Inorganica Chimica Acta, 188 (1991) 113–117

Further spectroscopic and electrochemical studies of pyrazolato-bridged dirhodium complexes that undergo a thermochromic isomerization

James L. E. Burn, Clifton Woods*
Department of Chemistry, University of Tennessee, Knoxville, TN 37996 (U.S.A.)

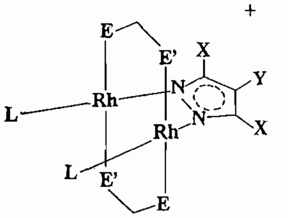
and D. Paul Rillema
Department of Chemistry, University of North Carolina at Charlotte, Charlotte, NC 28223 (U.S.A.)

(Received February 22, 1991; revised June 10, 1991)

Abstract

Paramagnetic Rh_2^{3+} complexes of the type $[Rh_2(\mu\text{-EE}')_2(\mu\text{-Z})L_2](PF_6)_2$ (Z = 3-methyl-5-trifluoromethylpyrazolate (mtmpz), 3,5-bis(trifluoromethyl)pyrazolate, (btmpz); EE' = bis(diphenylphosphino)methane (dppm), (diphenylarsino)(diphenylphosphino)methane (dapm); L = t-BuNC, CO) have been generated via electrochemical oxidation of the Rh_2^{2+} parent complexes $[Rh_2(\mu\text{-EE}')_2(\mu\text{-Z})L_2]PF_6$. Except for the diisocyanide complex containing dppm and btmpz, the complexes undergo isomerization which can be monitored by ESR spectroscopy down to −196 °C in CH_2Cl_2. For a given pyrazolate ligand the dppm complex undergoes isomerization at a lower temperature than the dapm complex, consistent with previous results that indicated that the dppm complex containing the 3,4,5-tribromopyrazolate (345Bpz) ligand did not isomerize down to −196 °C. Here we show that the low isomerization temperature for the complex containing the btmpz and dppm ligands is associated with the electronegativity of the CF_3 substituents on the pyrazolate ring. The ESR spectrum of the complex that contains the mtmpz and dppm ligands indicates that both the high-temperature and low-temperature isomers are present at −196 °C, supporting the correlation between low isomerization temperature and electronegativity of the substituents on the pyrazolate ring.

Recently we reported the results of some electrochemical and ESR studies of complexes of the general formula $[Rh_2(\mu\text{-EE}')_2(\mu\text{-Z})L_2]PF_6$ and of structure **I** where the EE' bridging ligand is bis(diphenylphosphino)methane (dppm), (diphenylarsino)(diphenylphosphino)methane (dapm) or bis(diphenylarsino)methane (dpam) [1].



I

L = t-BuNC

E=E'=P	E=As; E'=P	E=E'=As
1: X=Y=H	**6**: X=Y=H	**11**: X=Y=H
2: X=H; Y=CH_3	**7**: X=H; Y=CH_3	**12**: X=H; Y=CH_3
3: X=CH_3; Y=H	**8**: X=CH_3; Y=H	**13**: X=CH_3; Y=H
4: X=CH_3; Y=Br	**9**: X=CH_3; Y=Br	**14**: X=CH_3; Y=Br
5: X=Y=Br	**10**: X=Y=Br	**15**: X=Y=Br

For all complexes except **5** it was found that the one-electron oxidized species exhibit thermochromic behavior in solution as the temperature is lowered from room temperature to −196 °C. This behavior was attributed to an isomerization of a high-temperature green species designated as the α form and a low-temperature red species designated as the β form. The isomerization was monitored by noting the changes in *g* values of the ESR signals as a function of temperature. In solution at room temperature the isotropic *g* values are close to 2.2. In frozen solution the high-temperature forms have average *g* values near 2.2 and the low-temperature forms have average *g* values near 2.0. Similar variations in *g* values have been reported for a related triazenido-bridged dirhodium complex as a function of concentration [2].

Of the complexes we previously studied only the one-electron oxidized complex $\mathbf{5}^+$ remained in the α form down to −196 °C. It was demonstrated that the temperatures at which the α to β isomerizations occur are in the order dppm < dapm < dpam for a given pyrazolate ligand. It was also observed that the isomerization temperature varied as the sub-

---

*Author to whom correspondence should be addressed.

0020-1693/91/$3.50

stituent on the pyrazolate ring was changed. For a given transoid bridging ligand the 3,4,5-tribromopyrazolate (345Bpz) complex gave the lowest isomerization temperature.

