Contribution from the Department of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands, and School of Chemical Sciences, Dublin City University, Dublin 9, Ireland

Synthesis and Characterization of Orthometalated Rhodium(III) Complexes Containing Substituted Triazoles

John H. van Diemen,[†] Jaap G. Haasnoot,*[,†] Ronald Hage,[†] Jan Reedijk,[†] Johannes G. Vos,[‡] and Renji Wang[‡]

Received October 10, 1990

A number of orthometalated rhodium compounds of general formula $[Rh(ppy)_2(L)](PF_6)$, with ppy = pyridin-2-yl-2-phenyl and L = 3-(pyridin-2-yl)-1,2,4-triazole (L1), 1-methyl-5-(pyridin-2-yl)-1,2,4-triazole (L2), 1-methyl-3-(pyridin-2-yl)-1,2,4-triazole (L3), 4-methyl-3-(pyridin-2-yl)-1,2,4-triazole (L4), 3-methyl-5-(pyridin-2-yl)-1,2,4-triazole (L5), 3-(pyridin-2-yl)-5-phenyl-1,2,4-triazole (L6), 3-(pyridin-2-yl)-5-(3-nitrophenyl)-1,2,4-triazole (L7), and 3-(pyridin-2-yl)-5-(2-thienyl)-1,2,4-triazole (L8) are reported. NMR spectroscopy has been used to characterize the coordination modes of the ligands in the complexes. The reduction potentials of the coordinated triazole ligands have been determined electrochemically, and a linear correlation between the first reduction potentials of the several $[Rh(ppy)_2(L)]^+$ and $[Ru(L)_3]^{2+}$ complexes has been observed. The similar energies for the lowest energy absorption bands (ϵ = 6000 M^{-1} cm^{-1}) for all complexes suggest that this band is due to a Rh → ppy(π^*) MLCT transition. Emission measurements have revealed that phenylpyridine-based-ligand-centered luminescence is present at 77 K.

Introduction

A considerable part of inorganic photochemistry is devoted to investigations on polypyridine transition-metal complexes with possible photocatalytic activity.[1-4] To obtain more insight into the photophysical and electrochemical properties of coordination compounds, many research groups have focused their attention on understanding the factors which govern the electronic structure of ruthenium compounds, i.e. the ground-state and excited-state properties.[3,4] On the other hand, much less attention has been paid to the coordination characteristics of cyclometalated (orthometalated) analogues of 2,2'-bipyridine (bpy) type ligands with d^6 or d^8 metal ions (Ru,[5-8] Pt,[9-13] Pd,[9,12,14-16] Ir,[17,18] Rh[15,18-25]).

Recent studies on the photophysical aspects of low-spin d^6-metal rhodium(III) and iridium(III) complexes containing the orthometalating ligand 2-phenylpyridine (Hppy) revealed a considerable difference in their physical properties compared to those of the related ruthenium-bpy complexes.[21-25] Apart from the different metal ion, an important reason for this difference is the presence of metal-carbon bonds in the cyclometalated complexes, which will cause a very distinct charge distribution.

During recent years, we have been concentrating on the synthesis and characterization of mononuclear and dinuclear d^6-transition-metal complexes of the type $[\{M(bpy)_2\}_x(L)]^{n+}$ with x = 1, 2; M = Ru(II), Os(II); and L = a (substituted) pyridyl-1,2,4-triazole ligand.[26-32] The 1,2,4-triazole-type ligand is known to have strong σ-donor and weak π-acceptor properties. Furthermore, the asymmetry of the triazole ring potentially gives rise to two different coordination modes, namely via the N1 (or the equivalent N2) and the N4 nitrogen donor atoms.

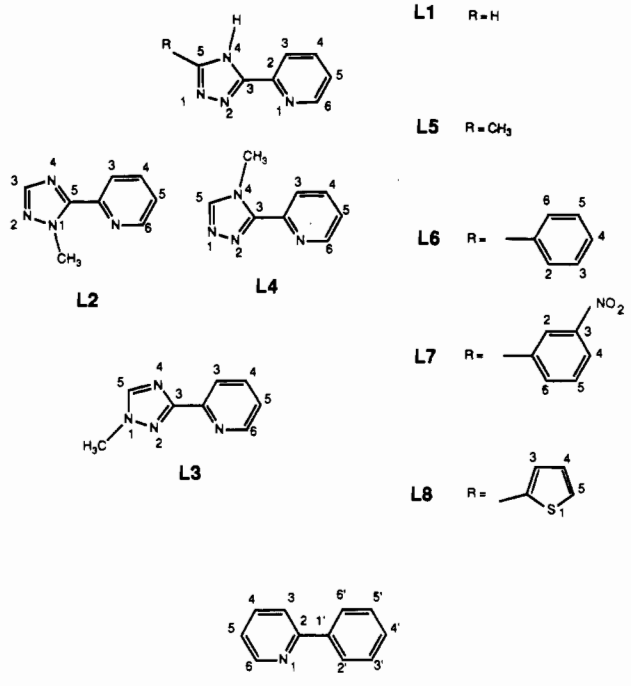
In this paper the synthesis, structure, and photochemical and electronic properties of a new series of mononuclear Rh(III) complexes, $[Rh(ppy)_2(L)](PF_6)$, with L being various pyridyl-1,2,4-triazole ligands are presented. The results obtained will be compared with those for earlier reported bis(pyridyl)ruthenium complexes. A structure analysis for a representative example (L = 3-(pyridin-2-yl)-5-phenyl-1,2,4-triazole) has been included in a footnote.[43]

Experimental Section

Materials. Hydrated rhodium trichloride and 2-phenylpyridine (Hppy) were obtained from Janssen Chimica and used without further purification.

The starting material, $[Rh(ppy)_2Cl]_2$, was prepared by following a slightly modified synthetic route reported in the literature.[33] A 2-mmol sample of $RhCl_3 \cdot H_2O$ was powdered and suspended in 75 mL of 2-methoxyethanol. Subsequently, an excess (5 mmol) of ppy was added.

Chart I. Various Triazole Ligands (L1-L8) and 2-Phenylpyridine (Hppy) with Atomic Numbering



After being stirred at room temperature for 24 h, the mixture was refluxed for 5 h. The resulting yellow precipitate was filtered out and

* To whom correspondence should be addressed.
[†] Leiden University.
[‡] Dublin City University.

