0.2882(6)	0.4411(8)	0.0769(7)	0.14(1)
C(11)	0.3482(6)	0.184(1)	0.1689(6)	0.07(1)
C(12)	0.3106(7)	0.3400(9)	0.2658(7)	0.07(1)
C(121)	0.3593(6)	0.1138(9)	0.3143(5)	0.041(8)
C(122)	0.3318(5)	0.0565(9)	0.3552(5)	0.03(1)
C(123)	0.4593(6)	0.054(1)	0.3872(7)	0.07(1)
C(124)	0.4311(6)	−0.007(1)	0.4267(6)	0.048(9)
C(125)	0.3677(6)	−0.004(1)	0.4114(6)	0.044(7)
C(126)	0.4240(6)	0.114(1)	0.3320(7)	0.059(7)
C(21)	0.2250(6)	−0.0925(9)	0.3486(6)	0.046(8)
C(22)	0.2201(6)	0.141(1)	0.3942(5)	0.050(9)
C(31)	0.2295(6)	−0.084(1)	0.0653(5)	0.048(9)
C(32)	0.3063(5)	−0.1395(9)	0.2063(6)	0.038(8)
C(341)	0.1680(5)	−0.1581(8)	0.1694(5)	0.027(7)
C(342)	0.1184(5)	−0.1138(8)	0.1862(5)	0.019(8)
C(343)	0.1260(6)	−0.3360(9)	0.1733(6)	0.042(9)
C(344)	0.0770(6)	−0.2926(9)	0.1902(6)	0.039(8)
C(345)	0.0731(5)	−0.1800(9)	0.1974(5)	0.030(8)
C(346)	0.1718(6)	−0.2706(9)	0.1623(5)	0.037(6)
C(41)	0.0709(5)	0.0620(9)	0.2643(5)	0.039(8)
C(451)	0.0578(5)	0.0936(9)	0.1128(5)	0.027(7)
C(452)	0.0807(5)	0.1715(8)	0.0772(5)	0.027(8)
C(453)	−0.0414(5)	0.0994(9)	0.0271(5)	0.034(8)
C(454)	−0.0212(6)	0.178(1)	−0.0098(6)	0.043(9)
C(455)	0.0403(6)	0.2122(9)	0.0159(6)	0.038(8)
C(456)	−0.0018(5)	0.0593(9)	0.0876(6)	0.036(7)
C(51)	0.1570(7)	0.3726(8)	0.1350(6)	0.051(9)
C(52)	0.1956(6)	0.223(1)	0.0399(5)	0.046(9)
C(61)	0.9733(8)	0.339(1)	0.1427(7)	0.06(1)
C(62)	0.9852(7)	0.430(1)	0.1089(9)	0.07(1)
C(63)	0.8718(7)	0.331(1)	0.0591(9)	0.06(1)
C(64)	0.8842(8)	0.420(1)	0.0266(7)	0.07(1)
C(65)	0.939(1)	0.469(1)	0.0511(9)	0.07(1)
C(66)	0.9160(9)	0.292(1)	0.1148(8)	0.06(1)
C(71)	0.7392(7)	0.126(1)	0.105(1)	0.07(1)
C(72)	0.7314(9)	0.098(1)	0.1669(9)	0.09(1)
C(73)	0.678(1)	0.125(1)	0.1816(8)	0.09(1)
C(74)	0.6332(9)	0.182(1)	0.133(1)	0.08(1)
C(75)	0.6400(8)	0.209(1)	0.0721(8)	0.07(1)
C(76)	0.6927(9)	0.181(1)	0.0587(8)	0.07(1)
C(81)	0.351(1)	0.178(3)	−0.014(2)	0.15(3)
C(82)	0.386(2)	0.265(2)	0.021(2)	0.17(2)
C(83)	0.454(1)	0.247(2)	0.032(1)	0.17(2)
C(84)	0.460(2)	0.171(3)	0.006(2)	0.37(5)
C(85)	0.434(2)	0.109(3)	−0.032(2)	0.17(3)
C(86)	0.374(2)	0.105(2)	−0.040(1)	0.12(2)
C(91)	0.544(1)	0.277(2)	0.287(2)	0.12(2)
C(92)	0.502(2)	0.336(3)	0.241(2)	0.19(3)
C(93)	0.487(2)	0.431(3)	0.253(2)	0.24(5)
C(94)	0.510(2)	0.469(3)	0.323(2)	0.21(4)
C(95)	0.550(1)	0.405(2)	0.370(1)	0.15(3)
C(96)	0.5655(8)	0.309(2)	0.351(1)	0.10(2)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **4**·4C_6H_6

