Pergamon

0277-5387(94)00405-6

Polyhedron Vol. 14, No. 10, pp. 1295–1298, 1995

0277-5387/95 $9.50+0.00

THE COMPETITION FOR RUTHENIUM(II) BETWEEN PHOSPHORUS(III) AND NITROGEN(III) BINDING SITES IN 2-CYANOETHYLDIPHENYLPHOSPHINE

WILKER CAETANO, JANETE J. F. ALVES, BENEDITO S. LIMA NETO* and DOUGLAS W. FRANCO

Instituto de Química de São Carlos, Universidade de São Paulo, C.P. 780, 13560/970,
São Carlos, SP, Brazil

(*Received* 6 *September* 1994; *accepted* 13 *October* 1994)

Abstract—FTIR, ^{31}P NMR and $Ru^{III}/Ru^{II}E^{\circ\prime}$ ($+0.20\pm0.10$ V vs ECS) data strongly suggest that the ligand 2-cyanoethyldiphenylphosphine (2-CEDP) is bound to Ru^{II} by the cyano group, while the P^{III} site remains uncoordinated. The stability of $[Ru(NH_3)_5(2\text{-CEDP})]^{2+}$ in aqueous medium has been studied and the binuclear complex ion $[Ru(NH_3)_5\,2\text{-CEDP})Ru(NH_3)_5]^{2+}$ was formed by reacting $[Ru(NH_3)_5(H_2O)]^{2+}$ with the $[Ru(NH_3)_5(2\text{-CEDP})]^{2+}$ species, $k_1 = 1.7\times10^{-1}$ M^{-1} s^{-1} ($\mu = 0.10$ M, $NaCF_3COO/CF_3COOH$; $C_{H^+} = 1.0\times10^{-3}$ M, CF_3COOH).

The high affinity of the Ru^{II} centre for ligands such as phosphanes[1–3] and nitriles[1,4–7] is well known. This behaviour is explained as due to the intense $Ru^{II}\rightarrow$ ligand backbonding interaction which is operative in such systems.[2]

The 2-cyanoethyldiphenylphosphine ligand (2-CEDP) has two possible coordination sites, the P^{III} atom from the diphenylphosphine group and the nitrogen from the nitrile function. Therefore, this ligand offers an excellent opportunity to compare the relative abilities of the $P(Ph)_2$— and N≡C— groups in the 2-CEDP to coordinate to a Ru^{II} centre. There are many examples in the literature of ambidentate molecules and ions where the competition between nitrogen and sulphur, nitrogen and oxygen, sulphur and oxygen coordination atoms is considered.[1] However, as far as we know, the $[Ru(NH_3)_5(2\text{-CEDP})]^{2+}$ complex ion is the first example in the literature where the competition between N^{III} and P^{III} coordinating sites, in the same ligand, is reported.

This paper describes the synthesis, characterization and reactivity aspects of the $[Ru(NH_3)_5(2\text{-CEDP})]^{2+}$ complex ion.

EXPERIMENTAL

Reagents

2-Cyanoethyldiphenylphosphine was purchased from Stream and $RuCl_3$ from Degussa, and were used without further purification. All other chemicals were purchased from the Aldrich Chemical Co. and were used as supplied. The solvents employed were freshly distilled before use. Doubly distilled water was used throughout.

All the preparations were carried out under argon (White Martins S.A.), previously purified using $Cr(ClO_4)_2$ solutions.

Syntheses

$[Ru(NH_3)_5Cl]Cl_2$ and $[Ru(NH_3)_5(H_2O)](PF_6)_2$ were prepared as described in the literature.[8]

$[Ru(NH_3)_5(2\text{-CEDP})](PF_6)_2$ was prepared by adding the 2-CEDP ligand (400 mg) to $[Ru(NH_3)_5(H_2O)](PF_6)_2$ (100 mg) dissolved in acetone (18 cm^3). The mixture was allowed to react in the dark for *ca* 8 h. After rotoevaporation of the excess of acetone, a white solid was precipitated on addition of cold ethanol–ether (1 : 2) mixture. The solid was filtered and washed successively with cold ethanol and ether. This product was recrystallized

---

* Author to whom correspondence should be addressed.

from hot water. The yield was better than 55%. Found: C, 25.5; N, 3.1; H, 11.4. Calc.: C, 25.2; N, 4.0; H, 11.7%.

