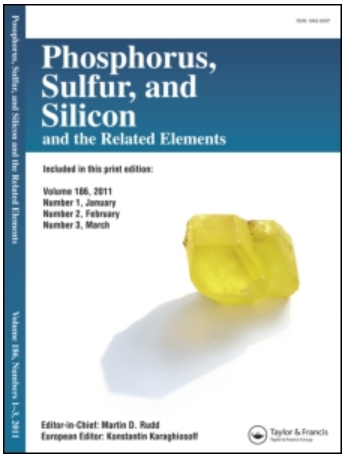


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Thiosemicarbazone Complexes of Ruthenium(II) and Rhodium(I) Containing Triphenylphosphine

G. Muthusamy[a]; P. Viswanathamurthi[b]; M. Muthukumar[b]; K. Natarajan[c]
[a] Department of Chemistry, Kongu Engineering College, Perundurai, India [b] Department of Chemistry, Periyar University, Salem, India [c] Department of Chemistry, Bharathiar University, Coimbatore, India

To cite this Article Muthusamy, G. , Viswanathamurthi, P. , Muthukumar, M. and Natarajan, K.(2009) 'Thiosemicarbazone Complexes of Ruthenium(II) and Rhodium(I) Containing Triphenylphosphine', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 8, 2115 — 2124
To link to this Article: DOI: 10.1080/10426500802429781
URL: http://dx.doi.org/10.1080/10426500802429781

Phosphorus, Sulfur, and Silicon, 184:2115–2124, 2009

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802429781

Taylor & Francis
Taylor & Francis Group

Thiosemicarbazone Complexes of Ruthenium(II) and Rhodium(I) Containing Triphenylphosphine

G. Muthusamy,[1] P. Viswanathamurthi,[2] M. Muthukumar,[2] and K. Natarajan[3]

[1]Department of Chemistry, Kongu Engineering College, Perundurai, India
[2]Department of Chemistry, Periyar University, Salem, India
[3]Department of Chemistry, Bharathiar University, Coimbatore, India

Several new hexa-coordinated ruthenium(II) and penta-coordinated rhodium(I) complexes of the types [RuCl(CO)(PPh$_3$)$_2$(TSC)], [RuH(CO)(PPh$_3$)$_2$(TSC)], and [Rh(PPh$_3$)$_3$(TSC)] (where TSC = anion of thiosemicarbazone Schiff bases) have been prepared by the reactions of [RuHCl(CO)(PPh$_3$)$_3$], [RuH$_2$(CO)(PPh$_3$)$_3$)], and [RhH(PPh$_3$)$_4$] with thiosemicarbazones of 2-furaldehyde (H-FTSC), thiophene-2-carboxaldehyde (H-TCTSC), p-anisaldehyde (H-ATSC), piperonaldehyde (H-PTSC), and cyclohexanone (H-CTSC). All the new complexes obtained have been characterized on the basis of elemental analysis, IR, ^{1}H NMR, ^{31}P NMR, and electronic spectral data.

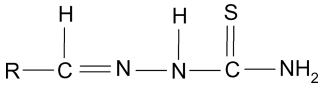
Keywords Ruthenium(II) and rhodium(I) complexes; Schiff base; spectroscopic studies; thiosemicarbazone

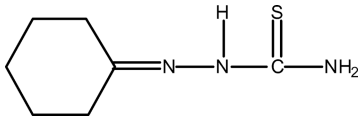
INTRODUCTION

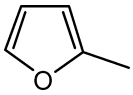
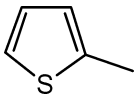
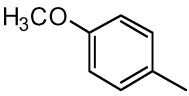
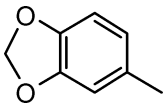
Mixed-ligand complexes of transition metals containing ligands with N,S and N,S,O donors are known to exhibit interesting stereochemical, electrochemical, and electronic properties.[1–3] Semicarbazones and thiosemicarbazones are among the most widely studied nitrogen and oxygen/sulfur donor ligands. In addition, thiosemicarbazones have emerged as an important class of sulfur ligands particularly for transition metal ions. The real impetus towards developing their coordination chemistry was due to their physicochemical properties[4–6] and significant biological activities.[7,8] Thiosemicarbazones usually bind to ruthenium metal ions either in the neutral thione form or as mono