From an analysis of the data from our previous study of complexes of structure **I**, it was concluded that isomerization might occur below −196 °C for the dppm complex that contains the 345Bpz ligand. Also, it was not clear from the previous data whether a very low isomerization temperature is the result of an inductive effect of the bromine substituents on the pyrazolate ring or a resonance effect involving the filled p-orbitals on the Br. In order to answer this question we have investigated the properties of complexes for which the pyrazolate ring has electronegative substituents that can exhibit an inductive effect but little or no resonance effect. The trifluoromethyl group was selected as this substituent and herein we report the results of our investigation of pyrazolato-bridged dirhodium complexes containing 3-methyl-5-trifluoromethylpyrazolate (mtmpz) and 3,5-bis(trifluoromethyl)pyrazolate (btmpz) ligands. The complexes which are the subjects of this study are identified in Table 1.

Results and discussion

The mtmpz and btmpz ligands were prepared according to literature procedures [3]. All other syntheses, spectroscopic and electrochemical techniques were essentially the same as those previously reported [1, 4]. The spectroscopic data for the complexes listed in Table 1 are given in Table 2 and are consistent with that of other complexes of structure **I** [2, 4].

The lowest-energy UV–Vis transitions for the mtmpz and btmpz complexes occur in the 470–485 nm region for the dicarbonyl complexes and in the 485–500 nm region for the diisocyanides. By analogy with previous assignments for analogous complexes [1], these absorption bands are assigned to transitions from a metal-based HOMO to a ligand-based LUMO.

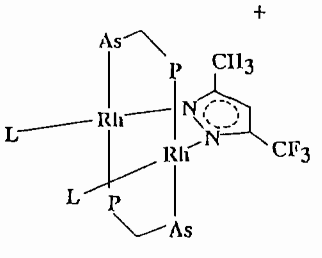
TABLE 1. Compounds of the type $[Rh_2(EE')_2(\mu\text{-}Z)L_2]PF_6$

Compound no.	EE' [a]	Z[a]	L
16	dppm	mtmpz	CO
17	dppm	btmpz	CO
18	dapm	mtmpz	CO
19	dapm	btmpz	CO
20	dppm	mtmpz	$(CH_3)_3CNC$
21	dppm	btmpz	$(CH_3)_3CNC$
22	dapm	mtmpz	$(CH_3)_3CNC$
23	dapm	btmpz	$(CH_3)_3CNC$

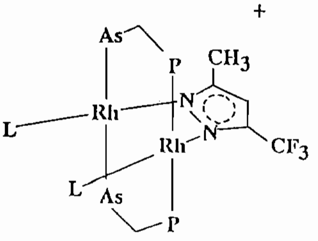
[a]dppm = bis(diphenylphosphino)methane, dapm = (diphenylarsino)(diphenylphosphino)methane, mtmpz = 3-methyl-5-trifluoromethylpyrazolate, btmpz = bis(trifluoromethyl)pyrazolate.

The $^{31}P\{^1H\}$ NMR spectra indicate that the dapm complexes exist as head-to-head (HH) and head-to-tail (HT) isomers with the dominant isomer being assigned as the HT isomer [5]. The $^{31}P\{^1H\}$ NMR spectra of **16** and **20** in CH_2Cl_2 exhibit the symmetrical AA'A"A'"XX' pattern that is typical of bis-dppm dirhodium complexes in which the four phosphorus atoms are in equivalent environments. Though the mtmpz ligand is asymmetrical, in the case of the dppm complexes **16** and **20** this asymmetry apparently does not result in sufficiently different environments for the two rhodium atoms to be detected by ^{31}P NMR techniques.

The $^{31}P\{^1H\}$ NMR spectra of the dapm carbon monoxide complex **18** and the analogous diisocyanide complex **22** are shown in Fig. 1 and the NMR parameters are given in Table 2. The spectrum of the carbon monoxide complex exhibits two doublets-of-doublets, one each for the HH and HT isomers. For each doublet-of-doublet, the large splitting is attributed to one-bond Rh–P coupling and the smaller splitting to three-bond Rh–P coupling. The more intense doublet-of-doublets is attributed to the isomer with structure **II**. Complexes of structure **III** and/or **IV**, for which the phosphorus environments are apparently indistinguishable by ^{31}P NMR, give rise to the less intense doublet.