Apparatus and techniques

UV and visible spectra were recorded using a Hewlett–Packard model 8452A diode array spectrophotometer. IR spectra were recorded on KBr pellets using a Bomen model MB-102 spectrophotometer.

The NMR spectra were recorded at 200 MHz on a Bruker AC-200 instrument; the spectra of the ligand and complexes were obtained in $(CD_3)_2CO$. Phosphoric acid was used as internal standard.

Electrochemical measurements were performed using a PARC model 173 potentiostat and a PARC model 175 universal programmer coupled to a computer system for data acquisition. A glassy carbon electrode, a platinum wire and a saturated potassium chloride calomel electrode (SCE) were used in cyclic voltammetric experiments as the working, auxiliary and reference electrodes, respectively. The reversibility[9] of the Ru^{III}/Ru^{II} redox couple was verified on the basis of the ratio of cathodic to anodic peak currents (i_{pa}/i_{pc}) and the peak-to-peak potential separation ($\Delta E_{pa,pc}$).

A Corning model 130 pH meter and a Methron EA-147 microglass electrode were used for the pH determinations. All measurements were performed at 25.0 ± 0.1°C.

Rate studies

The loss of NH_3 from $[Ru(NH_3)_5(2\text{-CEDP})]^{2+}$ was followed using pyrazine (pz, 0.10 M, as auxiliary ligand; 0.10 M $NaCF_3COO$, 1.0×10^{-3} M CF_3COOH) and monitoring changes in absorbance at $\lambda = 442$ nm in the electronic spectrum as a function of time.

The reaction between $[Ru(NH_3)_5(2\text{-CEDP})]^{2+}$ and excess $[Ru(NH_3)_5(H_2O)]^{2+}$ was followed spectrophotometrically. From time to time a sample was taken and isonicotinamide (isn) was added. The concentration of the unreacted aquo species was determined by measuring the absorbance at 476 nm ($\varepsilon = 1.2 \times 10^4$ M cm^{-1}) due to the $[Ru(NH_3)_5(isn)]^{2+}$ formed (0.1 M $NaCF_3COO$; 1×10^{-5} M, CF_3COOH). Values of k_{obs} were obtained from $\log(A_\infty - A_t)$ versus t plots[10] and the second order specific rate constants according to: $k_1 = k_{obs}/[Ru(NH_3)_5(H_2O)]^{2+}$, in the usual way.[10]

RESULTS AND DISCUSSION

The compound $[Ru(NH_3)_5(2\text{-CEDP})](PF_6)_2$ was isolated from the reaction between $[Ru(NH_3)_5(H_2O)]^{2+}$ and the 2-CEDP species.

The ion $[Ru(NH_3)_5(2\text{-CEDP})]^{2+}$ in water–acetone (4 : 1) solution exhibits a maximum absorption at 307 nm [$(2.9 \pm 0.3) \times 10^3$ M^{-1} cm^{-1}], probably intraligand (IL) in character and a shoulder at 334 nm [$(3.8 \pm 0.2) \times 10^2$ M^{-1} cm^{-1}] attributed tentatively to a ligand field transition (LF).

No immediate colour development was observed by dissolving the solid $[Ru(NH_3)_5(2\text{-CEDP})](PF_6)$ salt in aqueous isn or pz solutions, suggesting that no labilization of NH_3 ligand in positions *cis* or *trans* to the 2-CEDP molecule in the coordination sphere was taking place. The solution of $[Ru(NH_3)_5(2\text{-CEDP})](PF_6)_2$ only undergoes aquation on a time of weeks ($t_{1/2} > 3 \times 10^2$ h), suggesting that the 2-CEDP molecule behaves as a weak *trans* labilizing ligand. The electronic spectrum of these aged solutions (1 week old), after addition of pyrazine exhibit a characteristic metal-to-ligand charge transfer band at 442 nm, suggesting that the product of aquation is *trans*-$[Ru(NH_3)_4(2\text{-CEDP})pz]^{2+}$ instead of *trans*-$[Ru(NH_3)_5pz]^{2+}$ [$\lambda_{max} = 471$ nm in water–acetone (4 : 1) medium, $\mu = 0.10$, $NaCF_3COO$; 1.0×10^{-3} M CF_3COOH].[11]