Received 13 May 2008; accepted 25 August 2008.
Address correspondence to P. Viswanathamurthi, Department of Chemistry, Periyar University, Salem – 636 011, India. E-mail: viswanathamurthi@rediffmail.com

TABLE I Structures and Acronyms of the Ligands





R		Ligand	Abbreviation
	C_4H_3O	2-furaldehyde thiosemicarbazone	HFTSC
	C_4H_3S	thiophene 2-carboxaldehyde thiosemicarbazone	HTCTSC
	C_7H_7O	*p*-anisaldehyde thiosemicarbazone	HATSC
	$C_7H_5O_2$	piperonaldehyde thiosemicarbazone	HPTSC

negative thiolate form as bidentate N,S donor ligands forming a four-membered chelate ring with (N2) hydrazinic nitrogen.[9] In the majority of structurally characterized thiosemicarbazone complexes, five-membered chelate rings are thermodynamically more stable than the four-membered chelate rings.[10] Phosphine ligands play a central role in many reactions catalyzed by transition metals.[11–14] Although the metal complexes of thiosemicarbazones[15] and triphenylphosphine[16–20] have been studied extensively, there have been only very few reports concerning the metal complexes containing both thiosemicarbazone and triphenylphosphine. During the course of our systematic investigations on ruthenium(II) and rhodium(I) complexes containing mixed ligands, in the present work, we report the synthesis and characterization of ruthenium(II) and rhodium(I) complexes of thiosemicarbazones. The ligands shown in Table I were used in the present investigation.

RESULTS AND DISCUSSION

The new ruthenium(II) and rhodium(I) complexes of the general formulae $[RuX(CO)(PPh_3)_2(TSC)]$ and $[Rh(PPh_3)_3(TSC)]$ (X = H or Cl;

TABLE II Analytical Data of the Ruthenium(II) and Rhodium(I) Complexes

S. No.	Complex	Color	Mp (°C)	Found (Calcd), % C	H	N
1	$[RuCl(CO)(PPh_3)_2(FTSC)]$	Yellow	68	60.85(60.24)	4.34(4.23)	5.00(4.90)
2	$[RuCl(CO)(PPh_3)_2(TSTSC)]$	Yellow	122	59.53(59.14)	4.25(4.16)	4.78(4.81)
3	$[RuCl(CO)(PPh_3)_2(ATSC)]$	Pale yellow	142	59.01(59.45)	4.39(4.34)	4.64(4.52)
4	$[RuCl(CO)(PPh_3)_2(PTSC)]$	Yellow	154	59.04(58.56)	4.02(4.06)	4.54(4.45)
5	$[RuCl(CO)(PPh_3)_2(CTSC)]$	Yellow	136	61.96(61.44)	5.06(4.92)	4.94(4.88)
6	$[RuH(CO)(PPh_3)_2(FTSC)]$	Gray	184	62.28(62.77)	4.62(4.53)	5.14(5.10)
7	$[RuH(CO)(PPh_3)_2(TCTSC)]$	Light green	182	61.10(61.56)	4.42(4.45)	5.20(5.01)
8	$[RuH(CO)(PPh_3)_2(ATSC)]$	Light green	164	62.12(61.98)	4.51(4.48)	4.75(4.67)
9	$[RuH(CO)(PPh_3)_2(PTSC)]$	Light green	123	60.16(60.78)	4.21(4.33)	4.69(4.62)
10	$[RuH(CO)(PPh_3)_2(CTSC)]$	Light green	148	63.58(63.93)	5.42(5.25)	5.18(5.09)
11	$[Rh(PPh_3)_3(FTSC)]$	Brown	140	68.58(68.12)	4.59(4.86)	4.14(3.97)
12	$[Rh(PPh_3)_3(TCTSC)]$	Brown	196	67.44(67.10)	4.68(4.79)	3.98(3.91)
13	$[Rh(PPh_3)_3(ATSC)]$	Brown	242	66.68(66.96)	4.87(4.91)	3.78(3.72)
14	$[Rh(PPh_3)_3(PTSC)]$	Brown	198	65.78(66.14)	4.58(4.67)	3.78(3.67)
15	$[Rh(PPh_3)_3(CTSC)]$	Yellow	210	68.86(69.06)	5.44(5.42)	4.02(3.96)

