A Nuclear Magnetic Resonance Study of the Conformation of Six-membered Chelate Rings in Four-coordinate Complexes

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The ditertiary arsine $(CH_3)_2AsCH_2CH(C(CH_3)_3)CD_2As(CH_3)_2 (L-L)$ forms 'tetrahedral' $(L-L)Ni(CO)_2$ and square planar $(L-L)NiOC(CF_3)_2C(CF_3)_2O$. In both complexes the conformations of the chelate rings are locked with the *t*-butyl groups equatorial. The dihedral angles are very similar in spite of the anticipated differences in angles at the central atom. The square planar complexes $(L-L)'PtbipyCl_2$ and $(L-L)_2'PtCl_2$ and their palladium analogs $((L-L)' = H_2NCH_2CH(C(CH_3)_3)CD_2NH_2)$ also have their chelate rings in locked chair conformations. This results in the identification of isomers in the case of $(L-L)_2'M^{2+}$. The ${}^{3}J_{H-II}$ couplings indicate that the dihedral angles are similar in the group VIII complexes with a degree of puckering which could be less than in related complexes of L-L. The ${}^{3}J_{Pt-H}$ couplings indicate changes in the N...N axis.

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L'arsine ditertiaire $(CH_3)_2AsCH_2CH(C(CH_3)_3)CD_2As(CH_3)_2(L-L)$ forme des complexes $(L-L)Ni(CO)_2$ tétraédrique et $(L-L)NiOC(CF_3)_2C(CF_3)_2O$ plan carré. Dans chacun de ces complexes, les conformations des cycles des ligands sont bloquées avec les groupements *t*-butyles en positions équatoriales. Les angles dièdres sont très semblables malgré les différences que l'on aurait pu anticiper pour les angles vers l'atome central. Dans les complexes plan carré $(L-L)'PtbipyCl_2$ et $(L-L)_2'PtCl_2$ de même que dans leurs analogues avec du palladium $((L-L)' = H_2NCH_2CH(C(CH_3)_3)CD_2NH_2)$, les cycles des ligands sont aussi bloqués dans des conformations chaises. Ceci conduit à l'identification d'isomères dans le cas des complexes $(L-L)_2'M^{2+}$. Les constantes de couplage ${}^{3}J_{H-H}$ indiquent que les angles dièdres sont similaires dans les complexes du groupe VIII avec un degré de plissement qui pourrait être plus faible que dans les complexes apparentés contenant les groupes (L-L). Les constantes de couplage ${}^{3}J_{PL-H}$ montrent qu'il y a un changement dans le degré de plissement autour de l'axe N...N.

[Traduit par le journal]

Introduction

In earlier publications (1-5) we have discussed the conformation of five- and six-membered chelate rings in the octahedral metal carbonyl complexes $(L-L)M(CO)_4$ and $(L-L)M'(CO)_3X$, (M = Cr, Mo, W; M' = Mn, X = Cl, Br, I).The ligands, L-L, were specially prepared to allow studies by high resolution n.m.r. techniques and in particular were of the type $(CH_3)_2AsCH_2$ - $CHRCH_2As(CH_3)_2$ (R = H, 1; R = CH₃, 2; $R = C(CH_3)_3$, 3) for the studies on the sixmembered chelate rings (4, 5). We were able to show that complexes of 1 with the group VI carbonyls undergo fast conformational chair ⇒ chair interconversion while the similar complexes of 3 have locked chair configurations with the t-butyl group in an equatorial position. Similarly the $Mn(CO)_3X$ complexes of 3 were locked allowing the characterization of two isomers A and **B**, X = halogen. R = t-butyl. The preferred isomers have the same chair configuration as the



Can. J. Chem. Downloaded from www.nrcresearchpress.com by 8.26.113.34 on 11/17/14 For personal use only. analogous complexes of 1 (A, R = H) which, surprisingly, are also locked (5). This preferred configuration is the one that minimizes the interaction between the arsenic methyl groups and the axial halogen atom (6). Conformational calculations (7, 8) predict that the six-membered rings would be puckered chairs as we have found in solution (4, 5) and as others have found in the solid state (e.g. 6, 9–11).