Ni(1)−As(1)	2.276(2)	As(2)−C(22)	1.95(1)
Ni(1)−As(2)	2.303(2)	As(3)−C(41)	1.93(1)
Ni(1)−As(3)	2.266(2)	As(3)−C(346)	1.93(1)
Ni(1)−As(4)	2.400(2)	As(3)−C(451)	1.930(9)
Ni(1)−As(5)	2.296(2)	As(4)−C(31)	1.95(1)
As(1)−C(11)	1.93(2)	As(4)−C(32)	1.91(1)
As(1)−C(12)	1.93(1)	As(4)−C(341)	1.94(1)
As(1)−C(121)	1.93(1)	As(5)−C(51)	1.94(1)
As(2)−C(21)	1.94(1)	As(5)−C(456)	1.92(1)
As(2)−C(126)	1.93(1)	As(5)−C(52)	1.93(1)

As(1)−Ni(1)−As(2)	85.7(1)	Ni(1)−As(2)−C(126)	105.8(3)
As(1)−Ni(1)−As(3)	170.2(1)	Ni(1)−As(2)−C(21)	118.8(3)
As(1)−Ni(1)−As(4)	101.0(1)	Ni(1)−As(2)−C(22)	120.4(3)
As(1)−Ni(1)−As(5)	93.8(1)	Ni(1)−As(3)−C(346)	106.8(3)
As(2)−Ni(1)−As(3)	89.2(1)	Ni(1)−As(3)−C(41)	125.4(3)
As(2)−Ni(1)−As(4)	98.3(1)	Ni(1)−As(3)−C(451)	109.3(4)
As(2)−Ni(1)−As(5)	154.9(1)	Ni(1)−As(4)−C(31)	126.4(4)
As(3)−Ni(1)−As(4)	88.0(1)	Ni(1)−As(4)−C(32)	119.9(3)
As(3)−Ni(1)−As(5)	87.2(1)	Ni(1)−As(4)−C(341)	103.9(3)
As(4)−Ni(1)−As(5)	106.4(1)	Ni(1)−As(5)−C(456)	107.8(3)
Ni(1)−As(1)−C(11)	118.1(4)	Ni(1)−As(5)−C(51)	119.6(3)
Ni(1)−As(1)−C(12)	118.4(5)	Ni(1)−As(5)−C(52)	119.5(4)
Ni(1)−As(1)−C(121)	106.3(4)		

Electronic spectra of five-coordinate low-spin nickel(II) complexes have been examined in detail,[16,17] although mainly for systems containing tripod ligands.[18,19] In addition, electronic spectra have been reported for a number of nickel(II) complexes containing five arsenic donors.[19−21] Although complexes rarely exhibit ideal square-pyramidal or trigonal-bipyramidal geometries, the former typically displays an intense band at *ca.* 19 000−23 000 cm^{-1} with a less intense band at higher or lower energy, whereas the latter has a very intense band at *ca.* 15 000−20 000 cm^{-1} and a weaker band at higher energy. In these $[NiAs_5]^{2+}$ systems the bands of the approximately trigonal-bipyramidal complexes are the more intense by about a factor of 2. Our own work on such systems[22,23] supports the observation[16] that, typically, pseudo-trigonal-bipyramidal complexes are deep purple or blue and pseudo-square-pyramidal complexes are usually green or red. Finally, the electronic spectra of **4** have been investigated in detail[16] and were unequivocally interpreted as square-pyramidal even at low temperature. Complexes **4** and **5** have similar red colors and electronic spectra, indicating they most probably have similar pseudo-square-pyramidal structures. NMR spectral data (*vide infra*) lend support to this conclusion.