(1) Kalyanasundaram, K.; Grätzel, M.; Pelizetti, E. *Coord. Chem. Rev.* **1986**, *69*, 57.
(2) Krause, R. A. *Structure and Bonding*; Springer Verlag: Berlin, 1987; p 67.
(3) Juris, A.; Balzani, V.; Barigelletti, F.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
(4) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193.
(5) Reveco, P.; Schmehl, R. H.; Cherry, W. R.; Fronczek, F. R.; Selbin, J. *Inorg. Chem.* **1985**, *24*, 4078.
(6) Constable, E. C.; Holmes, J. M. *J. Organomet. Chem.* **1986**, *301*, 203.
(7) Hiraki, K.; Obayashi, Y.; Oki, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1372.
(8) Constable, E. C.; Henney, R. P. G.; Leese, T. R. *J. Chem. Soc., Dalton Trans.* **1990**, 443.
(9) Maestri, M.; Sandrini, D.; Balzani, V.; von Zelewsky, A.; Deuschel-Cornioley, C.; Jolliet, P. *Helv. Chim. Acta* **1988**, *71*, 1053.
(10) Chassot, L.; Müller, E.; von Zelewsky, A. *Inorg. Chem.* **1984**, *23*, 4249.
(11) Craig, C. A.; Watts, R. J. *Inorg. Chem.* **1989**, *28*, 309.
(12) Cornioley-Deuschel, C.; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 3354.
(13) Cockburn, B. N.; Howe, D. V.; Keating, T.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1973**, 404.

0020-1669/91/1330-4038$02.50/0

washed with two 20-mL portions of EtOH and ether, respectively. Yield: 70%.

(a) Preparation of the Ligands. The ligands 3-(pyridin-2-yl)-1,2,4-triazole (L1),[34] 1-methyl-5-(pyridin-2-yl)-1,2,4-triazole (L2),[35] 1-methyl-3-(pyridin-2-yl)-1,2,4-triazole (L3),[36] 4-methyl-3-(pyridin-2-yl)-1,2,4-triazole (L4),[37] 3-methyl-5-(pyridin-2-yl)-1,2,4-triazole (L5),[37] 3-(pyridin-2-yl)-5-phenyl-1,2,4-triazole (L6),[38] and 3-(pyridin-2-yl)-5-(3-nitrophenyl)-1,2,4-triazole (L7)[38] were prepared according to literature methods.

3-(Pyridin-2-yl)-5-(2-thienyl)-1,2,4-triazole (L8) was prepared according the following route. 2-Thiophenecarboxylic acid hydrazide (Janssen Chimica) and the methylimidate of picolinic acid (molar ratio 1:1.5) were heated at reflux for 3 h in 100 mL of MeOH. The yellow precipitate was cooled to room temperature, isolated, and carefully heated at 130 °C for 1 h. The off-white product was recrystallized from 2-methoxyethanol and washed with two 20-mL portions of ether. Yield: 75%. Mp: 214–215 °C. NMR [$(CD_3)_2SO$]: ^1H 8.70 (1 H, d, H^6), 8.13 (1 H, d, H^3), 8.01 (1 H, t, H^4), 7.67 (1 H, d, H^{3th}), 7.62 (1 H, d, H^{5th}), 7.52 (1 H, t, H^5), 7.17 (1 H, t, H^{4th}); ^{13}C 121.6 (C3), 125.2 (C5), 126.2 ($C5^{th}$), 127.3 ($C3^{th}$), 128.1 ($C4^{th}$), 133.3 ($C2^{th}$), 137.9 (C4), 146.5 (C2), 149.7 (C6), 155.6 (C3′), 156.8 (C5′).

(b) Syntheses of the Coordination Compounds. $[Rh(ppy)_2(L1)](PF_6)$ (**1**) was prepared by refluxing 0.25 mmol of $[Rh(ppy)_2Cl]_2$ and 0.65 mmol of the ligand L1 in 30 mL of $EtOH/CH_2Cl_2$ (2:1 v/v) for 4 h. The volume of the solution was reduced to 8 mL by evaporation, and subsequently 10 mL of water was added to the residue. The compound was precipitated by adding an excess of aqueous NH_4PF_6 to the solution. After filtration the crude product was recrystallized from water/acetone (1:1 v/v) or water/CH_3CN (1:1 v/v). Anal. Calcd for $[Rh(ppy)_2(L1)](PF_6)$: C, 49.59; H, 3.16; N, 11.96; P, 4.41. Found: C, 49.29; H, 3.24; N, 11.83; P 4.24.

(14) Craig, C. A.; Garces, F. O.; Watts, R. J.; Palmans, R.; Frank, A. J. *Coord. Chem. Rev.* **1990**, *97*, 193.
(15) Selbin, J.; Gutierrez, M. A. *J. Organomet. Chem.* **1981**, *214*, 253.
(16) Wakatsuki, Y.; Yamazaki, H.; Grutsch, P. A.; Santhanam, M.; Kutal, C. *J. Am. Chem. Soc.* **1985**, *107*, 8153.
(17) King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1431.
(18) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6647.
(19) Nonoyama, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 767.
(20) Nonoyama, M. *J. Organomet. Chem.* **1975**, *86*, 1263.
(21) Ohsawa, Y.; Sprouse, S.; King, K. A.; DeArmond, M. K.; Hanck, K. W.; Watts, R. J. *J. Phys. Chem.* **1987**, *91*, 1047.
(22) Sandrini, D.; Maestri, M.; Balzani, V.; Maeder, U.; von Zelewsky, A. *Inorg. Chem.* **1988**, *27*, 2640.
(23) Garces, F. O.; King, K. A.; Watts, R. J. *Inorg. Chem.* **1988**, *27*, 3464.
(24) King, K. A.; Finlayson, M. F.; Spellane, P. J.; Watts, R. J. *Sci. Pap. Inst. Phys. Chem. Res. (Jpn.)* **1984**, *78*, 97.
(25) Barigelletti, F.; Sandrini, D.; Maestri, M.; Balzani, V.; von Zelewsky, A.; Chassot, L.; Jolliet, P.; Maeder, U. *Inorg. Chem.* **1988**, *27*, 3644.
(26) Hage, R.; Dijkhuis, A. H. J.; Haasnoot, J. G.; Prins, R.; Reedjik, J.; Buchanan, B. E.; Vos, J. G. *Inorg. Chem.* **1988**, *27*, 2185.
(27) Hage, R.; Prins, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **1987**, 1389.
(28) Hage, R.; Turkenburg, J. P.; de Graaff, R. A. G.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Acta Crystallogr.* **1989**, *C45*, 381.
(29) Hage, R.; Prins, R.; de Graaff, R. A. G.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Acta Crystallogr.* **1988**, *C44*, 56.
(30) Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Inorg. Chim. Acta* **1986**, *118*, 73.
(31) Hage, R.; Haasnoot, J. G.; Stufkens, D. J.; Snoeck, T. L.; Vos, J. G.; Reedijk, J. *Inorg. Chem.* **1989**, *28*, 1413.
(32) Barigelletti, F.; de Cola, L.; Balzani, V.; Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Inorg. Chem.* **1989**, *28*, 4344.
(33) Nonoyama, M.; Yamasaki, K. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 943.
(34) Uda, M.; Hisazumi, G.; Sato, K.; Kubota, S. *Chem. Pharm. Bull.* **1976**, *24*, 3103.
(35) Lin, Y.; Lang, S. A., Jr.; Lovell, M. F.; Perkinson, A. A. *J. Org. Chem.* **1979**, *44*, 4160.
(36) Kubota, S.; Uda, M.; Nakagawa, T. *J. Heterocycl. Chem.* **1975**, *12*, 855.
(37) Kubota, S.; Uda, M.; Ohtsuka, M. *Chem. Pharm. Bull.* **1971**, *19*, 2331.
(38) Hergenrother, P. M. *J. Heterocycl. Chem.* **1972**, *9*, 131.