Neglecting the small differences in ligand field strength between the NH_3 and H_2O ligands,[1] a comparison among the spectral data of Table 1 for ruthenium complexes coordinated to the 2-CEDP, CH_3CH_2CN, CH_3CHCN, $P(Ph)_3$ and $(Ph)_2P(CH_2)_2P(Ph)_2$ ligands can be made. This analysis suggests that the 2-CEDP ligand behaviour is more like a nitrile than a phosphine. This is still more evident if we compare the energy of the MLCT bands for the pyrazine derivatives. For the phosphine complexes these $4d_\pi \rightarrow \pi^*$ transitions are in the 25.5 ± 0.1 kk range, whereas for the nitrile and acrylonitrile species the MLCT bands lie at lower energies (22.6–23.0 kk).

The IR spectrum of solid $[Ru(NH_3)_5(2\text{-CEDP})](PF_6)_2$ shows characteristic bands of the pentaammine moiety and of the 2-CEDP ligand. A small shift (10 cm^{-1}) relative to the free ligand [$\nu(C{\equiv}N) = 2252$ cm^{-1}] is observed for $\nu(C{\equiv}N)$ when the 2-CEDP ligand is coordinated to the Ru^{II} complex [$\nu(C{\equiv}N) = 2242$ cm^{-1}]. This behaviour is consistent with the coordination of a ligand to a metal centre through the nitrogen atom.[4,5,12]

The ^{31}P NMR spectrum of the new compound exhibits a singlet at 151.60 ppm due to the phosphorus atom of the 2-CEDP ligand. Since in the free 2-CEDP molecule, δ is 152.24 ppm, this

Table 1. UV-vis maxima bands, molar absorptivities and formal potentials for *trans*-$[Ru(NH_3)_4L_1L_2]^{2+}$ complexes

L_1	L_2	λ,[a] nm (ε,[b] $M^{-1}\ cm^{-1}$)	$E^{\circ\prime}_{Ru^{III}/Ru^{II}}$ (V vs SCE)[c]	Ref.
2-CEDP	NH_3	307 (2900), 334sh (380)	+0.20	[d]
CH_3CH_2CN	NH_3	262 (15000), 350sh (240)	+0.19	4,7
CH_2CHCN	NH_3	249 (8900), 352sh (4600), 372 (5200)	+0.30	5b,7
CH_3CH_2CN	H_2O	262 (4400), 378 (360)	+0.20	4
CH_2CHCN	H_2O	250 (5800), 378 (360)	+0.30	18
PPh_3	H_2O	386 (730)	+0.46	19,20
$(Ph)_2P(CH_2)_2P(Ph)_2$	H_2O	362 (650)	+0.50	21
2-CEDP	pz	442 (> 1400)		[d]
CH_3CH_2CN	pz	442 (800)	+0.64	4
CH_2CHCN	pz	434 (850)	+0.70	18
PPh_3	pz	393 (3000)	+0.77	20
$(Ph)_2P(CH_2)_2P(Ph)_2$	pz	392 (2200)		21

[a] ±2 nm.
[b] ±5–10%.
[c] ±0.01 V.
[d] This work.

result suggests that the point of attachment of the ligand in the Ru^{II} complex is not the phorphorus atom.

The voltammetric spectrum for the aqueous solution containing the $[Ru(NH_3)_5(2\text{-}CEDP)](PF_6)_2$ salt exhibits only the well defined and reversible $Ru^{III}+e \rightarrow Ru^{II}$ process, with $E^{\circ\prime} = 0.20 \pm 0.01$ V vs SCE, $\mu = 0.10$ $NaCF_3COO/CF_3COOH$, $C_{H^+} = 1.0 \times 10^{-3}$ M.

The IR and ^{31}P NMR data strongly suggest that the bonding site of the 2-CEDP ligand is the nitrogen and not the phosphorus atom. These data are in agreement with those obtained from the voltammetric spectra. Accumulated data for a long series of phosphanes[2,3] and nitrile[4–7] complexes indicate that the $E^{\circ\prime}_{Ru^{III}/Ru^{II}}$ in the *trans*-$[Ru(NH_3)_4P(III)(H_2O)]^{2+}$ complexes are in the +0.39 to +0.53 V range, and in the +0.20 to +0.30 V range for the $[Ru(NH_3)_5(NCR)]^{2+}$ species (some examples are cited in Table 1). Thus, as judged from the $E^{\circ\prime}_{Ru^{III}/Ru^{II}}$ data, the coordination site is more likely to be the nitrogen than the P^{III} atom.