X-ray Structure of 4·4C_6H_6. The structure of **4** has already been reported;[10] however, almost no structural details were given, and the structure determination has a high *R*-factor (0.18). Our redetermination of the structure of **4**, in a different crystal

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Table 4. Variable-Temperature ^{1}H NMR Data for Methyl Region of **4** in Various Solvents[a]

		δ							
solvent	T (K)		C(41)[b]	C(11)/C(12)	C(11)/C(12)/C(21)/C(22)	C(32)/C(51)	C(21)/C(22)	C(31)/C(52)	ref
DMF[c]						2.03		1.81	21
DMF-d_7	223		*ca.* 2.9[d]	2.45 (6 H)		2.05 (6 H)	1.96 (6 H)	1.77 (6 H)	*e*
	273		2.86 (3 H)	2.42 (6 H)		2.02 (6 H)	1.93 (6 H)	1.77 (6 H)	*e*
	298		2.84 (3 H)	2.41 (br, 6 H)		2.00 (6 H)	1.92 (br, 6 H)	1.76 (6 H)	*e*
	363		2.79 (3 H)		2.14 (vbr, 12 H)	1.97 (6 H)		1.77 (6 H)	*e*
DMSO-d_6		3.47[f]	2.68	2.2		1.77		1.59	10
	298		2.70 (3 H)	2.23 (br, 6 H)		1.83 (6 H)	1.75 (br, 6 H)	1.61 (6 H)	*e*
	363		2.65		1.99 (vbr, 12 H)	1.82 (6 H)		1.62 (6 H)	*e*
MeCN-d_3	243		2.53 (3 H)	2.15 (6 H)		1.74 (6 H)	1.67 (6 H)	1.58 (6 H)	*e*
	298		2.54 (3 H)	2.18 (br, 6 H)		1.77 (6 H)	1.70 (br, 6 H)	1.63 (6 H)	*e*
	333		2.49 (3 H)		*ca.* 1.9[d] (vbr, 12 H)	1.73 (6 H)		1.58 (6 H)	*e*

[a] δ, ppm. [b] Protons of methyl groups labeled from crystal structure of **4**. [c] Probably DMF-d_7. [d] Partially obscured by solvent peak. [e] This work. [f] Possibly H_2O in solvent.

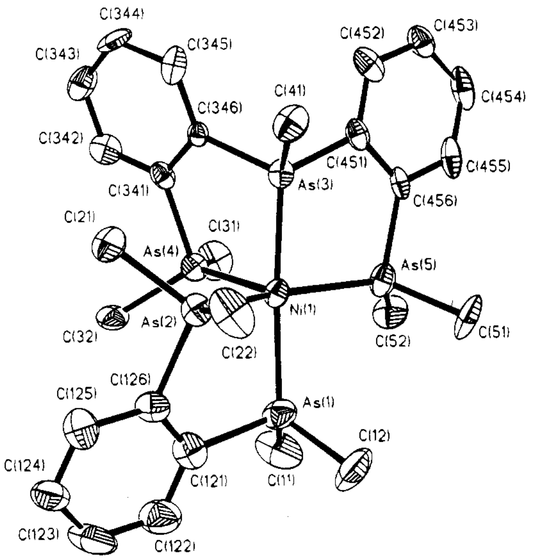

Figure 1. View of cation **4** (crystallographic numbering). Thermal ellipsoids are drawn with boundary surfaces at the 50% level.

modification from the original study, confirms the geometry about the Ni atom is that of a distorted square-pyramid (Figure 1). The structure parameter τ,[24] which measures the degree of trigonality, is 0.26. Tridentate ligand **1** coordinates facially to the central Ni, with the central and one terminal As donor occupying basal positions while the other terminal As donor occupies the apical position. The remaining basal sites are occupied by bidentate ligand **3**. The mean basal Ni−As distance is 2.285(2) Å. This value agrees with that originally found[10] and is consistent with reported values in related structures;[25,26] the sum of the covalent radii is 2.38 Å.[27,28] The shortest Ni−As distance is that of the more constrained, central As donor. Consistent with the square-pyramidal geometry of **4**, the apical Ni−As bond is longer than the basal bonds by 0.115(4) Å. Ligand **1** has moderate flexibility[29] and should be able to bind without difficulty in the apical position. There are no significant steric interactions that would restrict the approach of the apical donor. Thus, the increased apical bond length is attributed to the increase in metal−ligand repulsion in the axial direction as a result of the filling of the d_{z^2} orbital.[16] Apical bond lengthening is commonly observed in square-pyramidal low-spin d^8 complexes.[30]