Table I. ^1H NMR Data (ppm) for the Substituted Pyridyltriazole Ligands (L) in the $[Rh(ppy)_2(L)](PF_6)$ Complexes, Measured in CD_3CN[a]

compd	CH_3	H5[b]	H3	H4	H5	H6	H2
1		8.18	8.37	8.11	7.47	7.86	
		(−0.09)	(+0.26)	(−0.07)	(−0.04)	(−0.84)	
2	4.40	7.85	8.34	8.17	7.53	8.00	
	(+0.21)	(−0.14)	(+0.29)	(+0.26)	(+0.10)	(−0.65)	
3	3.92	8.08	8.29	8.07	7.45	7.85	
	(−0.05)	(−0.53)	(+0.23)	(+0.16)	(+0.02)	(−0.81)	
4	4.21	8.49	8.37	8.25	7.61	8.09	
	(+0.23)	(−0.13)	(+0.26)	(+0.30)	(+0.14)	(−0.57)	
5	1.75		8.32	8.07	7.44	7.84	
	(−0.61)		(+0.30)	(+0.17)	(+0.01)	(−0.79)	
6			8.50	8.22	7.62	8.25[c]	
			(+0.33)	(+0.19)	(+0.09)	(−0.50)	
			7.1	7.25	7.1	7.3	7.3[d]
			(−0.4)	(−0.25)	(−0.4)	(−0.83)	(−0.83)
7			8.44	8.12	7.45	7.78[e]	
			(+0.22)	(+0.10)	(−0.10)	(−0.95)	
				8.05	7.32	7.62	7.80[e]
				(−0.22)	(−0.47)	(−0.58)	(−1.00)
8			8.51	8.20	7.55	7.87[e]	
			(+0.38)	(+0.19)	(+0.03)	(−0.83)	
			7.05	6.81	7.48[f]		
			(−0.62)	(−0.36)	(−0.14)		

[a] Figures in parentheses are shifts compared to those of the free ligand, those to lower field being positive. [b] Triazole proton. [c] Bound pyridyl ring. [d] Phenyl ring. [e] Nitrophenyl ring. [f] Thiophene ring.

Table II. ^1H NMR Data (ppm) for the Pyridin-2-yl-2-phenyl (ppy) Ligands in the $[Rh(ppy)_2(L)](PF_6)$ Complexes, Measured in CD_3CN

compd	H3	H4	H5	H6
1	8.06	7.92	7.08 + 7.12	7.61 + 7.85
2	8.05	7.92	7.09	7.59 + 7.85
3	8.05	7.90 − 7.95	7.05 − 7.15	7.61 + 7.90
4	8.14	8.02	7.24	7.69 + 7.85
5	8.05	7.90 − 7.96	7.13	7.60 + 7.92
6	8.07 + 8.27	7.97 + 8.06	7.20 + 7.27	7.60 + 8.07
7	7.90 + 8.04	7.89 + 7.94	7.09 + 7.20	7.63 + 8.15
8	8.10 + 8.25	7.95 + 8.00	7.18 + 7.23	7.57 + 8.17

compd	H3′	H4′	H5′	H6′
1	6.30	6.91 + 6.96	7.05 + 7.10	7.80 + 7.83
2	6.27	6.93	7.05	7.81
3	6.29	6.93	7.01 − 7.10	7.81
4	6.34 + 6.41	6.97 + 7.07	7.10 + 7.20	7.86 + 7.93
5	6.30	6.94	7.08	7.82
6	6.03 + 6.13	6.75 + 6.92	6.82 + 7.07	7.61 + 7.95
7	5.94 + 6.34	6.47 + 6.90	6.63 + 7.05	7.29 + 7.79
8	6.26 + 6.36	6.90 + 7.07	7.06 + 7.21	7.70 + 7.93

Table III. Redox Properties[a] of the Rh(III) Complexes, As Obtained by Using DPP

compd	$V(ox)/V$	$V(red)^b/V$			
$[Rh(ppy)_2(L1)](PF_6)$ (**1**)	1.39	−1.60	−2.15	−2.37	−2.64
$[Rh(ppy)_2(L2)](PF_6)$ (**2**)	1.41	−1.59	−2.18[c]	−2.30	−2.63
$[Rh(ppy)_2(L3)](PF_6)$ (**3**)	1.44	−1.86	−2.26[d]		
$[Rh(ppy)_2(L4)](PF_6)$ (**4**)	1.47	−1.66	−2.15[c]	−2.26	−2.60
$[Rh(ppy)_2(L5)](PF_6)$ (**5**)	1.51	−1.69	−2.18	−2.54	
$[Rh(ppy)_2(L6)](PF_6)$·solv (**6**)	1.41	−2.08	−2.38	−2.61	
$[Rh(ppy)_2(L7)](PF_6)$·solv (**7**)	1.39	−1.18	−2.10	−2.40	
$[Rh(ppy)_2(L8)](PF_6)$·solv (**8**)	1.39	−2.10	−2.37	−2.65	
$[Rh(ppy)_2(bpy)](PF_6)$[e]	1.46	−1.41			

[a] Measured in CH_3CN containing 0.1 M NBu_4ClO_4 (V vs SCE). [b] First reduction wave is reversible for all complexes. [c] Shoulder. [d] Distorted waves below −2.3 V. [e] Reference 49.