TSC = FTSC, TCTSC, ATSC, or CTSC) were prepared from the reactions of $[RuHCl(CO)(PPh_3)_3]$, $[RuH_2(CO)(PPh_3)_3]$, or $[RhH(PPh_3)_4]$ with thiosemicarbazones in the molar ratio of 1:1. In all the reactions, it was found that the thiosemicarbazones bind to the β-nitrogen and sulfur atoms, though thiosemicarbazones can coordinate both through α-hydrogen as well as β-hydrogen with the replacement of one of the triphenylphosphine groups and the hydride from the ruthenium and rhodium complexes. The analytical data given in Table II are in good agreement with the proposed molecular formulae.

IR Spectra

The IR spectra of the ligands were compared with those of the new complexes (Table III) in order to confirm the coordination of ligand to the ruthenium and rhodium metals. The IR spectra of free ligands display two bands around 3450 and 3300 cm^{-1} corresponding to ν_{as} and $\nu_{sym}$of the terminal NH_2 group.[21] In the spectra of the metal complexes, these two bands appeared unaltered, showing noninvolvement of this

TABLE III IR and Electronic Spectral Data for Ruthenium(II) and Rhodium(I) Complexes

S. No.	ν(C≡O)	ν(Ru-H)	ν(C═N)	ν(C-S)	$\lambda_{max}(\varepsilon)(dm^3mol^{-1}cm^{-1})$
1	1940	–	1590	740	400(5843), 320(15984), 240(29851)
2	1930	–	1600	750	400(5843), 335(13693), 240(29851)
3	1940	–	1580	760	385(10238), 320(15984), 235(27358)
4	1940	–	1600	740	380(10973), 230(25947)
5	1930	–	1590	740	385(10238), 300(16825), 235(27358)
6	1920	1995	1580	740	390(9857), 325(14795), 235(27358)
7	1930	2010	1590	750	440(4978), 350(12498), 240(29851)
8	1940	2010	1590	720	390(9857), 230(25947)
9	1940	2010	1600	740	410(5639), 320(15984), 235(27358)
10	1930	2020	1590	740	390(9857), 235(27358)
11	–	–	1590	750	300(16825), 240(29851)
12	–	–	1600	750	300(16825), 240(29851)
13	–	–	1600	740	300(16825), 235(27358)
14	–	–	1590	750	300(16825), 230(25947)
15	–	–	1590	750	300(16825), 230(25947)

ν in cm^{-1}; λ in nm.

group in complexation. The band due to $\nu_{C=S}$ appeared around 840 cm^{-1} in the free ligands disappeared upon complexation, and a new band appeared around 740–760 cm^{-1}. These observations may be attributed to thio enolisation of the –NH-C=S group and subsequent coordination through the deprotonated sulfur atom.[22]

In the IR spectra of all the complexes, the absorptions due to νC=N are observed in the region 1590–1600 cm^{-1}, which is around 10 to 20 cm^{-1} lower than that observed for the free ligands. This shift certainly indicates the coordination of the nitrogen atom of the azomethine group to the metal atom.[23] Hence, the thiosemicarbazones coordinate to the metal atom via the azomethine nitrogen and sulfur atoms. In all the ruthenium complexes, the band due to the terminal C≡O group appeared at 1920–1940 cm^{-1}. In addition, the substitution of the hydride ligand in the starting complexes by the thiosemicarbazone ligand is confirmed by the absence of νM-H in the IR spectra of the complexes (M = Ru, Rh) except in the case of the reaction between $[RuH_2(CO)(PPh_3)_3]$ and thiosemicarbazones, where only one hydride is substituted under the experimental conditions. In the hydride complexes, the νM-H band appeared in the region 1995–2020 cm^{-1}. In addition to these bands, absorptions due to triphenylphosphine were also present in the expected regions. From the IR spectral data, it is inferred that the thiosemicarbazones behave as monobasic bidendate ligands and the coordination

sites are β-nitrogen and thiolatosulfur after deprotonation. Though thiosemicarbazones can coordinate both through α-hydrogen as well as β-hydrogen, for the present compounds, the IR data seem to show that probably the thiosemicarbazones coordinate through β-nitrogen.