The apical Ni−As bond is bent by 7.9° from the normal to the mean plane through the Ni and four basal As donors. This bending is a common feature of compounds of this type.[23] It appears to be unrelated to any steric interaction and may be an artifact of the description of distorted structures in terms of an ideal square pyramid. Bis(diphosphine) and -(diarsine) complexes have been found to adopt "stepped" structures.[31] In **4** the basal $NiAs_4$ plane makes angles of 18.1° and 5.5° with the planes through the basal As_2C_6 atoms of the bidentate and tridentate ligands, respectively. The smaller angle reflects the more constrained coordination of the tridentate ligand. The four benzenes of solvation are held in place by a variety of weak offset and edge-to-face π−π interactions with each other and with the arene rings of the coordinated ligands; close contacts between C atoms on adjacent rings are on average about 4 Å.

Variable Temperature ^{1}H NMR Spectra. The ^{1}H NMR data (Tables 4 and 5) indicate that **4** and **5** have similar structures. The ^{1}H NMR spectrum of **4** has previously been reported[10,21] in part but never assigned (Table 4). Our studies in DMSO-d_6 at room temperature show that **4** exhibits three sharp Me resonances for the tridentate ligand and two broad Me resonances for the bidentate ligand (*vide infra*). The broad resonances coalesce to a single broad peak at higher temperature while the sharp resonances remain unchanged. In DMF-d_7 (Figure 2) similar features are found for both complexes and the temperature range of this solvent is more useful for this study. At low temperatures the two broad peaks become sharp. No major changes in the other resonances are observed. The sharp resonances do not change in shape, although some undergo a small upfield shift and most of the resonances in the aromatic region do not broaden significantly as the temperature is raised. The main features of the spectra of the complexes in DMF-d_7 do not change with changes in concentration from 1.0 mM to saturation at about 40 mM. In both solvents the complexes show sharp peaks that correspond to the free ligands. These

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Table 5. Variable Temperature ^{1}H NMR Data for Methyl Region of **5** in Various Solvents[a]

		δ				
solvent	T (K)	C(11)/C(12)[b]	C(32)/C(51)	C(31)/C(52)	C(11)/C(12)/ C(21)/C(22)	C(21)/C(22)
DMF-d_7	223	2.47 (6 H)	2.21 (6 H)	1.91 (6 H)		1.30 (6 H)
	248	2.43 (6 H)	2.17 (6 H)	1.88 (6 H)		1.28 (6 H)
	298	2.43 (br, 6 H)	2.16 (6 H)	1.89 (6 H)		1.32 (br, 6 H)
	363		2.10 (6 H)	1.89 (6 H)	1.88 (vbr, 12 H)	
MeCN-d_3	238	2.09 (6 H)	1.83 (6 H)	1.63 (6 H)		1.05 (6 H)
	273	2.11 (br, 6 H)	1.84 (6 H)	1.65 (6 H)		1.09 (br, 6 H)
	298	2.13 (br, 6 H)	1.85 (6 H)	1.67 (6 H)		1.12 (br, 6 H)
	333		1.86 (6 H)	1.69 (6 H)	c	

[a] δ, ppm. [b] Protons of methyl groups labeled from crystal structure of **4**. [c] Peaks completely coalesced.