All other complexes were prepared as described for **1**. Anal. Calcd for $[Rh(ppy)_2(L2)](PF_6)$ (**2**): C, 50.22; H, 3.51; N, 11.71; P, 4.32. Found: C, 49.91; H, 3.38; N, 11.64; P, 4.03. Calcd for $[Rh(ppy)_2(L3)](PF_6)$ (**3**): C, 50.30; H, 3.38; N, 11.73; P, 4.32. Found: C, 49.94; H, 3.32; N, 11.54; P, 4.45. Calcd for $[Rh(ppy)_2(L4)](PF_6)$ (**4**): C, 50.22; H, 3.51; N, 11.71; P, 4.32. Found: C, 50.03; H, 3.34; N, 11.76; P, 4.11. Calcd for $[Rh(ppy)_2(L5)(PF_6)$ (**5**): C, 50.22; H, 3.51; N, 11.71; P, 4.32. Found: C, 49.97; H, 3.64; N, 11.46; P, 3.90. Calcd for $[Rh(ppy)_2(L6)](PF_6)\cdot(CH_3)_2CO$ (**6**): C, 54.56; H, 3.86; N, 10.05; P, 3.70. Found: C, 54.78; H, 3.86; N, 10.08; P, 3.85. Calcd for $[Rh(ppy)_2(L7)](PF_6)\cdot 2CH_3CN$ (**7**): C, 52.69; H, 3.51; N, 14.18; P, 3.49. Found:

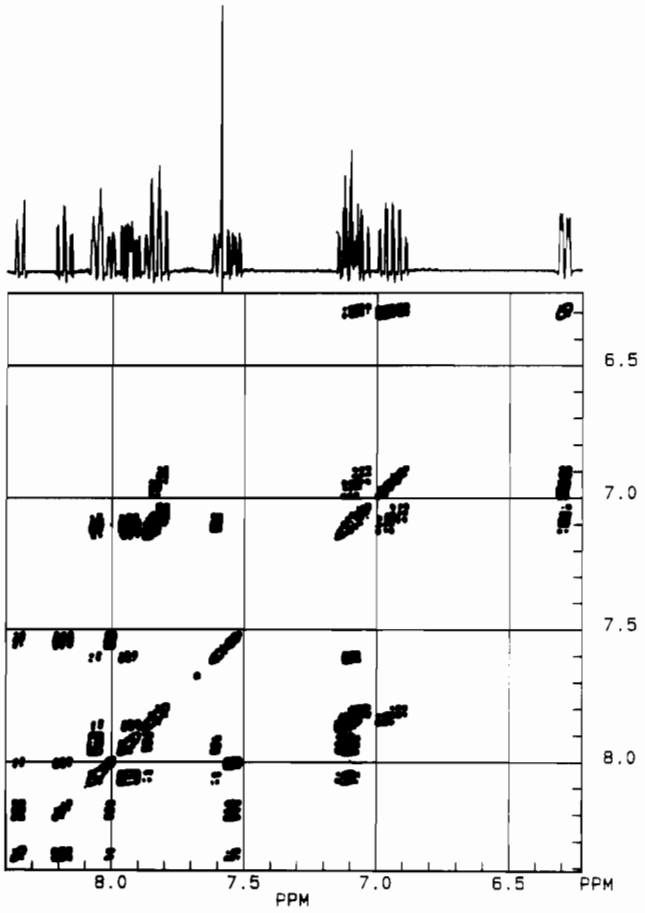


Figure 1. COSY NMR spectrum of $[Rh(ppy)_2(L2)](PF_6)$ recorded in CD_3CN.

C, 53.15; H, 3.45; N, 13.90; P, 2.98. Calcd for $[Rh(ppy)_2(L8)](PF_6)\cdot(CH_3)_2CO$ (**8**): C, 51.32; H, 3.59; N, 9.97; P, 3.68. Found: C, 51.68; H, 3.68; N, 10.06; P, 3.77.

Physical Measurements. ^1H and ^{13}C NMR spectra of the ligands were recorded on a JEOL JNM-FX 200 NMR spectrometer; ^1H NMR spectra of the metal complexes were recorded on a Bruker 300-MHz spectrometer. The measurements were carried out either in $(CD_3)_2SO$ (ligands) or in CD_3CN (complexes). The peak positions are relative to TMS.

For the COSY experiments 256 FID's of eight scans each, consisting of 1K data points, were accumulated. After digital filtering (sine bell squared), the FID was zero-filled to 512 words in the F_1 dimension. Acquisition parameters were $F_1 = \pm 500$ Hz and $t_{1/2} = 0.001$ s; the cycle decay was 1.5 s.

Electronic absorption spectra were recorded in ethanol on a Perkin-Elmer 330 UV–vis spectrophotometer and a Varian DMS 200 UV–vis spectrophotometer by using 1-cm quartz cells. Emission spectra were recorded on a Perkin-Elmer LS-5 luminescence spectrometer, equipped with a red-sensitive Hamamatsu R928 detector. Emission wavelengths are not corrected for photomultiplier monochromator response.

The differential-pulse polarographic (DPP) and cyclic voltammetric (CV) measurements were carried out by using an EG&G PAR C Model 303 instrument with an EG&G 384 B polarographic analyzer. The scan rate was 4 mV/s with a pulse height of 20 mV. A saturated calomel electrode (SCE) was used as a reference electrode. The solvent used was CH_3CN (spectroscopic grade) with 0.1 M tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. Before all measurements, the solutions were purged with argon.

Elemental analyses were carried out at University College Dublin.

Results

The proton NMR resonance signals (in ppm vs TMS) for the (substituted) pyridyltriazole ligands and the orthometalated ppy ligands in acetonitrile-d_3 are depicted in Tables I and II, respectively. A representative 2D NMR (COSY) spectrum of $[Rh(ppy)_2(L2)]^+$ is shown in Figure 1.

In Table III the results of the electrochemical experiments (CH_3CN solution, room temperature) are summarized. One

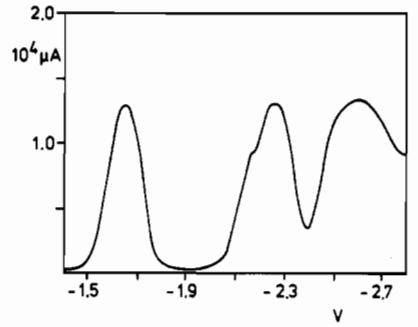


Figure 2. Differential-pulse polarograph of the reduction waves of $[Rh(ppy)_2(L4)]^+$ recorded in CH_3CN containing 0.1 M TBAP.

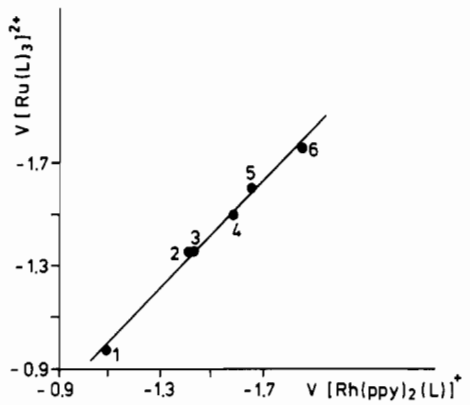


Figure 3. Correlation between the first reduction potentials of $[Ru(L)_3]^{2+}$ and $[Rh(ppy)_2(L)]^+$: (1) L = 2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole; (2) L = bpy; (3) L = phen; (4) L = L2; (5) L = L4; (6) L = L3. $r = 0.996$; slope = 1.016.