^{1}H NMR Spectra

In order to confirm the bonding of the thiosemicarbazone ligands to metal atoms, ^{1}H NMR spectra were recorded for selected examples of the new complexes (Table IV). The signal at 11.5 ppm due to the NH proton of the free thiosemicarbazone disappeared in the complexes confirming the thio enolisation. The signals due to NH_2 protons of the ligands are present in the expected regions (2.16–4.9 ppm) in the complexes, indicating the noninvolvement of the NH_2 group on complexation. The azomethine proton (-CH=N) appeared as a singlet at around the 8.2–8.6 ppm range. The peak due to the azomethine showed a high field shift compared to the free thiosemicarbazone after complexation

TABLE IV ^{1}H NMR Data for Some of the Ruthenium(II) and Rhodium(I) Complexes

S. No.	Complex	δ in ppm
1	[RuCl(CO)(PPh_3)$_2$(PTSC)]	8.7 (s) (1H, -CH=N) 7.0−7.7 (m) (33H, aromatic) 6.0 (s) (2H, >CH_2) 2.16(bs) (NH_2)
2	[RuCl(CO)(PPh_3)$_2$(ATSC)]	8.9 (s) (1H, -CH=N) 6.8−7.8 (m) (34H, aromatic) 3.83 (s) (3H, -OCH_3) 3.7(bs) (NH_2)
3	[RuH(CO)(PPh_3)$_2$(TCTSC)]	8.1 (s) (1H, -CH=N) 6.8−7.8 (m) (33H, aromatic) 4.9(bs) (NH_2) −12.15 (t) (Ru-H)
4	[RuH(CO)(PPh_3)$_2$(PTSC)]	8.7 (s) (1H, -CH=N) 7.0−7.6 (m) (33H, aromatic) 6.0 (s) (2H, >CH_2) 2.2 (bs) (NH_2) −12.25 (t) (Ru-H)
5	[Rh(PPh_3)$_3$(PTSC)]	8.2 (s) (1H, -CH=N) 6.8−7.7 (m) (48H, aromatic) 5.9 (s) (2H, >CH_2 2.7(bs) (NH_2)

s − singlet, bs − broad singlet, t − triplet, m − multiplet.

with the metal, confirming coordination through the azomethine nitrogen atom.[24] The multiplet observed at the 6.8–7.9 ppm range has been assigned to the aromatic protons of the thiosemicarbazones ligands and the phenyl groups of triphenylphosphine. In the hydrido ruthenium complexes, the hydride ligand appeared as a triplet at −12.15 ppm, indicating the presence of the hydride ligand.

^{31}P NMR Spectra

In order to confirm the presence and geometry of triphenylphosphine groups in the complexes, ^{31}P NMR spectra for few of the complexes were recorded. The observation of only one singlet at 46.86 ppm for the ruthenium(II) complex confirms the presence of the triphenylphosphine group and also suggests that the two triphenylphosphine groups must be *trans* to each other due to magnetic equivalence of two phosphorus atoms in triphenylphosphine groups.[25] The observation of two sharp singlets around the 24.95–24.99 ppm and 26.93–26.96 ppm region for all the rhodium(I) complexes indicates the presence of triphenylphosphine groups. The appearance of two peaks suggests that the three triphenylphosphine group present in two magnetic environments, i.e., two triphenylphosphine groups *trans* to each other in a magnetic environment and the other triphenylphosphine group in another magnetic environment.

Electronic Spectra

The electronic spectra of all the ruthenium(II) complexes (Table III) displayed two to three bands in the region 440–230 nm. The bands in the region 440–370 nm have been assigned to the MLCT transitions. The other high-intensity bands appearing around 350–230 nm are probably due to ligand-centered transitions, and are in good agreement with the assignments made earlier[26] for similar other octahedral complexes of ruthenium(II).