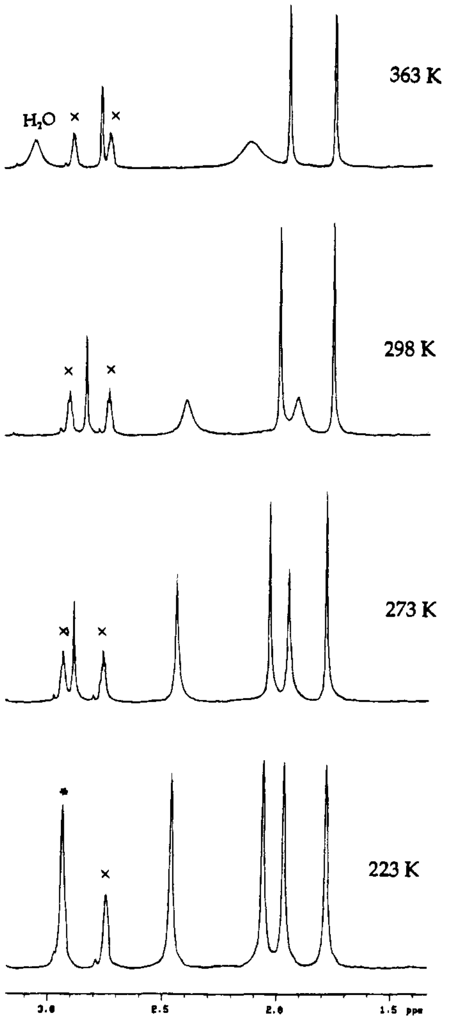

Figure 2. Variable-temperature ^{1}H NMR spectra of the methyl region of **4** (*ca.* 20 mM solution) in DMF-d_7: × solvent peaks; *, overlapped solvent and complex peaks.

peaks are small and only represent about 15 mol % of complex. They remain sharp at all but the very highest temperatures. Titration of a large excess of **3** (*ca.* 25-fold excess) caused no change to the resonances of the complexes in the ambient ^{1}H NMR spectra. ^{13}C NMR spectra (Experimental Section) in DMF-d_7 show only sharp resonances at low temperature, but at ambient temperature certain resonances, most probably due to **3**, broaden. Earlier electrochemical studies[29,32] of these complexes in MeCN had shown no evidence of the presence of the free ligands in solution. The ^{1}H NMR spectra of both complexes were recorded in MeCN-d_3 at various temperatures (Tables 4 and 5). The spectra show the same features as the other solvents except that there are no peaks in the Me or aromatic regions corresponding to the free ligands. The similarity of the MeCN-d_3 spectra to those in other solvents and the virtual temperature independence of the free-ligand peaks indicate that any processes involving the dissociated free ligands are of minor importance and are very slow on the NMR time scale. In all of the solvents the processes are reversible as the temperature is changed. Compound **4** is insoluble in CH_2Cl_2, and **5** has very limited solubility, thus making studies at lower temperature not possible.

In the spectra of **4** the peak corresponding to a single Me, which remains sharp throughout the temperature range, is assigned to that of the central As donor of the tridentate **1**; a corresponding peak is not present for **5**. The other peaks that remain sharp are assigned to the terminal methyls of **1** since these could not become equivalent without affecting the central group. The same assignments are made for **5**. Thus, in both complexes, it is the methyls of the bidentate ligand that become equivalent at higher temperature. The low temperature ^{1}H and ^{13}C NMR spectra indicate a high degree of symmetry in both complexes. In the Me region of the ^{1}H NMR spectra, with the exception of the unique Me on the central As in **4**, all of the resonances correspond to pairs of methyls. This is in contrast to the unsymmetrical solid-state structure of **4**, which implies that all methyls should be nonequivalent. Two possible explanations can be offered to account for this persistence of symmetry in solution. Firstly, at low temperature the complexes might exist in solution with a static geometry of C_s symmetry. This geometry, which would be different from that found for **4** in the solid state, could be either pseudo-trigonal-bipyramidal, with a facially bound ligand, or pseudo-square pyramidal, with a meridionally bound ligand. The former geometry is more likely since meridional binding by **1** and **2** is rare for first-row transition metals;[33] all crystallographically characterized complexes show facial coordination only.[22,34] However, a pseudo-trigonal-bipyramidal geometry would not be consistent with the fact that for **4** the solid-state electronic spectrum was found to be the same as the solution spectrum, both at room temperature and 77 K, implying the structure of the complex in the solid persists in solution.[16] Secondly, some facile process might exist that makes each pair of Me groups equivalent. Examination of CPK models and the crystal structure of **4** indicates that the only process that can account for the persistence of symmetry is a rapid oscillation of one of the bidentate $AsMe_2$ donors between equivalent vacant sites on pseudo-square-pyramidal enantiomers (Figure 3). The average geometry, at low temperature, on the NMR time scale, is that of a pseudo-trigonal-

