then the reduction potentials would be expected to be essentially the same. The enhanced ease of electron addition must be due to the unfilled d subshells of Fe(II).

Our results are partially at variance with the crystallographic data reported for $[Na(DB\text{-}18\text{-}crown\text{-}6)(THF)_2])^+[Fe(TPP)]^-$.[13] The latter complex, which was crystallized from a pyridine solution, does not give any evidence for axial ligation and has a different skeletal geometry from Fe(TPP). Indeed, our optical studies indicate that axial ligation apparently occurs only at low temperatures in frozen solutions. On the other hand, geometry differences of the reported magnitude should result in observable vibrational frequency differences.[18] Solid-state effects might be the origin of the geometric differences between crystalline Fe(TPP) and $[Fe(TPP)]^-$, since the present Raman studies do not indicate that there are substantial differences for the solution species at room temperature. Nevertheless, the explanation for the unusual optical spectrum of $[Fe(TPP)]^-$ remains unclear and must await a rigorous theoretical investigation.

Acknowledgment. We thank Dr. Hiroshi Sugimoto for assistance with the synthesis of $^{57}Fe(TPP)Cl$ and Professor Harold M. Goff for providing a preprint of the manuscript describing his deuterium NMR study. This work was supported by the National Science Foundation, under Grant No. CHE-8212299 (D.T.S.), and the National Institutes of Health, under Grant No. GM-30078 (D.F.B.).

Registry No. $[Fe(TPP)]^-$, 54547-68-1; $[Fe(TPP)](py)^-$, 96531-99-6; Fe(TPP), 16591-56-3.

Department of Chemistry
University of California
Riverside, California 92521

G. Susan Srivatsa
Donald T. Sawyer
Nancy J. Boldt
David F. Bocian*[1]

Received November 14, 1984

Solution Structure of Five-Coordinate Complexes of Ruthenium(II): Evidence for a Square-Pyramidal Geometry for the Cations $[RuXL_4]^+$ (X = H, C_2Ph; L = PMe_2Ph)

Sir:

We wish to report 32-MHz $^{31}P\{^1H\}$ NMR studies of the five-coordinate cations $[RuXL_4]^+$ (X = H, C_2Ph; L = PMe_2Ph), which, in conjunction with corresponding data from the closely related six-coordinate species $[RuX(PMe_2(MeO\text{-}2\text{-}C_6H_4))_4]^+$, provide the first direct evidence of the square-pyramidal geometry *in solution* for five-coordinate d^6 metal complexes containing phosphine ligands.

Although X-ray diffraction studies[1] and a theoretical treatment[2] indicate that the square pyramid is the more favored geometry for five-coordinate d^6 ions, experimental evidence for this structure *in solution* has proved elusive. For example, the catalytically important complexes $[RuCl_2(PPh_3)_3]$[3] and $[RuHCl(PPh_3)_3]$[4] in the solid state are square-pyramidal[5,6] but in solution at low temperature show an A_2X pattern of $^{31}P\{^1H\}$ signals[1] and cannot therefore rule out the alternative trigonal-bipyramidal structure. In complexes with four coordinated phosphorus nuclei, distinction between the two stereochemistries by ^{31}P NMR should be straightforward, the square-pyramidal geometry giving A_2MX or A_4 spectra and the trigonal-bipyramidal A_2X_2 or A_3X spectra. Thus, McAuliffe et al. have interpreted[7] the ^{31}P NMR spectra of $[RuX(L_2)_2][BPh_4]$ (L_2 = $Ph_2P(CH_2)_3PPh_2$, X = Cl; L_2 = $Ph_2P(CH_2)_3PMe_2$, X = H, Cl) as showing a rigid trigonal-bipyramidal structure for these complexes. Their observations do not, however, constitute "unambiguous findings", as claimed (vide infra).