II

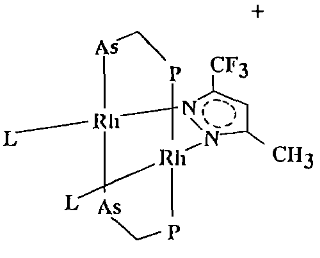


III

TABLE 2. Spectroscopic data for complexes of the type $[Rh_2(EE')_2(\mu\text{-}Z)L_2]PF_6$[a]

Compound no.	UV–Vis	IR		NMR	
	λ_{max} (nm) (ϵ)	ν(CO (cm^{-1})	ν(NC) (cm^{-1})	δ (ppm)	J(RhP) (Hz)[b]
16	485 (9000)	1991, 1975		17.3	127.0
17	480 (8000)	1996, 1983		18.5	124.5
18	478 (17000)	1993, 1979		26.8	148.9, 9.77 (HT)
				21.2	124.5, 9.77 (HH)
19	470 (10000)	1993, 1977		26.2	146.5 (HT)
				20.1	122.1 (HH)
20	500 (17000)		2108, 2072(sh)	18.3	139.2
	305 (1800)				
21	495 (15000)		2110, 2068	16.4	139.2
	300 (15000)				
22	496 (14000)		2123	26.4	168.5 (HT)
	304 (17000)			25.3	141.6 (HH)
23	485 (11000)		2114	25.8	156.0 (HT)
	299 (18000)			24.1	151.4 (HH)

[a] UV–Vis and NMR data were obtained on CH_2Cl_2 solutions and IR spectra were recorded for Nujol mulls. [b] The J(Rh–P) value reported for the dppm complexes are the separations of the major lines of the complex AA′A″A‴XX′ pattern.



IV

The spectrum of the isocyanide analogue, **22**, exhibits a doublet for the HT isomer and a weaker doublet for the HH isomer. It is not obvious why long range Rh–P coupling is observed for the dicarbonyl complexes and not for the analogous diisocyanide complexes. This difference may be related to the difference in the amount of electron density at the Rh atoms in the two complexes. More electron density would be expected at the Rh atoms in the t-BuNC complexes than in the CO complexes due to the better σ donor and the poorer π acceptor ability of t-BuNC compared to CO. It is possible that the extent to which nuclear spin information is transmitted between the Rh and P is sensitive enough to this variation in electron density at the rhodium atoms to account for such a difference in the long-range coupling constants.

The electrochemical behavior of mtmpz and btmpz complexes is very similar to that previously observed for other pyrazolato-bridged dirhodium complexes [1]. The cyclic voltammograms of **16** and **20** are shown in Fig. 2 and are typical of the CO and t-BuNC complexes. The voltammetric data are given in Table 3. These data indicate that the complexes exhibit a quasi-reversible wave followed by an irreversible wave at more positive potentials. The electronic structure of the pyrazolato-bridged complexes has been described in terms of a model derived by Hoffmann and coworkers [6]. The less positive $E_{1/2}$ values for the quasi-reversible couples of the t-BuNC complexes are attributed to a higher energy HOMO for the t-BuNC complexes resulting from

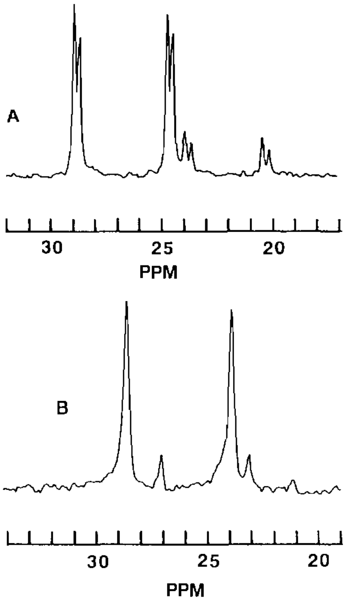


Fig. 1. ^{31}P NMR spectra of CH_2Cl_2 solutions of **18** (A) and **22** (B).

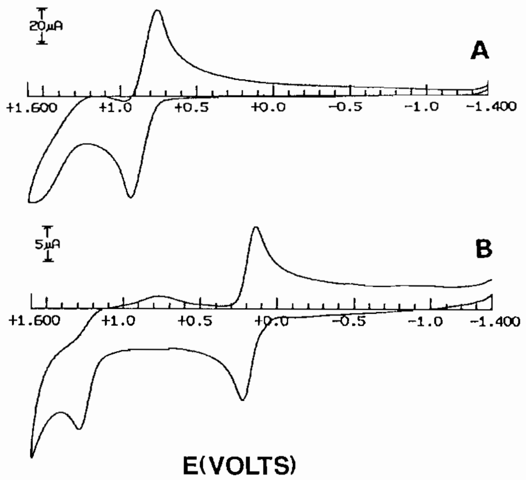


Fig. 2. Cyclic voltammogram of **16** (A) and **20** (B) in CH_2Cl_2 with 0.1 M $(n\text{-}Bu)_4NPF_6$ at a scan rate of 100 mV/s.