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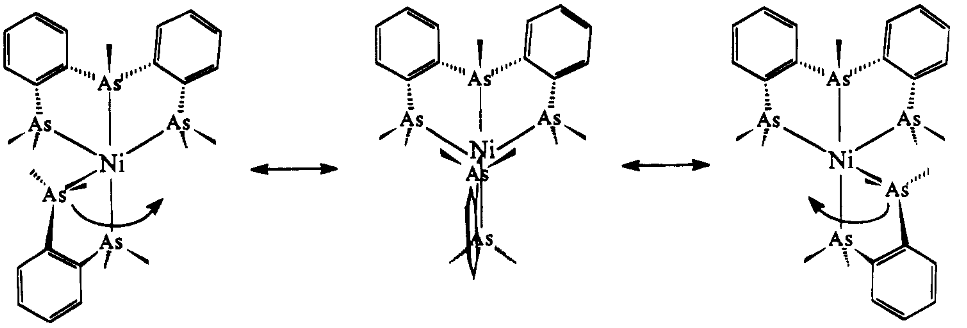

Figure 3. Low-energy donor-site exchange process showing proposed pseudo-trigonal-bipyramidal transition state.

Table 6. Significant Nuclear Overhauser Effects (NOE)[a] for **4** and **5**

methyl group(s) irradiated[b]	methyl group(s) enhanced	effect (%)	
		4	**5**
C(41)	C(21)/C(22)	5	
C(11)/C(12)	C(32)/C(52)	4	8
	C(31)/C(52)	5	6
C(32)/C(51)	C(31)/C(52)	9	8
	C(21)/C(22)	21	
C(21)/C(22)	C(32)/C(51)	18	
	C(31)/C(52)	4	
C(31)/C(52)	C(11)/C(12)	5	3
	C(32)/C(51)	9	5
	C(21)/C(22)	9	

[a] DMF-d_7 solution, temperature 223 K. [b] Protons of methyl groups labeled from the crystal structure of **4**.

bipyramid that would have a plane of symmetry making equivalent each pair of Me groups. Thus, provided the two pseudo-square-pyramidal enantiomers rapidly racemize via a pseudo-trigonal-bipyramidal transition state, the spectral data would be consistent with that reported for a pseudo-square-pyramidal complex.[16] This ease of exchange is consistent with the widely held view that there is only a small energy difference between these two limiting geometries.[35] One of the bidentate $AsMe_2$ peaks in **5** is considerably shielded with respect to the analogous peak in **4**, while the peaks for the other $AsMe_2$ group remain virtually unshifted between the complexes. The peaks that shift between the compounds are assigned to the oscillating $AsMe_2$ group. Only this group would experience shielding by the phenyl group rather than the Me group attached to the central As of the tridentate ligand in these compounds. The remaining assignments (Tables 4 and 5) were made by comparing the spectra of **4** and **5** and by using NOE experiments (Table 6). The very large NOE effect observed between the oscillating $AsMe_2$ and the pair of inward facing terminal methyls of the tridentate ligand in **4** is consistent with the rapid motion of that group between two sites. It is unlikely, given the distances that would be involved, that a static structure of C_s symmetry would provide for such a large NOE effect between the bidentate $AsMe_2$ and *both* inward facing methyls. The fact that a similar effect is not observed for **5** is surprising but may reflect different tumbling rates or relaxation processes in **5**.[36] Finally, while neither explanation can be established unequivocally, the latter would seem to be the more favored given the known structural preferences of the ligands, the previous interpretation of electronic spectra, and the closely related high-temperature behavior (*vide infra*) of the complexes. We are currently investigating the dynamic behavior of related complexes with other bidentate arsine ligands in the hope of resolving this ambiguity.