The present work extends our n.m.r. and conformational study of six-membered chelate ring systems to four-coordinate complexes of Ni, Pd, and Pt. Ligand **3** and the analogous diamine ligand (NH₂CH₂CH(C(CH₃)₃)CH₂NH₂, **4**) were used as chelating agents. Selectively deuterated ligands, **3**- d_2 and **4**- d_2 (CH₃)₂AsCH₂CH(C(CH₃)₃-CD₂As(CH₃)₂ and NH₂CH₂CH(C(CH₃)₃)-CD₂NH₂, were prepared in order to simplify the n.m.r. spectra of the chelate complexes.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 457 instrument. The n.m.r. spectra were run on an extensively modified Varian HA-100 instrument (12). The final refined n.m.r. parameters were obtained using the LAOCOON III program modified for use on the U.B.C. IBM 300-67 computer. Microanalyses were done by Mr. Peter Borda of this department.

Preparation of Ligands

The preparation of ligands 3 and 3- d_2 has been described previously (4). The preparation of 1,3-diamino-2-*t*-butylpropane, ligand 4, is described below. This and the analogous deuterated compound 4- d_2 were prepared in a similar manner starting with the appropriate diol, HOCH₂CH-(C(CH₃)₃)CH₂OH or HOCD₂CH(C(CH₃)₃)CH₂OH, which were prepared as previously reported (4). Perfluoropinacol (PFP) was prepared according to published procedures (13).

The Preparation of 2-t-Butyl-1,3-propanediol Ditosylate

2-*t*-Butyl-1,3-propanediol (15 g) was added slowly to tosyl chloride (50 g) in pyridine (200 ml) and the resulting solution stirred for 16 h at 5°. Water (100 ml) was added and the mixture maintained at a temperature of 5° for an additional hour before additional water (1 l) was added. The resulting precipitate was filtered to give a crude yield of 40 g (82%). The compound was recrystallized from ethanol and its n.m.r. spectrum measured on a sample dissolved in CDCl₃. Resonance signals centered at 7.6 (area 8), 4.2 (area 4), 2.5 (area 6), 1.8 (area 1), and 0.96 (area 9) p.p.m. correspond to the aryl, methylene, methyl, methyne, and *t*-butyl protons, respectively.

The Preparation of 1,3-Diamino-2-t-butylpropane

Sodium azide (35 g) was added to a solution of 2-*t*butyl-1,3-propanediol ditosylate (35 g) in dimethylformamide (300 ml). The temperature of the suspension was raised to $130-140^{\circ}$ and stirred continuously for 4 h. The cooled mixture was diluted with ether (300 ml) and then extracted with eight (100 ml) portions of water. The remaining ether layer was dried over anhydrous sodium sulfate for 2 h, filtered, and reduced in volume (to 50 ml). The resulting azide solution was diluted with anhydrous THF (50 ml) and added slowly to a suspension of excess LiAlH₄ (15 g) in anhydrous THF (50 ml) and stirred at room temperature for 2 h and at 50° for an additional 8 h. The THF suspension was cooled and treated with water (15 ml), 15% sodium hydroxide solution (15 ml), and again with water (45 ml). The resulting suspension was filtered and the filtrate dried over anhydrous sodium sulfate, filtered, then evaporated to leave a pale yellow liquid (6.3 g) (yield 60%).

The 1,1-dideutero-2-*t*-butyl-1,3-diaminopropane was prepared in a similar manner. This ligand's n.m.r. spectrum (CDCl₃ solution) shows resonance multiplets centered at 2.9 (area 2), 2.1 (area 4), 1.3 (area 1), and 1.0 (area 9) p.p.m. from TMS and represent the methylene, amine, methyne, and *t*-butyl protons, respectively. Upon the addition of D_2O , the signal at 2.1 p.p.m. disappeared while a new signal appeared at 4.7 p.p.m. attributable to the formation of HOD. The i.r. spectrum (liquid film) had adsorptions at 3370 (s), 3280 (s), 2960 (s), 2860 (s), 2200 (w), 2090 (w), 1595 (s), 1475 (s), 1395 (m), 1365 (m), and 900 (m) cm⁻¹. The bands at 2200 and 2090 cm⁻¹ are attributed to the C—D stretching absorptions and are not the result of an azide impurity. The diamine was used directly for complex formation without further purification.