In the electronic spectra of all the rhodium(I) complexes (Table III), two bands appeared in the region 325–230 nm. Generally, the Rh(I) species have been found to be strongly reducing in character, and because of this the d–d transitions are usually obscured by intense charge-transfer transitions.[27] Hence, all the transitions observed for the Rh(I) complexes must be due to charge-transfer transitions. Based on this, the bands observed around 325–300 nm have been assigned[28] to $e_g \rightarrow a_{2u}$. The bands around 260–230 nm may be due to $b_{2g} \rightarrow a_{2u}$. Moreover,

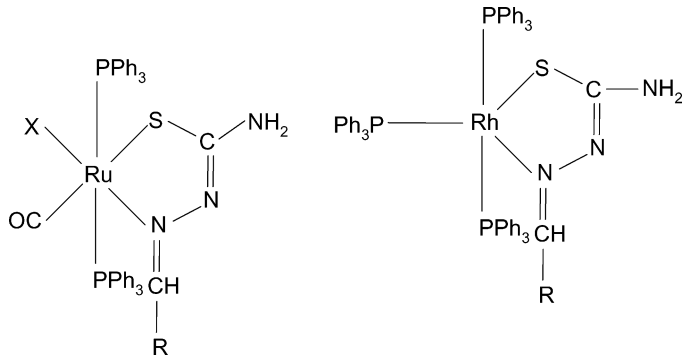


FIGURE 1 Structure of new ruthenium(II) and rhodium(I) complexes.

for a penta-coordinated Rh(I) complex, a trigonal bipyramidal structure is more favored than a square pyramidal one.[29–32]

Based on the analytical and spectral data, the structures in Figure 1 have been tentatively proposed.

Biocidal Study

The in vitro antibacterial screening against *E. coli* and *Salmonella typhi* and antifungal screening against *Aspergillus niger* of the ligand and some of their ruthenium(II) and rhodium(I) complexes have been carried out by the disc diffusion method.[33] The results (Tables V and VI) showed that the ruthenium(II) and rhodium(I) complexes are more toxic than their parent ligand against the same microorganisms and under identical experimental conditions. The increase in biological activity of the metal chelates may be due to the effect of the metal ion

TABLE V Antibacterial Activity Data of Ruthenium(II) and Rhodium(I) Complexes

	Diameter of inhibition zone (mm)			
	E. coli		*Salmonella typhi*	
Compound	0.25%	0.5%	0.25%	0.5%
FTSC	3	5	4	6
[RuCl(CO)(PPh_3)$_2$(FTSC)]	6	8	7	9
[RuH(CO)(PPh_3)$_2$(FTSC)]	12	14	10	12
[Rh(PPh_3)$_3$(FTSC)]	13	17	13	14
Streptomycin	18	23	19	22

TABLE VI Antifungal Activity data of Ruthenium(II) and Rhodium(I) Complexes

	Diameter of inhibition zone (mm)	
	Aspergillus niger	
Compound	0.25%	0.5%
FTSC	2	3
[RuCl(CO)(PPh_3)$_2$(FTSC)]	3	5
[RuH(CO)(PPh_3)$_2$(FTSC)]	3.1	7
[Rh(PPh_3)$_3$(FTSC)]	3.5	9
Bavistin	12	18

on the normal cell process. A possible mode for the toxicity increase may be considered in light of Tweedy's chelation theory.[34] Chelation reduces the polarity of the metal ion because of partial sharing of its positive charge with the donor groups and possible π-electron delocalization over the whole chelate ring. Such chelation could enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layers of the cell membrane.[35] Further, the toxicity of the compounds increases with increase in concentration. Though the complexes possess activity, they did not match the effectiveness of the standard drugs streptomycin or bavistin. The variation in the effectiveness of the different compounds against different organisms depends either on the impermeability of the cells of the microbes or differences in ribosomes of microbial cells.[36,37]

MATERIALS AND METHODS

All reagents used were of analar or of chemically pure grade. Solvents were purified and dried according to standard procedures.[38] The analyses of carbon and hydrogen were performed at the Central Drug Research Institute, Lucknow. Infrared spectra of the complexes were recorded in KBr pellets with a Perkin-Elmer 597 spectrophotometer in the range 4000–250 cm^{-1}. The electronic spectra were recorded in dichloromethane solutions with a Hitachi-Perkin Elmer 20/200 recording spectrophotometer in the range 900–200 nm. ^{1}H NMR spectra were recorded on a Bruker CXP-90 MHz or Bruker WH 270 MHz instrument. The ^{31}P NMR spectra were recorded on a Bruker CXP-90 MHz instrument. Melting points were recorded with a Mettler FP 51 instrument and are uncorrected. The starting compounds [RuHCl(CO)(PPh_3)$_3$],