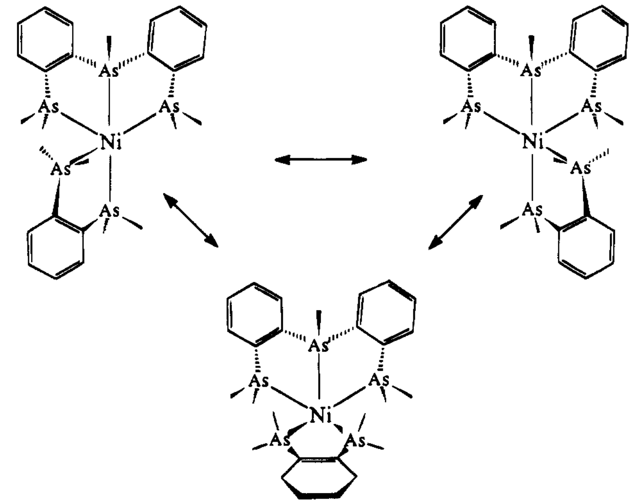

Figure 4. High-energy donor-site exchange process showing the spinning of **3** over a facial site.

As the temperature is increased, both $AsMe_2$ groups of **3** become equivalent. This is only possible if both of these groups are exchanging over all three positions of the facial site of the complex not associated with the tridentate ligand (Figure 4). Such a process very much resembles a turnstile mechanism.[37] Turnstile rotation, as opposed to the Berry pseudorotation, has been proposed to occur in a number of trigonal-bipyramidal metal complexes.[38] Peaks assigned to the central $AsMe_2$ group of **1** and the forward facing Me groups on both **1** and **2** show small upfield shifts as the temperature is increased (Tables 4 and 5). These inward pointing Me groups will be the ones most affected by the spinning of the bidentate ligand. The average environment of the inward pointing Me groups near the bidentate ligand changes as it begins to spin. The upfield shift arises from the increasing Me−Me interactions between the bidentate and tridentate ligands as the temperature is increased. The free-energy barriers $\Delta G^{\ddagger}$ for this spinning of the bidentate ligands over the facial sites of the complexes are calculated[39] to be 65.8 ± 0.5 kJ mol^{-1} for **4** (T_c = 333 K) and 66.5 ± 0.5 kJ mol^{-1} for **5** (T_c = 353 K) in DMF-d_7. The similarity of the energy barriers

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is consistent with **4** and **5** having similar structures. Examination of CPK models suggests that a phenyl group on the central As is unlikely to provide any more of a barrier to either the oscillatory or spinning processes than a Me group. Intramolecular ligand exchange processes have been observed for complexes of the type $[Ni(bidentate)_2X]^+$.[6,7] Where the energy barriers to exchange could be determined, they are similar to those above. No mechanism for the process was given, but it would seem possible that it might involve the same exchange of bidentate ligands over a facial site. In the case of the $[Ni(bidentate)_2X]^+$ complexes this exchange would have to be geared in some way to the very rapid halide exchange which is also occurring; otherwise there would be no continuously accessible vacant coordination site. The rapid exchange of donor sites by the bidentate ligand may explain why no isomers of **4** and **5** have been isolated in the solid state. Only the arrangement of ligands which leads to the most insoluble form of the complex in a solvent would be isolated. That arrangement of ligands must be the same for the organic solvents in which **4** and **5** are soluble.

Conclusion

While fluxional processes involving intramolecular ligand exchange are now well established for five-coordinate metal complexes, most of the examples involve complexes with approximate trigonal-bipyramidal geometries.[40] Our work has shown that square-pyramidal nickel(II)−arsine complexes also undergo fluxional processes. The temperature dependent processes we have identified seem to be closely related to fluxional behavior in trigonal-bipyramidal systems.[38] In addition, the use of symmetrical bi- and tridentate arsine ligands has demonstrated that in these unsymmetrical complexes a detailed investigation of their dynamic behavior is possible without the need to deal with synthetically difficult asymmetric ligands. We are currently investigating[23] the fluxional behavior of the unsymmetrical homoleptic Ni complexes of **1** and **2**. The complexes are five coordinate and display even more complex fluxional processes.

Acknowledgment. We thank the University of Otago and the John Edmond Postgraduate Scholarship Fund (D.A.M.) for financial support. We thank Perkin-Elmer (Auckland, New Zealand) for provision of software. We are grateful to Prof. Ward T. Robinson (University of Canterbury) for X-ray data collection and to Prof. David A. Buckingham and Dr. Alan R. Hayman (University of Otago) for helpful discussions.

Supporting Information Available: Tables of data collection and refinement details, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom parameters (5 pages). Ordering information is given on any current masthead page.

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