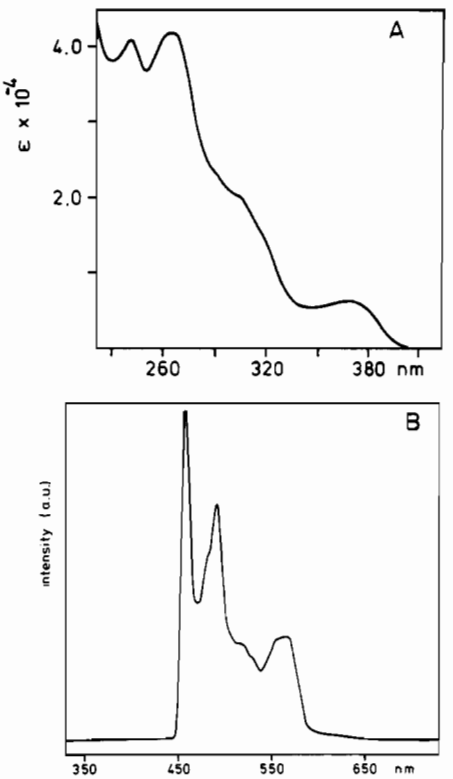


Figure 4. (A) Absorption spectrum (EtOH) and (B) emission spectrum (MeOH at 77 K) of $[Rh(ppy)_2(L4)]^+$.

irreversible oxidation wave and several reduction waves are observed. Only the first reduction appeared to be reversible. The oxidation potential and (first) reduction potential of $[Rh(ppy)_2(bpy)]^+$ are included for comparison purposes. A differ-

Table IV. Absorption and Emission Data for the $[Rh(ppy)_2(L)](PF_6)$ Complexes

compd	absorption[a] λ_{max}/nm ($\epsilon/10^4$ M^{-1} cm^{-1})					emission[b] λ_{max}/nm
1	371 (0.57)	295[c]	264 (4.0)	243 (3.5)	207 (5.0)	453[d]
2	367 (0.61)	290[c]	264 (4.0)	240 (4.2)	207 (5.3)	455
3	371 (0.57)	295[c]	264 (3.5)	239 (3.8)	205 (6.7)	455
4	368 (0.62)	300[c]	264 (4.2)	238 (4.1)	206 (5.7)	460
5	373 (0.86)	295[c]	265 (6.0)	241 (5.3)	207 (7.7)	456
6	377 (0.54)	310[c]	264 (5.2)	243 (4.5)	204 (8.9)	458
7	370 (0.62)	320[c]	264 (6.8)	247 (sh)	205 (8.6)	455
8	375 (0.60)	320[c]	266 (3.8)	242 (3.3)	204 (5.9)	462

[a] Measured in EtOH. [b] Measured in MeOH at 77 K (excitation wavelength 280 nm). [c] Shoulder (ϵ values around 2×10^4 M^{-1} cm^{-1}). [d] Highest energy feature of the luminescence emission maxima.

ential-pulse polarograph of the reduction of $[Rh(ppy)_2(L4)]^+$ is shown in Figure 2. The first reduction potentials of $[Rh(ppy)_2(L)]^+$ and $[Ru(L)_3]^{2+}$, with L = a pyridine-type ligand, have been compared. The observed linear correlation is illustrated in Figure 3.

The absorption maxima (in EtOH at room temperature) and emission maxima (in MeOH at 77 K) are summarized in Table IV. A representative example is given in Figure 4.

Discussion

NMR Spectroscopy. NMR techniques (especially COSY experiments) have proven to be an important tool in elucidating the structure of d^6-transition-metal complexes. The present Rh(III) complexes, like the Ru(II) complexes reported earlier, may chelate to the substituted pyridyltriazole ligands in two different modes. One is via the nitrogen atom of the pyridyl ring and the N1 (or N2) atom of the triazole ring.[28] The second coordination mode is via the pyridyl nitrogen and the N4 of the triazole ring.[27,28] Both types of complexes will give rise to different proton NMR shifts compared to the free ligand. For the $Rh(ppy)_2$ complexes with the triazole ligands L2 and L4, however, only one coordination mode is possible because of the methyl group attached to N1 and N4, respectively. The metal ion in **2** must be attached to N4 of the triazole ring, while for **4** the triazole ring can only be bound to the metal ion via N2. Comparing the details of the NMR data for these two complexes, one sees that this difference in binding has little influence on the positions of the resonances of the pyridine ring of the pyridyltriazole ligands. On the other hand, the position of the H5 triazole proton, relative to that of the free ligand, does provide more information about how the metal ion is coordinated, i.e. via N1 (N2) or N4. In general, the resonance positions of the substituents adjacent to a coordinating nitrogen atom will be significantly upfield shifted, compared to the resonance signal of the free ligands.[39-41] For the $[Rh(ppy)_2(L3)]^+$ complex an upfield shift of only 0.05 ppm for the methyl group is observed, which strongly suggests N4 coordination. This coordination mode for L3 has been observed previously for $[Ru(L3)(CH_3CN)Cl_3]$[29] and $[Ru(L3)_2(CO)Cl](PF_6)$.[42]

$[Rh(ppy)_2(L1)]^+$ shows a very small shift for the 5-substituent after coordination (−0.09 ppm). To derive which coordination mode is present in this case for **1**, the results of the related bis(pyridyl)ruthenium complex were taken into account. Contrary to the case of the rhodium complex, for the analogous $[Ru(bpy)_2(L1)](PF_6)_2$ both isomers were found. After chromatographic separation, the H5 resonance could be assigned for each isomer (N2, 8.65 ppm; N4, 8.38 ppm).[41,42] On basis of these results, the N4 coordination mode seems more likely in our case.

The considerable upfield shift observed for the 5-substituent (CH_3) in $[Rh(ppy)_2(L5)]^+$ of −0.61 ppm relative to the free ligand indicates that the methyl group is adjacent to a coordinating nitrogen atom. Therefore, a Rh–N4 bond is most likely.

^1H NMR spectra of **6** and **8** reveal that both isomers are formed in an N2:N4 ratio of 20:80. The preference for the N4 coordination mode is supported by the X-ray structure analysis for $[Rh(ppy)_2(L6)](PF_6)$: the pyridyltriazole ligand is found to be coordinated to the $Rh(ppy)_2$ moiety via N4 of the triazole ring.[43]

Compared to the case of the analogous $Ru(bpy)_2$ complexes with substituted triazole ligands, a remarkable difference is observed. While for the analogous Ru(II) complexes a N1 (or N2) coordination mode has been reported,[27] the present isoelectronic $Rh(ppy)_2$ complexes are preferably bound to the N4 atom of the triazole ring. Space-filling models even reveal that for complexes with L6 and L8 N4 coordination is sterically less favorable than N1/N2 coordination, because in that case the bulky 5-substituent (phenyl; thienyl) of the triazole ring is close to a phenyl ring of one of the ppy ligands. A reasonable explanation for this difference in coordination is related to the σ-donor activity of N4 versus N1 (N2). Hage et al.[44,45] concluded that N1 (N2) is a significantly better σ-donor in comparison with N4 in $[Ru(bpy)_2]^{2+}$ complexes. In the case of the Rh(III) complexes, the negatively charged ppy ligands will induce a higher electron density on the metal ion. Complexation via the stronger σ-donor N2 atom would further enhance the electron density on the metal ion, and therefore coordination via N2 seems less favorable for $[Rh(ppy)_2L]^+$, the weakest σ-donor site (N4) of the triazole ring coordinates to the rhodium ion.

