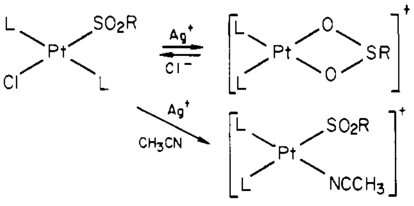
Scheme I



L = PPh_3, PMe_2Ph

$(CH_3C_6H_4SO_2)]PF_6$ gave the original sulfinato-*S* complex $[Pt(PMe_2Ph)_2(CH_3C_6H_4SO_2)Cl]$.

The addition of $AgPF_6$ in acetonitrile to the sulfinato complexes did not give the rearranged sulfinato-*O,O′* complexes but instead gave the complexes $[Pt(PPh_3)_2(CH_3CN)(SO_2R)]PF_6$, which have intense sulfinato S=O absorption in the 1230- and 1060-cm^{-1} regions (see Table I) and nitrile C≡N absorption in the 2300–2310 cm^{-1} region. These compounds also have the very intense PF_6 absorption centered at 840 cm^{-1}.

The products of reactions conducted in this study are summarized in Scheme I. In contrast to the facile migration of alkyl or aryl R′ groups from CO to Pt upon treatment of $[Pt(PR_3)_2Cl(R'CO)]$ with silver ion,[5] the reaction of $[Pt(PR_3)_2Cl(R'SO_2)]$ with silver ion does not lead to migration of R′ from SO_2 to Pt but rather to rearrangement of the sulfinato-*S* to the sulfinato-*O,O′* complex. The difficulty of elimination of SO_2 from sulfinato complexes and a significant barrier to desulfonylation may thus be attributed to the possible rearrangement of the sulfinato-*S* to the sulfinato-*O,O′* complex, which will utilize vacant coordination sites needed for alkyl or aryl migration.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. R.K.R. and M.R.K. were National Science Foundation Undergraduate Research Participants.

Registry No. $Pt(PPh_3)_2Cl(CH_3SO_2)$, 57692-69-0; $Pt(PPh_3)_2Cl(C_2H_5SO_2)$, 80975-57-1; $Pt(PPh_3)_2Cl(C_3H_7SO_2)$, 80964-52-9; $Pt(PPh_3)_2Cl(C_6H_5SO_2)$, 57692-70-3; $Pt(PPh_3)_2Cl(p\text{-}ClC_6H_4SO_2)$, 80975-56-0; $Pt(PPh_3)_2Cl(p\text{-}CH_3C_6H_4SO_2)$, 80964-51-8; $Pt(PPh_3)_2Cl(p\text{-}CH_3OC_6H_4SO_2)$, 80964-50-7; $Pt(PPh_3)_2Cl(p\text{-}NO_2C_6H_4SO_2)$, 80964-49-4; $[Pt(PPh_3)_2(CH_3SO_2)]PF_6$, 80964-57-4; $[Pt(PPh_3)_2(C_3H_7SO_2)]PF_6$, 80964-59-6; $[Pt(PMe_2Ph)_2(CH_3C_6H_4SO_2)]PF_6$, 80964-61-0; $[Pt(PPh_3)_2(CH_3CN)(CH_3SO_2)]PF_6$, 80964-48-3; $[Pt(PPh_3)_2(CH_3CN)(p\text{-}ClC_6H_4SO_2)]PF_6$, 80975-55-9; $[Pt(PPh_3)_2(CH_3CN)(p\text{-}CH_3OC_6H_4SO_2)]PF_6$, 80964-46-1; $Pt(PMe_2Ph)_2Cl_2$, 38928-82-4; $(Ph_3P)_4Pt$, 14221-02-4; $Pt(PPh_3)_2C_2H_4$, 12120-15-9.

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Cyclometalation of Arylazo Compounds. 3.[1] Determination of the Chelate Ring Size in a Peri-Palladated 1-Arylazonaphthalene by Nitrogen-15 Nuclear Magnetic Resonance

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Received December 7, 1981

Our interest in regiospecific cyclopalladation has been stated before.[1,3] By altering substituents in the arylazonaphthalene ligand, the site of metalation at either of the three ortho positions could partially be governed. Cyclopalladation at the peri position in the naphthyl moiety was achieved only after all the ortho positions had been substituted by methyl groups. Thus, the azo ligand **3** reacted with Na_2PdCl_4 to complex **4** with a Pd–arene σ bond at carbon atom C(8), as was confirmed by ^{1}H NMR[1] and by cleaving the Pd–C bond with $NaBD_4$.[2] No decision could be made, however, as to which of the azo nitrogen atoms had been coordinated: closure of the chelate ring at N_α[4] would result in a five-membered ring structure, whereas cyclopalladation at N_β[4] would lead to a six-membered chelate.