$[RuH_2(CO)(PPh_3)_3]$, $[RhH(PPh_3)_4]$, and thiosemicarbazones were prepared by methods reported in the literature.[39–45]

Preparation of New Ruthenium(II) and Rhodium(I) Complexes $[RuX(CO)(PPh_3)_2(TSC)]$ and $[Rh(PPh_3)_3(TSC)]$ (X = H or Cl; TSC = Anion of Thiosemicarbazone)

To a hot solution of $[RuHCl(CO)(PPh_3)_3]$, $[RuH_2(CO)(PPh_3)_3]$, or $[RhH(PPh_3)_4]$ (0.1 g) in dry benzene (25 mL), a hot solution of the appropriate thiosemicarbazone in ethanol (5 mL) was added (1:1 mole ratio) and refluxed for 2 h. The resulting solution was concentrated to about 3 mL, and petroleum ether was slowly added, whereby the new complex separated out. The complex was filtered, washed with petroleum ether, and dried. It was then recrystallized from CH_2Cl_2/petroleum ether (60–80°C). Yield: 70–75%.

CONCLUSIONS

New hexa coordinated ruthenium(II) and penta-coordinated rhodium(I) complexes have been prepared. Based on the analytical and spectral studies, an octahedral structure for ruthenium(II) complexes and trigonal bipyramidal structure for rhodium(I) complexes have been tentatively proposed.

REFERENCES

[1] R. Prabhakaran, A. Geetha, M. Thilagavathi, R. Karvembu, V. Krishnan, H. Bertagnolli, and K. Natarajan, *J. Inorg. Biochem*., **98,** 2131 (2004).
[2] S. Dhar, M. Nethaji, and A. R. Chakravarty, *Inorg. Chim. Acta*, **358,** 2437 (2005).
[3] N. Bharti, B. Shailendra, S. Sharma, F. Naqvi, and A. Azam, *Bioorg. Med. Chem*., **11,** 2923 (2003).
[4] J. L. Dearling, J. Blower, and J. Philip, *Chem. Commun*., **22,** 2531 (1998).
[5] D. X. West, G. A. Bain, R. J. Butcher, J. P. Jasinski, and R. Y. Pozdniakiv, *Polyhedron*, **15,** 665 (1996).
[6] J. G. Tojal, L. Lezama, J. Pizarro, M. Insausti, and M. I. Arriortua, *Polyhedron*,**18,** 703 (1999).
[7] P. Bindhu, M. R. P. Kurup, and T. R. Satyakeerty, *Polyhedron*, **18,** 321 (1999).
[8] R. W. Brockman, J. R. Thomson, M. J. Bell, and H. E. Skipper, *Cancer Res*., **16,** 167 (1956).
[9] (a) F. Basuli, S. M. Peng, and S. Bhattacharya, *Inorg. Chem*., **36,** 5645 (1997); (b) F. Basuli, M. Ruf, C. G. Pierpont, and S. Bhattacharya, *Inorg. Chem*., **37,** 6113 (1998); (c) F. Basuli, M. Ruf, C. G. Pierpont, and S. Bhattacharya, *Inorg. Chem*., **39,** 1120 (2000); (d) I. Pal, F. Basuli, T. C. W. Mak, and S. Bhattacharya, *Angew. Chem., Int. Ed. Engl*., **113,** 3007 (2001).