For the Rh complex with L7, more than 95% of the N4 isomer is formed. The strong electron-withdrawing effect of the nitrophenyl substituent could further diminish the σ-donating power mostly on the neighboring N4 atom of the triazole ring and thus would make N4 coordination much more likely.

It is a very interesting result that the triazole ring remains protonated after coordination to the $M(ppy)_2$ moiety. Previous

(39) Steel, P. J.; Lahousse, F.; Lerner, D.; Marzin, C. *Inorg. Chem.* **1983**, *22*, 1488.
(40) Lytle, F. E.; Petrosky, L. M.; Carlson, L. R. *Anal. Chim. Acta* **1971**, *57*, 239.
(41) Buchanan, B. E.; Wang, R.; Vos, J. G.; Hage, R.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **1990**, *29*, 3263.
(42) Foster, R. J.; Boyle, A.; Vos, J. G.; Hage, R.; Dijkhuis, A. H. J.; de Graaff, R. A. G.; Haasnoot, J. G.; Prins, R.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1990**, 121.

(43) $[Rh(ppy)_2(L6)](PF_6)\cdot(CH_3)_2O$: yellow, bar-shaped single crystal, 0.15 × 0.15 × 0.10 mm^3, monoclinic, $P2_1/n$, a = 18.0812 (6) Å, b = 13.6253 (4) Å, c = 14.5311 (7) Å, β = 93.9478 (4)°, Z = 4, V = 3570.2 Å^3, ρ_{calc} = 1.550 g cm^{-3}, ρ_{obs} = 1.547 g cm^{-3}, T = 293 K, μ = 5.80 cm^{-1}, Enraf-Nonius CAD 4, graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å), cell constants determined from setting angles of 24 reflections (θ between 10 and 12°), intensities determined from $\omega/2\theta$ scans and corrected for Lorentz and polarization effects, 4588 unique reflections, 1524 reflections in refinement ($I > 2\sigma(I)$), R_{int} = 0.056, R (R_w) = 0.042 (0.044), 508 parameters refined. Solution and refinement of the structure: The position of the rhodium atom was derived from a Patterson synthesis. The structure was solved by automatic Fourier techniques, by using the computer program AUTOFOUR. After several cycles of isotropic refinement, an empirical absorption correction was applied and, subsequently, a least-squares refinement on F of positional and anisotropic thermal parameters of non-hydrogen atoms. Hydrogen atoms were coupled to the adjacent carbon atoms (C–H = 1.00 Å). Hydrogen atoms were refined isotropically. Scattering factors and corrections for anomalous dispersion were taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974. Programs written or modified by Mrs. E. W. Rutten-Keulemans and Dr. R. A. G. de Graaff were used on the Leiden University IBM 3083 computer. Description of the structure: The Rh(III) ion has an octahedral coordination, consisting of four nitrogen and two cis-oriented anionic carbon atoms, which agrees with the proposal of Sprouse et al.[18] Selected relevant bond distances and angles: Rh–C = 1.97 (1) and 1.98 (1) Å with the cyclometalated carbon atoms of the pyridin-2-yl-2-phenyl ligands cis; both Rh–N(ppy) = 2.03 (2) Å with these nitrogen atoms trans to each other. The origin of this coordination mode of ppy is probably the trans effect of the nitrogen donor atoms (which has also been suggested in earlier reports).[10,18,49] The triazole ligand is coordinated via the pyridyl nitrogen (Rh–N(py) = 2.19 (2) Å) and via the triazole N4 (Rh–N4 = 2.25 (2) Å). Both distances are significantly larger than the observed Rh–N(bpy) bond lengths in the related complex $[Rh(ppy)_2(bpy)]^+$ (2.14 Å),[44] most probably as a result of weak π-back-bonding between the metal ion and the ligand. The bite angles of the two ppy ligands and of the L6 ligand are 80.8 (4), 81.2 (4), and 76.5 (3)°, respectively, and are in the range as observed before.[5,28,29] Further details of the structure determination are available as supplementary material.
(44) Hage, R.; Haasnoot, J. G.; Nieuwenhuis, H. A.; Reedijk, J.; de Ridder, D. J. A.; Vos, J. G. *J. Am. Chem. Soc.* **1990**, *112*, 9245.
(45) Hage, R., Ph.D. Thesis, Leiden University, 1991.

work on the Ru(II) complexes with different pyridyltriazole ligands has revealed that the triazole ring becomes much more acidic after coordination to the metal center.[26,27] This is caused by the strong σ-donating properties of the triazole ligand: after binding to the metal center occurs, less electron density on the ligand is present, resulting in an increased acidity. This effect has not clearly been observed for the Rh(III) complexes, presumably due to the fact that the metal center already is coordinated by two negatively charged phenyl rings. As a result, less density is transferred from the triazole ring to the Rh(III) center, and therefore the ligand pK_a has not been changed much.

Although the NMR data of the ppy ligands do not provide additional information for determining the coordination mode, a remark can be made about the splitting of the resonance signals. This is due to the difference in chemical environment, which is most clearly visible for the H6 protons. The two signals are different because one proton is in the vicinity of the triazole ring, while the other is pointing to the pyridine ring of the pyridyltriazole ligand.

Electrochemistry. For all compounds, one irreversible oxidation wave around 1.4 V has been observed, which has been assigned to a metal-centered oxidation process. Due to the irreversibility, it is difficult to derive whether a different coordination geometry (N1(2) vs N4) or electronic ligand effects cause the observed small differences in peak positions.