Preparation of Complexes

The Preparation of $(CO)_2NiAs(CH_3)_2CH_2CH_{((CH_3)_3)CH_2As(CH_3)_2}$

1,3-Bis(dimethylarsino)-2-t-butylpropane (0.5 g) was added to a stirred solution of nickel carbonyl in benzene and was maintained under a nitrogen atmosphere. After heating the mixture to 40° for 30 min, the resulting yellow solution was filtered and evaporated to dryness. The residue was sublimed (80° at 0.01 mm) to yield a cream-colored solid (0.55 g, 81%) m.p. 135°. The i.r. spectrum of a sample dissolved in cyclohexane had two carbonyl stretching vibrations at 2005 (s) and 1944 (vs) cm⁻¹.

Anal. Calcd. for $C_{13}H_{26}As_2NiO_2$: C, 36.7; H, 6.12. Found: C, 36.6; H, 6.29.

The Preparation of $O(CF_3)_2CC(CF_3)_2ONiAs(CH_3)_2$ - $CH_2CH(C(CH_3)_3)CH_2As(CH_3)_2$

Upon the addition of ligand 3 to a solution of potassium bis(perfluoropinacolato)nickel(II) in benzene (30 ml) at 40° under a nitrogen atmosphere a change in color from violet to orange was observed. The orange solution was extracted with two portions of water (10 ml), dried over anhydrous sodium sulfate, filtered, and evaporated to dryness. The orange residue was recrystallized from CH_2Cl_2 – petroleum ether to give orange crystals, m.p. 245° (yield 80%). The ¹⁹F n.m.r. spectrum of the complex measured in CHCl₂ solution showed a sharp resonance at 73.0 p.p.m. upfield from CFCl₃.

Anal. Calcd. for $C_{17}H_{26}As_2F_{12}NiO_2$: C, 29.1; H, 3.70. Found: C, 29.0; H, 3.70.

The Preparation of $NH_2CH_2CH(C(CH_3)_3)CH_2NH_2-MCl_2$ (M = Pd or Pt)

An equimolar quantity of the diamine ligand (0.2 g) was added to an aqueous solution of K_2MCl_4 and stirred at 50° for 2–3 min. The precipitate of complex chloride was filtered and washed with water until no chloride ion could be detected by silver nitrate solution. This almost colorless material was used directly for further syntheses. The Preparation of $(NH_2CH_2CH(C(CH_3)_3)CH_2)$ - NH_2)₂ MCl_2

The diamine ligand was added to an equimolar quantity of (NH₂CH₂CH(C(CH₃)₃)CH₂NH₂)MCl₂ in water (15 ml), then stirred and heated (80°) until most of the insoluble material had dissolved. The solution was filtered and the filtrate reduced in volume (1 ml). The white product was precipitated by the addition of acetone, then recrystallized from concentrated solutions of water (5°) (yield ~85%).

Anal. Calcd. for C₁₄H₃₆Cl₂N₄Pt: C, 31.9; H, 6.8; N, 10.6. Found: C, 31.8; H, 7.0; N, 10.9

Anal. Calcd. for C14H36Cl2N4Pd: C, 38.4; H, 8.3; N, 12.8. Found: C, 38.4; H, 9.0; N, 12.9.

The deuterated analogs were prepared similarly.