Table I. ^{31}P NMR Data for $[RuXL_4][PF_6]$ Complexes

L	X	T^a	$\delta_A{}^b$	δ_M	δ_X	$J_{AM}{}^c$	J_{AX}	J_{MX}
PMe_2Ph	C≡CPh	183	4.7	−3.1	30.4	26	33	26
$PMe_2(oA)^d$	C≡CPh	303	−0.5	6.2	28.2	33	28	33
PMe_2Ph	H	193	9.2	−8.2	33.8	20	37	20
$PMe_2(oA)$	H	273	4.5^e		38.2		38	20

[a] Temperature in kelvins. [b] Chemical shifts relative to external H_3PO_4. [c] Coupling constants in hertz. [d] oA ≡ $MeO\text{-}2\text{-}C_6H_4$. [e] Second-order system not analyzed.

The salt $[Ru(C{\equiv}CPh)L_4][PF_6]$ (**1**; L = PMe_2Ph),[8a] prepared from $[RuHL_5][PF_6]$[9] and PhC≡CH, shows a single ^{31}P resonance (15 ppm) at 30 °C in CD_2Cl_2 which at −60 °C separates into three signals of intensity 1:2:1 (X:A_2:M) and at −90 °C resolves into three multiplets characterized by the parameters in Table I. The line widths of ~6 Hz prevent distinction between the values of J_{AM} and J_{MX}. The color of the solution at all temperatures is the same as observed in the solid state, viz. purple, which discounts the possibility of strong solvation.[8b]

The NMR pattern is clear evidence[8c] in favor of the square-pyramidal geometry for this complex and the substantial deshielding of the signal assigned as the apical phosphorus P_X is reminiscent of the data for $[RuCl_2(PPh_3)_3]$ and $[RuHCl(PPh_3)_3]$ in which the great difference in ^{31}P chemical shifts suggests that the square-pyramidal structure is maintained as it is characterized by widely different bond lengths $Ru\text{–}P_{basal} > Ru\text{–}P_{apical}$.[5,6] The crystal structure determination[8] of complex **1** gives the metal–phosphorus bond lengths $Ru\text{–}P_A$ = 2.40 Å, $Ru\text{–}P_M$ = 2.34 Å, and $Ru\text{–}P_X$ = 2.22 Å, reaffirming the correlation with $\delta(^{31}P)$ values.

The room-temperature ^{31}P spectrum of complex **1** [L = $PMe_2(MeO\text{-}2\text{-}C_6H_4)$] is also of the A_2MX type, but in this case an OMe group is weakly coordinated[11] cis to the alkynyl ligand, thus generating a pseudooctahedral geometry.

The hydride complexes show changes with temperature similar to those of their alkynyl analogues; the solution in CD_2Cl_2 of six-coordinate $[RuHL_4]^+$ [**2**; L = $PMe_2(MeO\text{-}2\text{-}C_6H_4)$], which has a structure[11] analogous to the corresponding alkynyl complex,

---

(1) Hoffman, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 4221.
(2) Pearson, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 4947.
(3) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945.
(4) Hallman, P. S.; McGarvey, B. R.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3143.
(5) La Placa, S. J.; Ibers, J. A. *Inorg. Chem.* **1965**, *4*, 778.
(6) Skapski, A. C.; Troughton, P. G. H. *J. Chem. Soc., Chem. Commun.* **1968**, 1230.
(7) Briggs, J. C.; McAuliffe, C. A.; Dyer, G. *J. Chem. Soc., Dalton Trans.* **1984**, 423.
(8) (a) Ashworth, T. V.; Kruger, G. J.; Singleton, E., unpublished results. ^1H NMR showed samples did not contain solvent of crystallization (e.g. ethanol), which might have affected the ^{31}P NMR results. (b) In acetone solution, however, the complex is colorless at −50 °C showing solvation. (c) A reviewer has suggested the possibility that the observed pattern may arise from a trigonal-bipyramidal structure in which restricted rotation about the metal–phosphorus bonds gives rise to rotamers. We do not consider this a viable alternative since such a structure would render *all* phosphorus atoms nonequivalent and give rise to very different coupling constants. In addition, the salt $[RuH(Ph_2P(CH_2)_4PPh_2)_2][PF_6]$,[10] in which the use of bidentate ligands precludes rotamer complications, also gives rise to an A_2MX ^{31}P pattern (acetone-d_6, −80 °C): δ 78.6 (t), 37.9 (dd), −14.7 (t); J_{AM} = 21, J_{AX} = 30, $J_{MX} \leqslant 6$ Hz (M, X signals broadened); color of solution dark red.
(9) Ashworth, T. V.; Laing, M.; Nolte, M. J.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1977**, 1816.
(10) Ashworth, T. V.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1976**, 705.
(11) The X-ray crystal structures of both **1** and **2** [L = $PMe_2(MeO\text{-}2\text{-}C_6H_4)$] have been determined,[12] and the Ru–O distances of the coordinated methoxy group are 2.33 (3) and 2.31 (4) Å, respectively. This indicates weak bonding.[13] That the Ru–O interaction is maintained in solution is shown by the downfield shift of a methoxy carbon atom in the ^{13}C NMR spectrum of each of the compounds.[14]
(12) Ashworth, T. V.; Levendis, D. C.; Singleton, E., unpublished results.
(13) Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1979**, *18*, 2658.
(14) Roundhill, D. M.; Roundhill, S. G. N.; Beaulieu, W. B.; Baghi, U. *Inorg. Chem.* **1980**, *19*, 3365.