According to Cope and Friedrich,[5] the formation of a five-membered chelate seems to be a necessary prerequisite for cyclopalladation to occur. This has been corroborated by numerous cyclopalladated complexes,[6-8] and to our knowledge only three examples of six-membered Pd chelates with Pd–C σ bonds have been reported in the literature.[9,10,20] In other cases, an intermediate formation of a six-membered palladacycle in a Pd(II)-catalyzed reaction can be postulated.[11,12]

^{15}N NMR spectroscopy has proved to be a promising method for distinguishing between the two possible structures of complex **4**: as bonding to a nitrogen lone pair (by a proton[13] or by a metal center[14]) causes dramatic changes in ^{15}N chemical shifts, ^{15}N labeling of either N_α or N_β and comparing the ^{15}N resonances of the ligands with those of the palladated complexes would offer conclusive proof of the chelate ring size.

Experimental Section

^{15}N NMR Spectra. Ligands and complexes were measured as 2% $(CH_3)_2SO$[15] solutions on a Bruker WM-250 spectrometer[16] operating at 25.33 MHz in the FT mode. ^{15}N chemical shifts are related to formamide as external reference (112.4 ppm with respect to 0 ppm for anhydrous liquid ammonia at 25 °C[17]).

^{15}N-labeled ligands **1** ($^{15}N_\beta$) and **3** ($^{15}N_\beta$) and Pd(II) complexes **2** ($^{15}N_\beta$) and **4** ($^{15}N_\beta$) were synthesized in the same way as their unlabeled analogues.[1] The $^{15}N_\beta$ label was introduced by diazotization of 1-aminonaphthalene with $Na^{15}NO_2$ (Stohler Isotope Chemicals, 99% ^{15}N). For the $^{15}N_\alpha$-labeled azo ligand **3** ($^{15}N_\alpha$), a partially different method was applied: 1-[^{15}N]amino-2-methylnaphthalene was synthesized by nitration of 2-methylnaphthalene[18] with $H^{15}NO_3$ (60.2% solution, Stohler Isotope Chemicals, 99% ^{15}N) and Béchamp reduction of the resulting nitro compound.[19] Diazotization of 1-

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(1) This is the third communication on compounds with a metal–arene σ bond; Part 2: Hugentobler, M.; Klaus, A. J.; Mettler, H.; Rys, P.; Wehrle, G. *Helv. Chim. Acta* **1982**, *65* (4).

(2) Results taken from: Hugentobler, M. Ph.D. Dissertation No. 7020, ETH, Zürich, Switzerland, 1982.

(3) Klaus, A. J.; Rys, P. *Helv. Chim. Acta* **1981**, *64*, 1452–1466.

(4) The naphthalene moiety was chosen as parent component (IUPAC rule no. C-912); therefore N_α is the azo nitrogen adjacent to the naphthyl and N_β the one adjacent to the phenyl ring (see Figure 1).

(5) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909–913.

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(15) $(CH_3)_2SO$ was partially deuterated (15% ^{2}H).

(16) We thank F. Bangerter for the NMR spectroscopic measurements and P. S. Pregosin for helpful discussions of the interpretation of the NMR spectra.

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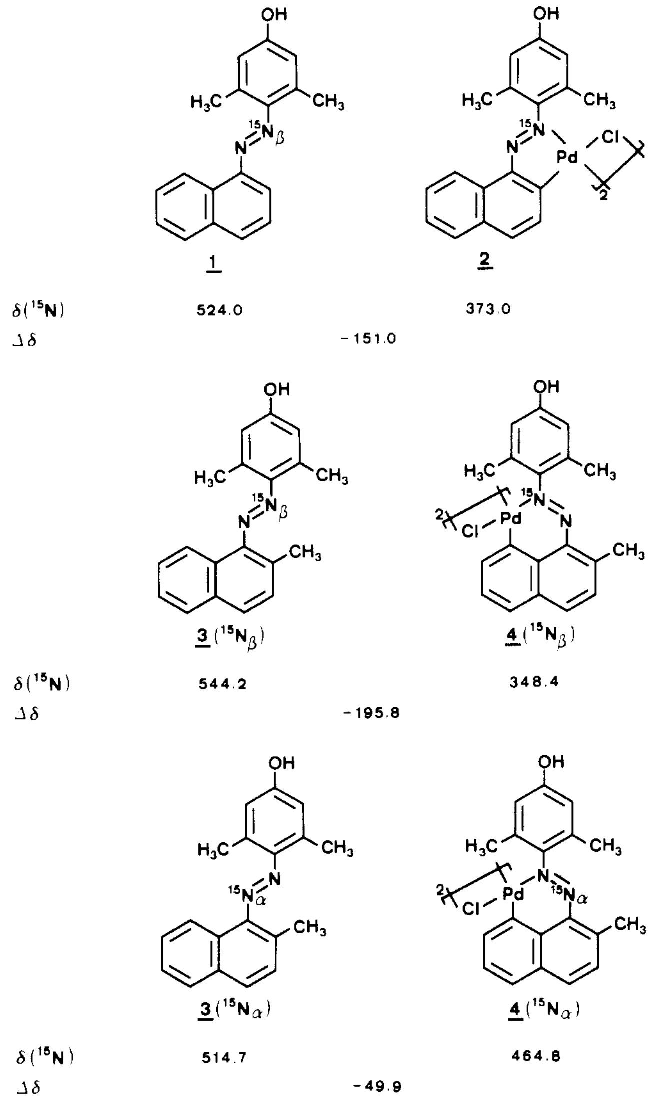