The Preparation of $[(bipy)MNH_2CH_2CH(C(CH_3)_3) CH_2NH_2]Cl_2$

 α, α' -Dipyridyl (0.2 g) was added to an equimolar quantity of NH2CH2CH(C(CH3))CH2NH2MCl2 in water (20 ml) then stirred and heated (90°) for 1 h under an atmosphere of nitrogen. The resulting solution was filtered, then reduced in volume (1 ml) before acetone was added to precipitate the product. The pure (yellow) products were obtained by recrystallizing twice from concentrated solutions of acetone-water at 5° (yield 80%). Anal. Calcd. for C17H26Cl2N4Pd.2H2O: C, 40.9; H,

6.0; N, 11.2. Found: C, 40.5; H, 6.2; N, 11.0. Anal. Calcd. for $C_{17}H_{26}Cl_2N_4Pt.2H_2O$: C, 34.6; H,

5.1; N, 9.5. Found: C, 34.2; H, 5.6; N, 9.4.

The n.m.r. spectra of the Pd and Pt complexes have signals attributed to the dipyridyl group at 8.21 and 8.75 p.p.m. and 8.14 and 8.75 p.p.m., respectively, from external TMS. The signals attributed to the six-membered ring protons are summarized in Table 1.

Results and Discussion

The new ligand 1,3-diamino-2-t-butylpropane, 4, was prepared from the appropriate diol via the azide (Scheme 1). Althought the method is not original (14, 15) it is given in detail since deviations result in diminished yields.

The n.m.r. spectrum of the amine was as expected and, although it was not subjected to microanalysis, the complete characterization of its complexes leaves no doubt that it is formulated correctly.

The bis dimethylarsino analog 3 reacts with nickel tetracarbonyl to afford the expected chelate complex $(L-L)Ni(CO)_2 (L-L = 3)$. This complex which contains nickel in the zero oxidation state is probably pseudo tetrahedral. The diamagnetic square planar complex (L-L)Ni(PFP) (L-L =3, $PFP = ^{-}O - C(CF_3)_2 - C(CF_3)_2 - O^{-})$ which contains nickel(II) was also prepared.

In order to simplify the n.m.r. spectra the complex $(L-L)Ni(CO)_2$ $(L-L = 3-d_2)$ was measured in a saturated benzene solution (the complex decomposes in $CHCl_3$). The spectrum of the ring protons is of the ABX type. The downfield





Both nickel complexes have vicinal coupling constants for the protons on the ring carbons with values of approximately 12 and 1 Hz (Table 1). The former value is representative of an axial-axial interaction between the two vicinal protons and indicates that the *t*-butyl group occupies an equatorial position with respect to the 'locked' ring. The values are comparable to those found in the analogous group VIB complexes which are thought to have puckered chair configurations (4). The ${}^{3}J_{H_{nx} - H_{eq}}$ coupling (~1 Hz) for these nickel complexes are slightly smaller than they are for the analogous manganese tricarbonyl halides ($\sim 2 \text{ Hz}$) (5) and may indicate that the nickel compounds are slightly

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TABLE 1. Selected n.m.r. parameters of complexes^a

			8					J _{H-H}			1
					-CH ₃	As(N)	Vic	inal		J _{P1}	Ŧ
	As(C)	H ₃) ₂	C(CH ₃) ₃	-CHR-	H _{ax}	Heq	Jax-cq	J _{ax-ax}	J	J _{Pt-Heq}	J _{Pt-flax}
(CO) ₂ NiAs(CH ₃) ₂ CH ₂ CH(C(CH ₃) ₃)CD ₂ As(CH ₃) ₂	1.01	1.02	0.71	0.94	0.70	1.66	6.0	11.7	- 12.4		
PFPNiAs(CH ₃) ₂ CH ₂ CH(C(CH ₃) ₃)CD ₂ As(CH ₃) ₂	1.34	1.39	0.88	1.07	1.04	1.78	1.2	12.3	- 12.9		
Cl ₂ Pt[NH ₂ CH ₂ CH(C(CH ₃) ₃)CD ₂ NH ₃] ₂ A isomer			1.352	1.94	2.99	3.48	2.9	11.2	-12.5	62.0	22.0
B ISOMET			766.1	1.94	06.7	5.48	4.7	c.11	- 12.5	0.20	0.22
Cl ₂ Pd[NH ₂ CH ₂ CH(C(CH ₃) ₃)CD ₂ NH ₂] ₂ A isomer			1.354	1.88	2.87	3.39	2.9	11.2	-12.7		
B isomer			1.354	1.88	2.85	3.39	2.9	11.2	- 12.7		
bipyPt[NH2CH2CH(C(CH3)3)CD2NH2]			1.40	2.23	3.17	3.54	3.5	10.9	-12.8	54.5	30.5
bipyPd[NH2CH2CH(C(CH3)3)CD2NH2]			1.41	2.12	2.96	3.46	3.13	11.0	-12.8		
"Chemical shifts are given downfield from external TMS in p.	p.m. The	couplings	involving platinur	n were measured	from spec	tra obtait	ned from	a Varian	XL-100 spect	rometer usin	g Fourier