Several reduction peaks are observed in the region below −1.0 V (Figure 2). Except for that of complex **6**, the first peak appeared to be (quasi-)reversible ($E_p^{ox} - E_p^{red}$ = 80–150 mV). This reversible character is an indication that the reduction process is ligand centered. In these mixed-ligand complexes, two rather different types of ligands are present, i.e. the negatively charged orthometalated ppy ligands (indicated as NC) and the neutral substituted triazole ligand (NN). As was pointed out previously, the coordinating NN ligands are much easier to reduce than the orthometalated NC ligands.[22] Therefore, the first (reversible) reduction would be expected to be located on the pyridyltriazole ligand. From a comparison of the first reduction potentials of the various complexes, a few remarkable differences are observed. For L1–L5 (except L3) the peak position is around −1.65 V. L3 appeared to be much more difficult to reduce compared to L2, although the structural differences are quite small and the coordinating mode of the triazole ligand is the same. This anodic shift has been observed for $[Ru(L3)_3]^{2+}$ and $[Ru(bpy)_2(L)]^+$, where L is the analogous pyrazinyltriazole.[45,46] Considering the first reduction wave of L6–L8, an enormous variation is observed. The potentials of L6 and L8 are about the same (−2.1 V), but the value for L7 is shifted 0.9 V toward less negative potential. Undoubtedly, the strong electron-withdrawing power of the nitro substituent on the phenyl ring causes this dramatic shift compared to the case of the related L6. A similar effect has been described by Balzani and co-workers[47] for $[Ru(bpy)_2(4\text{-}NO_2\text{-}bpy)]^{2+}$ with respect to $[Ru(bpy)_3]^{2+}$. By diminishing the electron density on the triazole system, it will be easier to reduce the ligand; i.e., the lowest π^* orbital of L7 will be lower compared to the LUMO of L6. The more negative reduction potentials for the aryl-substituted pyridyltriazoles (L7 and L8) compared to the methyl-substituted ones (L2–L5) probably originate from a greater amount of electron donation of the aromatic rings. The nature of the second reduction wave can be 2-fold. Depending on its position, either a further reduction of the pyridyltriazole ligand or a ppy-based reduction can be envisioned. In general, reduction of the negatively charged ppy ligands takes place at potentials below −2.4 V.[22] The second reduction waves observed in **1**, **2**, **4**, **5**, and **7** are most likely pyridyltriazole based, as they are observed at much less negative potentials than expected for a ppy-based reduction. Due to the very negative first reduction potentials of L6 and L8 and the positions of the second peaks (−2.4 V), it seems likely that the second reduction wave corresponds to a ppy reduction. For the present metal complexes, one or two peaks found below −2.4 V can reasonably be assigned to reduction of the ppy ligand(s). Broad peaks around −2.3 V observed for **2**–**4** might be due to a combination of NN and NC reduction.

A detailed analysis of the first reduction potentials of $[Ru(ppy)_2(L)]^+$ and those of $[Ru(L)_3]^{2+}$ has shown a very interesting correlation (Figure 3). Some of the redox data of both types of complexes were obtained by our group;[45] others were published elsewhere.[3,22,48] A linear relationship has been found when the first reduction waves for these different types of complexes were considered. This provides further evidence that the first reduction waves of $[Rh(ppy)_2(L)]^+$ complexes indeed reflect pyridyltriazole-based reductions.

Absorption and Emission Spectroscopy. The positions and extinction coefficients of the absorption maxima obtained for the triazole-containing $Rh(NC)_2$ complexes are similar to those reported previously.[49] There has been some controversy concerning the assignment of the band around 370 nm. Ohsawa et al. have concluded that the lowest energy band is a Rh → bpy transition,[21] but Sandrini et al. have shown that this band most probably can be assigned to a Rh → ppy transition.[22] As it is well established that triazole ligands have much stronger σ-donor properties than bpy, it would be expected that the low-energy band should be shifted for all complexes **1**–**8** compared to $[Rh(ppy)_2(bpy)]^+$. The maxima around 360 nm, depicted in Table IV, in fact are very similar to those reported for $Rh(ppy)_2$ complexes with bpy, biq, and phen.[22] These observations agree with the assignment that the lowest energy absorption is a Rh → ppy transition, which, as a result, is rather insensitive toward the nature of the NN-donor ligand. The intense bands at higher energy are LC transitions, as shown previously for other Rh orthometalated systems.[49]

All compounds show highly structured emission spectra at 77 K at ~450 nm (see Figure 4 for a representative example). All complexes show similar emission maxima, nearly the same as that observed for $[Rh(ppy)_2(bpy)]^+$, which shows an emission maximum at 454 nm.[22] This observation supports the conclusion of Maestri et al.[48] that in these systems a $^3LC\ \pi \rightarrow \pi^*$ excited state is present.

The emission intensities of the complexes are very weak at room temperature and are located at 420 nm. It is surprising that the emission maxima of the complexes are at higher energies than those observed at 77 K (454 nm). This has not been anticipated, as usually the emission band is located at lower energy at 300 K. At higher temperatures, the solvent molecules can relax to the most favorable state and the energy of emission decreases. At this stage, the origin of this anomaly is not clear, but it is possible that, at higher temperature, other, higher lying emitting states can be populated.[50] Temperature-dependent lifetime measurements have revealed that, at higher temperatures, nonemitting ^3MC states are populated and, therefore, the emission at room temperature is weak or absent.[25] The stronger σ-donor properties of the pyridyltriazole ligands probably cause an increase in the energy of the ^3MC state. The energy difference between the (emissive) LC states and (nonemissive) MC state becomes larger, and emission may be present in our case. Another possibility is that an impurity is present in these samples, yielding the very weak emission at room temperature. Detailed temperature-dependent measurements are necessary to fully reveal the luminescence properties of these compounds.

Concluding Remarks

The results described above indicate that significant differences are present between the ruthenium(II) and rhodium(III) complexes containing pyridyltriazole ligands. The most remarkable difference is that for the $Ru(bpy)_2$ complexes mainly coordination via N1(2) of the triazole ring takes place, while the $Rh(ppy)_2$ systems show mainly N4 coordination. Due to the weaker σ-donor

(46) Nieuwenhuis, H. A.; Haasnoot, J. G.; Hage, R.; Reedijk, J.; Snoeck, T. L.; Stufkens, D. J.; Vos, J. G. *Inorg. Chem.* **1991**, *30*, 145.
(47) Balzani, V.; Juris, A.; Barigelletti, F.; Belser, P.; von Zelewsky, A. *Sci. Pap. Inst. Phys. Chem. Res. (Jpn.)* **1984**, *78*, 78.
(48) Maestri, M.; Sandrini, D.; Balzani, V.; Maeder, U.; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 1323.
(49) Maeuder, U. Ph.D. Thesis, University of Fribourg, 1987.
(50) Balzani, V. Private communication, University of Bologna, 1990.

capability of the N4 donor atom, this coordination mode is more favorable, as the Rh(III) center already contains two very strong σ-donating phenyl rings. This work shows that the most favorable coordination mode for the triazole ligands can be changed by the properties of the metal groups. Furthermore, in all cases the pyridyltriazole ligand remains protonated after coordination to the Rh(III) center, which is in contrast to the case of the $Ru(bpy)_2$ analogues. The latter observation is important for determining the reduction potential of the neutral ligand. So far, reliable reduction potentials of the free pyridyltriazole ligand could not be obtained. The correlation of the first reduction potentials between $[Ru(L)_3]^{2+}$ and $[Rh(ppy)_2(L)]^+$ clearly shows that in all cases a L-based reduction is present for the $[Rh(ppy)_2(L)]^+$ complexes, indicating that the LUMO in these complexes is centered on the pyridyltriazole ligand. This correlation is of importance for the assignment of reduction waves of $[Ru(bpy)_2(L)]^{2+}$ complexes, when it is not clear whether the reduction processes are bpy based or L based. Finally, in agreement with the measurements carried out on the $[Ru(bpy)_2(L)]^{2+}$ complexes, the pyridyltriazole ligands appear to have weaker π-acceptor properties compared to 2,2′-bipyridine. A possible exception is the pyridyltriazole ligand with the nitrophenyl substituent (L7), most likely due to the strong electron-withdrawing power of the substituent. The luminescence observed at 77 K for the $[Rh(ppy)_2(L)]^+$ complexes investigated so far appeared to be rather independent of the σ-donor/σ-acceptor properties of the chelating ligand L. Except for the case of L = biq,[22] a ppy-based $\pi \rightarrow \pi^*$ emission could be assigned.