Figure 1. ^{15}N NMR data for azo ligands and corresponding Pd(II) complexes. ^{15}N chemical shifts are measured in ppm relative to formamide (112.4 ppm with respect to 0 ppm for anhydrous liquid ammonia), with 2% solutions of ligands and complexes in partially deuterated $(CH_3)_2SO$ (15–20% deuterium content). All ^{15}N signals appear as singlets. $\Delta\delta = \delta(^{15}N)_{complex} - \delta(^{15}N)_{ligand}$; negative sign means shift to high field of the ligand ^{15}N resonance.

[^{15}N]amino-2-methylnaphthalene with unlabeled $NaNO_2$ and subsequent coupling on 3,5-dimethylphenol led to **3** ($^{15}N_\alpha$), which formed complex **4** ($^{15}N_\alpha$) upon cyclopalladation with Na_2PdCl_4.

Results and Discussion

The ^{15}N chemical shifts of $^{15}N_\alpha$- and $^{15}N_\beta$-labeled ligands and complexes are presented and compared in Figure 1. Direct coordination of the palladium(II) center to the labeled azo nitrogen atom as in complex **2** causes a high-field shift of the ^{15}N resonance by 151 ppm. This difference in chemical shift ($\Delta\delta$) is in the same range and has the same direction toward higher field as was reported for protonated azobenzene compared with azobenzene (−150 ppm)[13] or for a Pt(II) complex with an *o,o′*-dihydroxyazobenzene ligand (−180 ppm).[14] When the ^{15}N-labeled ligand **3** ($^{15}N_\beta$) is cyclopalladated, the $^{15}N_\beta$ resonance is shifted toward high field by almost 200 ppm, which suggests a ring closure at N_β and the formation of a six-membered ring structure. We cross-checked this result with the $^{15}N_\alpha$-labeled ligand **3** ($^{15}N_\alpha$): cyclopalladation still results in a high-field shift of the resonance of $^{15}N_\alpha$ adjacent to the unlabeled, coordinated nitrogen atom, but to a lesser extent (−50 ppm). This result, too, is compatible with other data ($\Delta\delta$ = −60 ppm for coordination of Pt(II) to the adjacent, unlabeled azo nitrogen).[14]

Conclusion

The data discussed above (see Figure 1) unambiguously assign the *six-membered* chelate structure **4** to the Pd(II) complex obtained by peri palladation of the tri-ortho-methylated azo ligand **3**. To the best of our knowledge, the formation of a six-membered in preference of a five-membered chelate ring upon cyclopalladation of an N-donor ligand is unique. Our results do not exclude an intermediate cyclopalladation via a five-membered chelate and subsequent recoordination at N_β to the thermodynamically more stable complex **4** with the six-membered palladacycle.

Registry No. **1**, 1778-72-9; **2**, 81205-90-5; **3**, 81205-85-8; **4**, 81205-91-6.

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ω,ω′-Dialkylated Tetraaza Linear Ligands as More Appropriate Reference Ligands for Tetraaza Macrocycles. A Comparison of 1,4,7,10-Tetraazadodecane with 3,6-Diaza-1,8-diaminooctane

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and Piero Paoletti*

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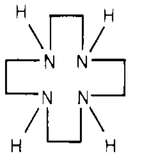
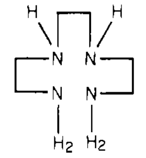
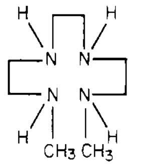
In making comparisons of the thermodynamic properties of metal complexes of tetraaza macrocyclic ligands with analogous noncyclic ligands, all authors to date have chosen simple linear tetraamines containing unsubstituted nitrogen atoms as reference ligands.[1] Thus for the smallest tetraza macrocyclic ligand, 1,4,7,10-tetraazacyclododecane (L_1) (I), the noncyclic tetraamine 3,6-diaza-1,8-diaminooctane (L_2) (II) has been used as a reference.[2]



I



II



III

This practice, which undoubtedly originates from the ready availability of compounds such as L_2, is open to some criticism since L_1 contains four secondary nitrogen atoms whereas L_2 contains two primary and two secondary nitrogen atoms. Previous studies with N-methylated ethylenediamines indicated that replacing one primary with one secondary nitrogen caused the enthalpy of formation of the copper(II) complexes to become between 0.4 to 1.0 kcal mol^{-1} less negative per substituted nitrogen atom.[3] Thus one might reasonably expect that the enthalpy of formation of the copper(II) complex of 1,4,7,10-tetraazadodecane (L_3) (III) would be between some 1 or 2 kcal mol^{-1} less negative than that of L_2.

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