0020-1669/85/1324-2125$01.50/0

required only slight cooling before the A_2BX spectrum (Table I) was shown, whereas the CD_2Cl_2 solution of **2** (L = PMe_2Ph)[15] failed to give a slow-exchange spectrum at the lowest temperature available (173 K). However, the slow-exchange A_2MX spectrum (Table I) was achieved for **2** (L = PMe_2Ph) in acetone solvent, suggesting an important role for solvation in slowing the exchange process. The pattern of chemical shifts resembles that for the alkynyls, and assignment of square-pyramidal stereochemistry seems assured.

Our observations are therefore at variance with the conclusions drawn by McAuliffe and co-workers regarding the unequivocal establishment of the trigonal-bipyramidal geometry for a complex of ruthenium(II). The supposed mononuclear complexes $[RuCl(L_2)_2][BPh_4]$, which contain ^{31}P NMR signals at +45.7 ppm (L_2 = $Ph_2P(CH_2)_3PPh_2$) and +35.7 ppm (L_2 = $Ph_2P(CH_2)_3PMe_2$), may well be dimeric with chloride bridges analogous to those of the known complex $[RuCl(PMe_3)_4]_2Cl_2$[17] or at least undergo a rapid-exchange process with such a dimer, since *cis*-$[RuCl_2(Ph_2P(CH_2)_3PPh_2)_2]$ exhibits[18] a chemical shift value of +42.0 ppm for the phosphorus nuclei trans to chlorine and chloro complexes of ruthenium have a well-known tendency to form chloro-bridged species.[17–19] This interpretation would also explain the "absence" of fluxional behavior of the five-coordinate compounds reported in ref 7. We have synthesized $[Ru(C\equiv CCO_2Et)(Ph_2P(CH_2)_3PPh_2)_2][PF_6]$,[8] which is closely similar to $[RuCl(Ph_2P(CH_2)_3PPh_2)_2][BPh_4]$ except that the $-C\equiv CCO_2Et$ group would not be expected to bridge as readily as Cl^-. Our complex is fluxional in CD_2Cl_2 with a single ^{31}P resonance at 30 °C. At −80 °C, however, two triplets are observed, but rather than ascribing this to a trigonal-bipyramidal structure, we suggest two other possibilities: (i) a weak association of mononuclear units via coordination of the ketonic oxygen atom; (ii) a square-pyramidal structure with the alkynyl ligand at the apex and a pair of trans phosphorus atoms bent slightly away from the alkynyl group. The latter possibility has been described[20] for the compound *trans*-$[RuHCl(diop)_2]$. Of relevance to the proposals made herein is that the observed pair of triplets in the ^{31}P NMR spectrum of the latter complex was originally interpreted[21] as indicating a salt $[RuH(diop)_2][Cl]$ containing a trigonal-bipyramidal cation.

Finally, we have found that $[RuH(Ph_2P(CH_2)_3PPh_2)_2][PF_6]$[10] reacts with $CDCl_3$ to give a product that exhibits a doublet of triplets in the ^{31}P NMR (δ 43.2 and −3.8; J = 32 Hz), and it is very likely therefore that the similar pattern observed[7] for $[RuH(Ph_2P(CH_2)_3PMe_2)_2]^+$ is the result of reaction with the solvent.