Acknowledgment. We wish to thank Mr. S. Gorter for collecting the crystallographic data and C. Erkelens and A. W. M. Lefeber for performing the 300-MHz (COSY) NMR experiments. Finally, we gratefully acknowledge Unilever Research Laboratories for the permission to use their electrochemical equipment.

Registry No. **1**, 136115-72-5; **2**, 136115-74-7; **3**, 136115-76-9; **4**, 136144-67-7; **5**, 136115-78-1; **6**, 136115-80-5; **6**·$(CH_3)_2CO$, 136115-85-0; **7**, 136115-82-7; **8**, 136115-84-9; L8, 136115-94-1; $[Rh(ppy)_2Cl]_2$, 33915-80-9; $[Rh(ppy)_2(L1)]$, 136115-86-1; $[Rh(ppy)_2(L2)]$, 136115-87-2; $[Rh(ppy)_2(L3)]$, 136115-88-3; $[Rh(ppy)_2(L4)]$, 136115-89-4; $[Rh(ppy)_2(L5)]$, 136115-90-7; $[Rh(ppy)_2(L6)]$, 136115-91-8; $[Rh(ppy)_2(L7)]$, 136115-92-9; $[Rh(ppy)_2(L8)]$, 136115-93-0; 2-thiophenecarboxylic acid hydrazide, 2361-27-5; methyl picolinimidate, 19547-38-7.

Supplementary Material Available: Tables of crystallographic data, positional parameters, thermal parameters, and bond distances and angles for $[Rh(ppy)_2(L6)](PF_6)\cdot(CH_3)_2CO$ and an ORTEP diagram of $[Rh(ppy)_2L_6]^+$ (9 pages); a listing of structure factors (6 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055, and University of Delaware, Newark, Delaware 19716

Synthesis and Structure of $(C_5H_4CH_3)Ta(SPh)_4$ and an EHMO Analysis of Its Distorted Four-Legged Piano-Stool Structure

Owen J. Curnow,[†] M. David Curtis,*[,†] Arnold Rheingold,[‡] and Brian S. Haggerty[‡]

Received March 13, 1991

Reaction of $(\eta^5\text{-}C_5H_4Me)TaCl_4$ with 4 equiv of NaSPh at −78 °C gave $(\eta^5\text{-}C_5H_4Me)Ta(SPh)_4$ (**1**). Single-crystal X-ray crystallography showed the molecule to have a distorted four-legged piano-stool structure with two Cp′–Ta–S angles averaging 117.2° and the other two averaging 104.1°. EHMO calculations on $(C_5H_5)Ta(SH)_4$ showed the distortion to be largely electronic in nature as well as showing that cis-ligand interactions in $CpML_4$ complexes cannot be ignored. The Cp–M interaction also has an effect on Cp–M–L angles. Crystal data for **1**: space group $P\bar{1}$; $Z = 2$; $a = 9.817$ (3), $b = 10.458$ (3), $c = 15.612$ (4) Å; $\alpha = 78.78$ (2), $\beta = 71.98$ (2), $\gamma = 67.59$ (2)°; $V = 1404.0$ (6) Å^3; $R = 4.22$, $R_w = 4.30$ based on 4154 reflections with $F_o \geq 5\sigma(F_o)$.

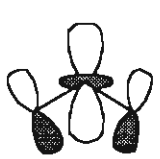
Introduction

Compounds of the formula $CpML_4$ have structures described as "four-legged piano stools". They may also be viewed as square pyramids if the Cp ligand is considered to occupy a single coordination site.

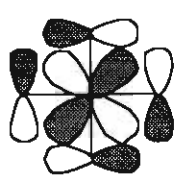
Hoffmann et al. have done an EHMO analysis of the structure of $CpML_4$ compounds to rationalize the preference for the four-legged piano-stool structure over other possible conformers.[1] The major d-orbital interactions are as follows:[1-3] The $d_{x^2-y^2}$ orbital is used up in σ bonding with the four L ligands. The d_{xz} and d_{yz} orbitals are mostly involved with the Cp ligand, although some σ-bonding interactions with the L ligands are also possible. For 18-electron compounds with π-donating ligands, the HOMO is found to be a π^* interaction between the metal d_{z^2} orbital and the p_z orbital on each of the L ligands (I*). The SHOMO is also a π^* interaction, but between the metal d_{xy} orbital and the p_x or p_y orbital on each of the L ligands (II*). For a 14-electron compound these MOs will be empty; i.e., II* will be the LUMO. The corresponding bonding MOs, I and II, are found much lower in energy.

Poli has recently described the distortions of individual L ligands in terms of the Cp–M–L angle, θ.[2,3] He found the distortions to be largely dependent on the π-bonding ability of the ligand, the nature of the ligand trans to it, and the metal electron count.

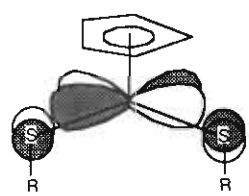
For a thiolate ligand, SR, the orientation of the R substituent will determine with which d orbital the π-donor orbital of the sulfur atom is able to interact. Hence, an orientation with R directed away from the Cp ligand will favor π bonding with the d_{xy} orbital, while R oriented into the plane of the four L ligands will favor π bonding with the d_{z^2} orbital.[1,4]

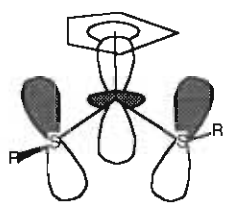


(I*)



(II*)





[†] University of Michigan.
[‡] University of Delaware.

(1) Kubáček, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.
(2) Poli, R. *Organometallics* **1990**, *9*, 1892.
(3) Krueger, S. T.; Poli, R.; Rheingold, A. L.; Staley, D. L. *Inorg. Chem.* **1989**, *28*, 4599.

0020-1669/91/1330-4043$02.50/0