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transform techniques. Couplings are given in Hz.

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more puckered. The small differences, however, may be caused by inductive effects and not by conformational distortions. It is not surprising to find that the conformation of the chelate ring in the octahedral and square planar complexes is very similar since the As-M-As angle is expected to be $\sim 90^{\circ}$ and this, together with the As—M distance is expected to have the greatest effect on ring conformations (2, 7). The 'tetrahedral' nickel complex (L-L)Ni(CO)₂ could be expected to have a different degree of puckering because the As-Ni-As could be greater than 90° but it seems that the angle subtended by a ligand at a metal is more a function of of the ligand than the metal. For example the P-Fe-P angle in the isoelectronic complex $(C_6H_5)_2PC = CP(C_6H_5)_2CF_2CF_2CF_2Fe(NO)_2$ is 87° (16).

The n.m.r. spectra of the nickel complexes were not measured in the same solvents as the analogous $M(CO)_4$ and $M(CO)_3X$ complexes because of solubility and stability problems. This makes it difficult to make a detailed comparison of the chemical shifts of the ring protons. It is probably significant that H_{ax} is considerably upfield of H_{eq} in the $-CH_2$ - group as is the case for the $(L-L)M(CO)_4$ complexes of ligands 1 and 3 (4). However in the 'locked' $(L-L)M'(CO)_3X$ complexes of ligand 1, H_{ax} (2.24 p.p.m.) is downfield of H_{eq} (1.77 p.p.m.) (values are for X = Br) and the same trend is seen in the isomer of the $(L-L)M'(CO)_3X$ complex of ligand 3 which has the same conformation (A, R = H or *t*-butyl). In the case where X = Br, H_{ax} is at 1.86 p.p.m. and H_{eq} at 1.91 p.p.m. This downfield shift for H_{ax} when it is adjacent to an axial halogen on the metal may indicate some interaction between the two.

The diamine 4 reacts with MCl_4^- (M = Pt, Pd) to afford the insoluble MCl_2 derivatives which were not suitable for n.m.r. studies. Fortunately further reaction of 4 afforded the ionic $(L-L)_2M^{2+}2Cl^-$ which could be investigated in aqueous solution. In order to obtain a complex with only one ligand 4 chelated to the group VIII metal, the insoluble MCl_2 derivatives were treated with α, α' -dipyridyl to afford the water soluble $(L-L)M(bipy)^{2+} 2Cl^-$ complexes.

Figure 1 shows the n.m.r. spectrum of the ring protons of the platinum-bipy complex dissolved in D_2O . The upfield (X) portion of this ABX spectrum is considerably sharpened when the sample is deuterium decoupled and is associated with the proton on the central ring carbon. The AB portion of the spectrum is assigned to the protons on the ring carbon atom that is adjacent to a nitrogen atom. The equatorial proton has a chemical shift at lower field than the axial proton on the same carbon. The magnitudes of the coupling constants (Table 1) indicates an axial-axial interaction between protons 2 and 3, A which requires the *t*-butyl group to have taken an equatorial position and effectively locked the six membered ring. The n.m.r. spectrum of the diamine metal complexes definitely eliminates the possibility of any existence of skew-boat con-

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formers because a locked configuration of this type would lead to two conformers (depending upon the positions of the $-CD_2$ and $-CH_2$ -groups relative to the ring). The ${}^{3}J_{Pt-H}$ couplings also provide evidence for a locked chair configuration as will be described below.