We are continuing our studies on the solution structures of five-coordinate phosphine complexes of ruthenium(II) and hope to disclose further results in the near future; the evidence for a trigonal-bipyramidal geometry for such complexes remains inconclusive.

Registry No. **1** (L = PMe_2Ph), 96227-16-6; **1** (L = $PMe_2(oA)$), 96227-18-8; **2** (L = PMe_2Ph), 96211-42-6; **2** (L = $PMe_2(oA)$), 96227-20-2.

---

(15) Complex **2** (L = PMe_2Ph) was generated in situ by warming either a CD_2Cl_2 or an acetone-d_6 solution of the formato complex $[Ru(O_2CH)(PMe_2Ph)_4][PF_6]$.[16] Alternatively, it may be obtained by reaction of **1** (L = PMe_2Ph) with H_2.

(16) Ashworth, T. V.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1976**, 204.

(17) Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Abdul Malik, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 511.

(18) Jung, C. V.; Garrou, P. E.; Hoffman, P. R.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 726.

(19) Armit, P. W.; Boyd, A. S. F.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1663.

(20) Ball, R. G.; James, B. R.; Trotter, J.; Wang, D. K. W.; Dixon, K. R. *J. Chem. Soc., Chem. Commun.* **1979**, 460.

(21) James, B. R.; Wang, D. K. W. *Inorg. Chim. Acta* **1976**, *19*, L17.

National Chemical Research Laboratory
Council for Scientific and Industrial Research
Pretoria 0001, Republic of South Africa

Terence V. Ashworth
Anthony A. Chalmers
Eric Singleton*

Received November 2, 1984

Articles

Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

(Trifluoromethyl)sulfenyl, (Trifluoromethyl)sulfinyl, and (Trifluoromethyl)sulfonyl Derivatives of Heterocyclic Amines

O. D. GUPTA, WAN AHMAD KAMIL, and JEAN'NE M. SHREEVE*

Received December 10, 1984

1,8-Bis((trifluoromethyl)sulfenyl)-1,8,10-triaza-9-boradecalin, 1,4,7,10-tetrakis((trifluoromethyl)sulfenyl)-1,4,7,10-tetraazacyclododecane, 1,5,9-tris((trifluoromethyl)sulfenyl)-1,5,9-triazacycloundecane, 1,5-bis((trifluoromethyl)sulfenyl)octamethylcyclotetrasilazane, 1,3,5-tris((trifluoromethyl)sulfenyl)hexamethylcyclotrisilazane, 1,4-bis((trifluoromethyl)sulfenyl)piperazine, and 1,4,8,11-tetrakis((trifluoromethyl)sulfenyl)-1,4,8,11-tetraazacyclotetradecane result when CF_3SCl is reacted with the respective heterocyclic amines. Piperazine and 1,4,8,11-tetraazacyclotetradecane form analogous compounds with CF_3SO_2Cl and with $CF_3S(O)Cl$. The latter also forms 1,3,5-tris((trifluoromethyl)sulfinyl)hexamethylcyclotrisilazene with hexamethylcyclotrisilazane.

Introduction

(Trifluoromethyl)sulfur(II, IV, VI)-containing molecules have attracted considerable attention because of their biologically active nature. To date this has been particularly true for compounds where a sulfur–nitrogen bond is present, e.g., as secondary or tertiary amine derivatives.[1] The substituted amines are most often acyclic or aromatic, and only rarely is the nitrogen atom found as the heteroatom in the latter ring or in a saturated ring system.[2,3]

In this paper we report the syntheses of a variety of (trifluoromethyl)sulfenyl, (trifluoromethyl)sulfinyl, and (trifluoromethyl)sulfonyl N-substituted heterocyclic amines. The reagents of choice for the introduction of these groups into such compounds

---

(1) Newbold, G. T. In "Organofluorine Chemicals and Their Industrial Applications"; Banks, R. E., Ed.; Ellis Harwood Ltd: Chichester, England, 1979; Chapter 8.

(2) Haas, A.; Niemann, U. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 143 and references therein.

(3) Haas, A.; Kortmann, D. *J. Fluorine Chem.* **1978**, *11*, 337.

0020-1669/85/1324-2126$01.50/0 © 1985 American Chemical Society