TABLE 3. Peak potentials in mV vs. SCE for dirhodium pyrazolato-bridged complexes of the type $[Rh_2(\mu\text{-}EE')_2(\mu\text{-}Z)L_2]PF_6$[a]

L	dppm E=E'=P			dapm E=P; E'=As		
	$E_{p1,a}$	$E_{p1,c}$	$E_{p2,a}$[b]	$E_{p1,a}$	$E_{p1,c}$	$E_{p2,a}$
Z = 3-methyl-5-trifluoromethylpyrazolate						
CO	895	732	[c]	991	844	1418
t-BuNC	234	91	1369	327	204	1322
Z = 3,5-bis(trifluoromethyl)pyrazolate						
CO	1031	885	[c]	1062	917	1460
t-BuNC	377	254	1415	405	265	1367

[a] These data were obtained at 25 °C and 100 mV s^{-1} for CH_2Cl_2 solutions containing 0.10 M TBAH. [b] Complexes **20** and **21** exhibit broad cathodic waves, $E_{p2,c}$, of low peak current at 0.780 and 0.950 V, respectively. [c] These waves occurred at the solvent limit near 1600 mV and an accurate value of the peak potential could not be obtained.

the poorer π acceptor ability of t-BuNC versus CO [1]. Controlled-potential oxidation at potentials just past the peak potential of the first oxidation wave results in a one-electron oxidation and the generation of a paramagnetic Rh_2^{3+} complex. The Rh_2^{3+} complexes exhibit ν(CO) and ν(NC) values that are *c.* 60–80 cm^{-1} higher than those given in Table 2 for the parent complexes. The increases in ν(CO) and ν(NC) are expected since there is a decrease in backbonding to CO and t-BuNC as the metal centers are oxidized.

The ESR spectra of the Rh_2^{3+} diisocyanide complexes obtained from the electrochemical oxidation of **20**–**23** were obtained in 4:1 CH_2Cl_2/toluene solutions at 22, −130 and −196 °C. The room-temperature spectra consist of a single isotropic signal with g values at 2.15 ± 0.02 (except for $\mathbf{20}^+$ where $g = 2.09$). The low-temperature spectra exhibit anisotropic signals consisting of three components. These components can be split if hyperfine coupling is observed to the P or Rh atoms. In frozen-solution ESR spectra of the α forms the signals consist of three components near g values of 2.22, 2.19 and 2.03. The β forms exhibit signals whose components have g values near 2.06, 2.00 and 1.99.

The mtmpz and btmpz complexes adhere to the trend observed for the previously studied complexes in that the α to β isomerization temperatures are in the order dppm < dapm. Table 4 contains a summary of the occurrence of the two forms at various temperatures. Figure 3(A) indicates that at −196 °C the dppm complex $\mathbf{21}^+$ exists only as the α isomer, thus indicating that the α to β isomerization does not occur above −196 °C. By analogy to previous interpretations of similar spectra [1, 2, 7], the com-

TABLE 4. Summary of the existence of α and β forms of $[Rh_2(\mu\text{-}EE')_2(\mu\text{-}Z)(t\text{-}BuNC)_2](PF_6)_2$ (Z = mtmpz, btmpz; EE' = dppm, dapm) at 22, −130 and −196 °C[a]

Temperature (°C)	EE' = dppm		EE' = dapm	
	mtmpz	btmpz	mtmpz	btmpz
22	α	α	α	α
−130	α + (β)	α	(α) + β	α + (β)
−196	a + β	α	β	β

[a] The symbol in parentheses indicates that according to ESR signal intensities very little of that form is present.

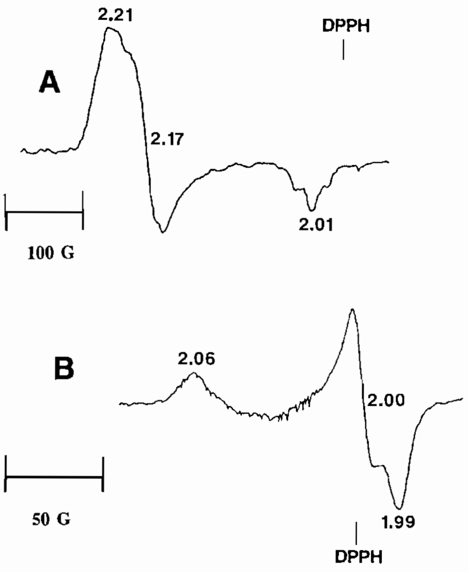


Fig. 3. X-band frozen-solution ESR spectra of $\mathbf{21}^+$ (A) and $\mathbf{23}^+$ (B) in 4:1 CH_2Cl_2/toluene solution at −196 °C.

ponent in Fig. 3(A) at $g = 2.01$ is an unresolved triplet resulting from hyperfine coupling to the two Rh atoms. The feature observed at lower field results from the overlap of the remaining two magnetic components with approximate g values of 2.17 and 2.21. Additional hyperfine coupling to the Rh atoms is unresolved for these components but in previous work was clearly observed for **5**$^+$ [1].