[10] D. Mishra, S. Naskar, M. G. B. Drew, and S. K. Chattopadhyay, *Polyhedron*, **24,** 1861 (2005).
[11] G. B. W. L. Ligthart, R. H. Meijer, and M. P. Hulshof, *Tetrahedron Lett*., **44,** 1507 (2003).
[12] C. Y. Lo, H. Guo, J. J. Lian, F. M. Shen, and R. S. Liu, *J. Org. Chem*., **67,** 3930 (2002).
[13] A. A. Danopoulos, S. Winston, and W. B. Motherwell, *Chem. Commun*., 1376 (2002).
[14] A. Dijksman, A. M. Gonzalez, A. M. I. Payeras, I. W. C. E. Arends, and R. A. Sheldon, *J. Am. Chem. Soc*., **123,** 6826 (2001).
[15] N. Bharti, S. Sharma, F. Nagui, and A. Azam, *Bioorg. Med. Chem*., **11,** 2923 (2003).
[16] Y. Matsuo and E. Nakamura, *Organometallics*, **22,** 1554 (2003).
[17] R. Acharyya, S.-M. Peng, G.-H. Lee, and S. Bhattacharya, *Inorg. Chem*., **42,** 7378 (2003).
[18] H. Kawano, Y. Nishimura, and M. Onishi, *J. Chem. Soc., Dalton Trans*., 1808 (2003).
[19] K. Majumder, S.-M. Peng, and S. Bhattacharya, *J. Chem. Soc., Dalton Trans*., 284 (2001).
[20] S. Dutta, S.-M. Peng, and S. Bhattacharya, *J. Chem. Soc., Dalton Trans*., 4623 (2000).
[21] D. M. Boghaei and S. Mohebi, *J. Mol. Cat*., **179A,** 41 (2002).
[22] S. K. Dutta, M. Conville, W. J. Youngs, and M. Chaudhury, *Inorg. Chem*., **36,** 2517 (1997).
[23] V. Mahalingam, R. Karvembu, V. Chinnusamy, and K. Natarajan, *Spectrochim. Acta*, **64A,** 886 (2006).
[24] R. Karvembu, S. Hemalatha, R. Prabhakaran, and K. Natarajan, *Inorg. Chem. Commun*., **6,** 486 (2003).
[25] R. Karvembu and K. Natarajan, *Polyhedron*, **21,** 1721 (2002).
[26] M. V. Kaveri, R. Prabhakaran, R. Karvembu, and K. Natarajan, *Spectrochim. Acta*, **61A,** 2915 (2005).
[27] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd ed. (Elsevier, New York, 1984).
[28] G. L. Geoffroy, M. S. Wrighton, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc*., **96,** 3105 (1974).
[29] J. P. Jesson and P. J. Meakin, *J. Am. Chem. Soc*., **95,** 1344 (1973).
[30] J. P. Jesson and P. J. Meakin, *J. Am. Chem. Soc*., **96,** 5760 (1974).
[31] G. L. Geoffroy, H. Isci, J. Litrenti, and W. R. Mason, *Inorg. Chem*., **16,** 1950 (1977).
[32] P. Meakin and J. P. Jesson, *J. Am. Chem. Soc*., **96,** 5751 (1974).
[33] C. H. Collins and P. M. Lyne, *Microbial Methods* (University Park Press, Baltimore, 1970).
[34] B. G. Tweedy, *Phytopathalogy*, **55,** 910 (1964).
[35] S. C. Singh, N. Gupta, and R. V. Singh, *Ind. J. Chem*., **34A,** 733 (1995).
[36] N. Dharmaraj, P. Viswanathamurthi, and K. Natarajan, *Trans. Met. Chem*., **26**, 105 (2001).
[37] P. G. Lawrence, P. L. Harold, and O. G. Francis, *Antibiot. Chemother*., **5,** 1597 (1980).
[38] A. I. Vogel, *Textbook of Practical Organic Chemistry*, 5th ed. (ELBS, London, 1989).
[39] N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Syn*., **15,** 48 (1974).
[40] N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Syn*., **15,** 58 (1974).
[41] K. Mukkanti, K. B. Pandeya, and R. P. Singh, *Indian J. Chem*., **21A,** 641 (1982).
[42] K. Singh, R. V. Singh, and J. P. Tandon, *Synth. React. Inorg. Met. Org. Chem*., **16,** 1341 (1986).
[43] K. K. Aravindakshan, *Indian J. Chem*., **26A,** 241 (1987).
[44] S. Chandra, K. B. Pandeya, and R. P. Singh, *Indian J. Chem*., **18A,** 476 (1979).
[45] M. S. Raizada and M. N. Srivatsava, *Synth. React. Inorg. Met. Org. Chem*., **22,** 393 (1992).