The coordination through the nitrogen atom is consistent with the fact that the coordinated NH_3 molecule only undergoes aquation slowly. If the P^{III} group were coordinated to the Ru^{II} centre, due to the well known strong *trans* effect of P^{III} ligands in coordination complexes,[2,3] this aquation reaction should be a lot faster than observed in the present system. In all the reactions between the $[Ru(NH_3)_5(H_2O)]^{2+}$ and P^{III} ligands, one always observed the labilization of the NH_3 ligand in the position *trans* to P^{III} in the Ru^{II} coordination sphere, and the formation of the corresponding bisphosphite or bisphosphine complex.[2] This is not observed when L is 2-CEDP; indeed, in this system only one substitution is observed. Therefore, the inertness of the NH_3 molecule *trans* to L is consistent with the coordination of 2-CEDP through the nitrile group.

A question could be raised about how the relative affinities of the $N{\equiv}C$— and $P(Ph)_2$— groups are reflected by the $E^{\circ\prime}_{Ru^{III}/Ru^{II}}$ data. The use of the formal reduction potential values for the Ru^{III}/Ru^{II} couple as an indicator of the relative $Ru^{II} \rightarrow L$ back-bonding[2,3,13] is quite widespread; the more positive the potential, the more stabilized will be the Ru^{II} respecting the Ru^{III} centre by the $Ru^{II} \rightarrow L$ back-bonding interaction. Therefore, one can conclude that the $Ru^{II} \rightarrow P^{III}$ back-bonding interaction is stronger than the $Ru^{II} \rightarrow N{\equiv}C{-}R$ one. This is not correct, since $E^{\circ\prime}_{Ru^{III}/Ru^{II}}$ is the ratio of the relative affinities of the Ru^{III}/Ru^{II} centres for the ligand L. The fact that $E^{\circ\prime}_{Ru^{III}/Ru^{II}}$ for the nitrile species are less positive than the observed values for the similar phosphane complexes could be only a consequence of the high affinity of the nitrile group for both the Ru^{II} and Ru^{III} centres (see Table 1).

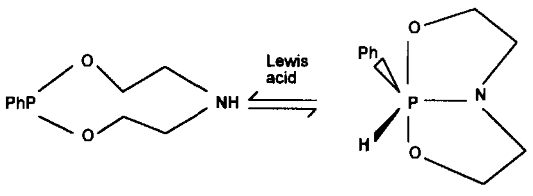
Despite the fact that 2-CEDP is an ambidentate ligand with the possibility of formation of six-membered metal chelates, our experimental data suggest that it acts as a monodentate ligand in the title compounds.

The accessibility of the P^{III} atom for coordination in the $[Ru(NH_3)_5(2\text{-}CEDP)]^{2+}$ complex ion has been evaluated through its reaction with $[Ru(NH_3)_5(H_2O)]^{2+}$:

$$[Ru(NH_3)_5(2\text{-CEDP})]^{2+} + [Ru(NH_3)_5(H_2O)]^{2+} \xrightarrow{k_1} [Ru(NH_3)_5(2\text{-CEDP})Ru(NH_3)_5]^{4+} + H_2O.$$

The numerical value of k_1, calculated from three independent experiments, is $(1.7 \pm 0.2) \times 10^{-1}\ M^{-1}\ s^{-1}$, which lies[14,15] in the range of the k_1 values observed for substitution reactions in $[Ru(NH_3)_5(H_2O)]^{2+}$.

The coordinating ability of phosphorus/nitrogen ambidentate ligands has also been investigated[16] with other species that display donor sites of distinctive character. This is the situation in the open eight-membered cyclic aminophosphane tautomer **1** of bicylic phosphane **2**.