The ESR spectrum of the dapm complex **23**$^+$ is shown in Fig. 3(B) and illustrates that **23**$^+$ exists only as the β isomer at −196 °C; thus, an isomerization temperature for **21**$^+$ is presumed to be below −196 °C while that for **23**$^+$ is above −196 °C. These data indicate that substitution of an As atom for a P atom increases the isomerization temperature.

The only other pyrazolato-bridged complex studied thus far that appears to have an isomerization temperature below −196 °C is **5**$^+$. The features that **5**$^+$ and **21**$^+$ have in common are electronegative substituents on the pyrazolate ring, Br in the case of **5**$^+$ and CF_3 in the case of **21**$^+$. Since CF_3 is not likely to be strongly involved in resonance, it is concluded that the low isomerization temperatures of **5**$^+$ and **21**$^+$ are due to the inductive effect of the electronegative groups on the pyrazolate ring.

The above conclusion is supported by a comparison of isomerization temperatures for the mtmpz and btmpz complexes **20**$^+$ and **21**$^+$. The net electron withdrawing effect of one CF_3 group is expected to be less than that of two CF_3 groups; thus, a higher isomerization temperature was expected for the mtmpz complex **20**$^+$ than for the btmpz complex **21**$^+$. The ESR spectrum of **20**$^+$ shown in Fig. 4 clearly indicates the presence of both α and β isomers at −196 °C and indeed, **20**$^+$ is the only Rh_2^{3+} species derived from a pyrazolato-bridged dirhodium complex of structure **I** that has been studied that clearly exists as both the α and β isomer at −196 °C. The ESR spectrum of **20**$^+$ at −130 °C indicates that only a small amount of the β isomer is present at this temperature; thus, the isomerization temperature is higher for the species with the less electronegative substituents on the pyrazolate ring.

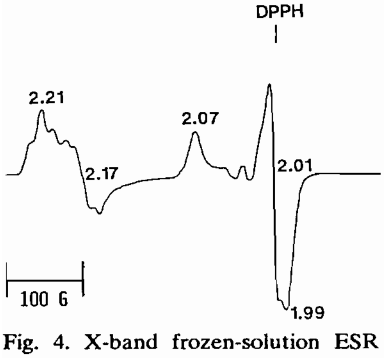


Fig. 4. X-band frozen-solution ESR spectra of **20**$^+$ 4:1 CH_2Cl_2/toluene solution at −196 °C.

Acknowledgements

The authors wish to thank the National Science Foundation, the Department of Energy, and Research Corporation for support of this work. We also wish to thank Johnson Matthey, Inc. for a generous loan of rhodium(III) chloride.

References

1 C. Woods, L. J. Tortorelli, D. P. Rillema, J. L. E. Burn and J. C. DePriest, *Inorg. Chem., 28* (1989) 1673.
2 N. G. Connelly and G. Garcia, *J. Chem. Soc., Chem. Commun.,* (1987) 246.
3 S. Trofimenko, *J. Am. Chem. Soc., 89* (1967) 3165.
4 C. J. Janke, L. J. Tortorelli, J. L. E. Burn, C. A. Tucker and C. Woods, *Inorg. Chem., 25* (1986) 4597.
5 P. Enlow and C. Woods, *Organometallics, 2* (1983) 64; R. R. Guimerans and A. L. Balch, *Inorg. Chim. Acta, 77* (1983) L177.
6 D. M. Hoffman and R. Hoffmann, *Inorg. Chem., 20* (1981) 3543.
7 D. C. Boyd, P. A. Matsch, M. M. Mixa and K. R. Mann, *Inorg. Chem., 25* (1986) 3333; M. Y. Chavan, T. P. Zhu, X. Q. Lin, M. Q. Ahsan, J. L. Bear and K. M. Kadish, *Inorg. Chem., 23* (1984) 4538; J. L. Bear, T. P. Zhu, T. Malinski, A. M. Dennis and K. M. Kadish, *Inorg. Chem., 23* (1984) 674; A. R. Chakravarty, F. A. Cotton, D. A. Tocher and J. H. Tocher, *Inorg. Chim. Acta, 101* (1985) 185; J. L. Bear, L. M. Liu and K. M. Kadish, *Inorg. Chem., 26* (1987) 2927.