The parameters from the analogous palladium complex indicate a very similar structure in solution.

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The n.m.r. spectrum of the ion $(L-L)_2 Pt^{2+}$ (L-L = 4) is shown in Fig. 2. Analysis of the spectrum shows that two isomers are present in solution in equal amounts. The derived parameters for the two isomers are nearly identical indicating both isomers have their six-membered rings locked in chair configurations with the t-butyl group equatorial (for the same reasons as those given for the dipyridyl complexes). The two isomers undoubtedly have the structures shown in Fig. 3 where both rings are locked with the t-butyl groups equatorial. The chemical shifts of the axial protons on the N-CH2-group differ slightly for each isomer and examination of Fig. 3 shows that these are the protons whose magnetic environment changes most in the two isomers. The palladium analog shows the same isomer distribution and the n.m.r. parameters indicate identical structures in solution. In a similar study of $(L-L)_2 M^{2+}$ complexes Appleton and Hall (17, 18) isolated isomeric compounds for $L-L = meso-H_2NCH(CH_3)CH_2CH(CH_3)NH_2.$ These are probably related as in Fig. 3 with the equatorial methyl groups providing the locking force. However the 60 MHz n.m.r. spectra did not reveal the difference. Their vicinal ${}^{3}J_{H-H}$ couplings of 2.5 Hz (ax-eq) and 11.0 Hz (ax-ax)



FIG. 3. Structures of the two isomers of $[Pt(NH_2-CH_2CH_2NH_2)_2]^{2+}$.

are similar to those obtained in the present investigation. In another paper (19) n.m.r. evidence for geometric isomerism was obtained by these workers when L-L is H_2NCH_2 -CHOHCH₂NH₂.

It seems that ${}^{3}J_{Pt-H}$ couplings follow a Karplus type relationship where the *trans* coupling is expected to be ~90 Hz and the *gauche*, ~31 Hz from amino acid derivatives (20) or ~65 and ~15 Hz, respectively, from diamine complexes (19, 21). In the platinum complexes of **4** both isomers of $(L-L)_2Pt^{2+}$ have the same values indicating that there is little steric interaction between the two halves of the ion. Furthermore the ratio ${}^{3}J_{Pt-Heq}/{}^{3}J_{Pt-Hax}$ is ~3. This indicates that the very similar values obtained by Appleton and Hall do indicate locked six-membered rings in the complexes of $H_2NCH_2CHXCH_2NH_2$ (X = Cl, OH) (19). In the dipyridyl complex of **4** the ${}^{3}J_{Pt-H}$ couplings are considerably changed although their sum (54.5 + 30.5) Hz is much the same as in the $(L-L)_2Pt^{2+}$ complexes of the same ligand. This suggests that a conformational change involving the N—Pt—N and CNNC planes, has taken place since the ${}^{3}J_{H-H}$ are invarient.

Although it is difficult to compare coupling constants obtained from different compounds in different solvents, it seems that the ditertiary arsine complexes have slightly larger ${}^{3}J_{H_{ax}-H_{ax}}$ and smaller ${}^{3}J_{H_{ax}-H_{eq}}$ values than the diamine complexes. This could indicate that the diamine complexes are less puckered.

Our study indicates that the chemical shift of protons attached to ring carbons bonded to nitrogen are at lower field than those bonded to the central ring carbon and agreee with the results of Appleton and Hall (17, 19, 21). For a pair of geminal protons, the axial proton is as usual (22, 23) at higher field than the equatorial proton. In the arsenic complexes investigated the protons on the carbon bonded to arsenic are at much higher field than in the nitrogen complexes. This is presumably caused by the more electropositive nature of the arsenic atom relative to nitrogen.

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