1 2

The product of the reaction of $[Ru(NH_3)_5(H_2O)]^{2+}$ with ligand **1** shows a voltammetric spectrum exhibiting a reversible process with $E^{\circ\prime} = +0.45 \pm 0.01$ V vs SCE. As discussed above, this more positive $E^{\circ\prime}$ value is typical of coordination on the metal centre by a P^{III} site. In the case of ligand **1**, the characteristics of the nitrogen atom are not adequate for back-bonding exhibiting as a consequence, when compared with 2-CEDP, a quite diverse behaviour.

In the ligand **1** derivative compounds obtained so far,[17] the metal is always coordinated to phosphorus. The bridging ability of ligand **1**, with simultaneous coordination to nitrogen, depends on the experimental conditions and the ligand to metal ratio. This is accounted for by the higher donor character of P^{III} with respect to the nitrogen site in ligand **1**, which is not the case in the ligand 2-CEDP.

The complex ion $[Ru(NH_3)_5(2\text{-CEDP})]^{2+}$ is the first example in the literature where comparison is made between nitrogen (nitrile) and phosphorus (phosphine) coordination sites in the same ligand.

The results obtained in the present study, with the $[Ru(NH_3)_5]^{2+}$ moiety, are in agreement with the position of nitriles and phosphine in the π-acceptor series of monodentate ligands.[1] Studies with ligand **1** are now in progress at this laboratory and will be reported later.

Acknowledgements—We thank the CNPq, FAPESP, FINEP and CAPES for support of this work, and Professor Edson Rodrigues for reading the English manuscript.

REFERENCES

1. E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium*. Elsevier, Amsterdan (1984) and references therein; (b) G. Wilkinson, R. D. Gillard and J. A. McCleverty (Eds), *Comprehensive Coordination Chemistry*, Vols 2 and 4. Pergamon Press, Oxford (1987).
2. D. W. Franco, *Coord. Chem. Rev.* 1992, **119**, 199 and references therein.
3. J. C. Nascimento Filho, J. B. Lima, B. S. Lima Neto and D. W. Franco, *J. Molec. Catal.* 1994, **90**, 257.
4. J. J. F. Alves, A. M. G. Plepis, C. U. Davanzo and D. W. Franco, *Polyhedron* 1993, **12**, 2215.
5. (a) R. E. Clarke and P. C. Ford, *Inorg. Chem.* 1970, **9**, 227; (b) P. C. Ford, R. D. Foust and R. E. Clarke, *Inorg. Chem.* 1970, **9**, 1933.
6. R. J. Allen and P. C. Ford, *Inorg. Chem.* 1972, **11**, 679.
7. T. Matsubara and P. C. Ford, *Inorg. Chem.* 1976, **15**, 1107.
8. (a) L. H. Vogt, J. L. Katz and S. E. Wiberley, *Inorg. Chem.* 1965, **4**, 1157; (b) C. G. Kuehn and H. Taube, *J. Am. Chem. Soc.* 1976, **98**, 689.
9. R. S. Nicholson, *Analyt. Chem.* 1966, **38**, 1406.
10. R. G. Wilkins, *Kinetics and Mechanism of Reaction of Transition Metal Complexes*, 2nd edn. VCH, Weinheim (1991).
11. P. C. Ford, F. P. Rudd, R. Gaunder and H. Taube, *J. Am. Chem. Soc.* 1968, **90**, 1187.
12. K. Nakamoto, *Infrared and Raman Spectra of Inorganic Chemistry and Coordination Compounds*, 3rd edn. John Wiley, New York (1978).
13. D. K. Lavalee and E. B. Fleischer, *J. Am. Chem. Soc.* 1972, **94**, 2583.
14. S. S. Isied and H. Taube, *Inorg. Chem.* 1976, **15**, 3070.
15. H. Taube, *Commun. Inorg. Chem.* 1981, **1**, 17.
16. B. S. Lima Neto and D. W. Franco, unpublished results.
17. L. Mordenti, J. L. Roustan and J. G. Riess, *Organometallics* 1983, 843.
18. J. J. F. Alves and D. W. Franco, manuscript in preparation.
19. J. M. Rezende and D. W. Franco, *Transition Metal Chem.* 1987, **12**, 267.
20. J. C. Nascimento Filho, J. M. Rezende, B. S. Lima Neto and D. W. Franco, *Inorg. Chim. Acta* 1988, **145**, 111.
21. J. M. Rezende and D. W. Franco, unpublished results.