Asian Journal of Chemistry Vol. 13, No. 1 (2001), 128–136

Synthesis and Characterization of Some Transition Metal Complexes with Thiourea Derivatives

FATIMA ESMADI* and W. AL-MASRY
Chemistry Department, Faculty of Science, Yarmouk University, Irbid, Jordan

Reactions of mono-, di-and tri-substituted thiourea with chloride salts of palladium, platinum, rhodium and iridium and with chlorocarbonyls of rhodium and iridium were carried out. The complexes were characterized by elemental analysis, spectroscopic data (UV and IR) and conductivity measurements. According to infrared data, thiourea derivatives are suggested to be sulfur bonded in all cases.

INTRODUCTION

Thiourea and its derivatives have been devoted much attention since they are important ligands for transition metals, especially platinum[1–6]. The spectroscopic properties of these ligands and their complexes have been studied thoroughly in order to confirm mode of coordination and the conformation of the ligand in the complexes[7]. Infrared spectroscopy is used for assigning structure of the thiourea complexes, although it is difficult sometimes to draw a conclusion due to overlap between the different bands in the spectra of the complexes. It has been found that lowering of ν(C═S) value compared to free ligands in some complexes is an evidence for monodentate ligation through sulfur as in case of $[PtCl_2(TMeTU)]$ (TMeTU = tetramethylthiourea) and consequently it is proposed to have a dimeric structure[8]. Kukushkin et *al.*[1] assigned (Pt—N) bonding for allylthiourea in the platinum complex $[Pt(ATU)Cl_2]_2$ (ATU = allylthiourea) depending on the appearance of a strong absorption band at 515 cm^{-1} in the infrared spectrum of the complex.

X-ray crystallography is the most reliable method that can be used to elucidate the bonding mode of such ligands. It has been found in complexes of copper[9, 10], gold[11], nickel[12], palladium[11, 13] and platinum[14], the thiourea derivatives are sulfur bonded. In these complexes the average C—N bond distance is shorter than those in free ligands while the C—S bond distance is longer which is an indication of metal-sulfur bond formation. Ligands as N-aryl-N′(2-pyridyl) thiourea have been characterized to act as bidentate through sulfur and nitrogen in their complexes of Co(II) and Ni(II) according to their infrared spectral analysis[15].

Although many transition metal complexes of thiourea derivatives have been synthesized and characterized spectroscopically, little is known about complexes of rhodium and iridium with such ligands. In order to know more about bonding modes of such ligands, series of complexes have been synthesized and characterized with these ligands. The ligands were mostly disubstituted where one nitrogen has a phenyl group and the other nitrogen substituent was varied. In addition, some trisubstituted thiourea ligands have been used. The ligands were reacted with rhodium and iridium chlorides and with their chlorocarbonyl anions. Since much attention has been paid to platinum and palladium complexes in the last decades, we tried to prepare and characterize such complexes with thiourea derivatives that have not been reported before.

RESULTS AND DISCUSSION

A series of N,N′-disubstituted thiourea derivatives have been synthesized according to the method reported in the literature[2]. These ligands were reacted with platinum, palladium, rhodium and iridium chlorides and also with chlorocarbonyls of rhodium and iridium. The physical properties of these complexes are listed in Tables 1 and 2.

Palladium and platinum complexes: Some of the prepared complexes of these two metals are formulated as neutral $[MCl_2L]_2$ and $[MCl_2L_2]$; others as ionic $[MClL_3]Cl$ and $[ML_4]Cl_2$. The isolated complexes are coloured solids and stable in air. The complexes were formulated according to their elemental analysis, conductivity measurement and infrared spectral data.

The complexes which are suggested to have MCl_2L formula might have a dimeric structure $[MCl_2L]_2$ since their IR spectra show a weak band in the 300–235 cm^{-1} range which can be attributed to bridging M—Cl bond[2, 17]. Another band appearing in the range 370–350 cm^{-1} could be assigned to terminal (M—Cl) stretching[17]. A previous study indicated that the platinum complex of tetramethylthiourea ligand may have the dimeric structure $[PtCl_2(TMTU)]_2$ with either (M—Cl) or (M—S) bridge. However, metal chloride bridge is usually more common than metal-sulfur bridge in such complexes[8].

Infrared spectra of the complexes that were formulated as $[ML_2Cl_2]$ where (M = Pt, L = BPTU; M = Pd, L = PMPTU) indicate the presence of a terminal (M—Cl) bond which appears in the range 370–330 cm^{-1} and a band in the range 460–380 cm^{-1} which can be assigned to (M—S) bond stretching. Based on steric effects, these complexes are more likely to have *trans* arrangement[18].

Infrared spectra of the complexes that are formulated as $[PdLCl_3]Cl$ where L = MPTU, n-BPTU and BPTU indicate the presence of (Pd—Cl) and (Pd—S) bonds which appear in the 370–340 cm^{-1} and 490–400 cm^{-1} range respectively.

Other bands have appeared in the infrared spectra of the isolated complexes which have been shifted to lower or higher frequencies compared to those in the free ligand. The band which appears in the range 1530–1515 cm^{-1} due to (N—H) deformation and (N—C—N) antisymmetric stretching is shifted to higher frequency range 1590–1560 cm^{-1} which indicates a greater double bond character of carbon-nitrogen bond caused by bonding of the ligand to the metal through sulfur[12, 17]. Another difference in the spectra of the ligands and that of the metal complexes appears in the region around 1000 cm^{-1}, where the free ligands usually show a strong band in the range 1050–970 cm^{-1} due to (N—C—N) symmetric stretching and (C═S) bond stretching. This bond usually disappears upon complexation due to weakening of (C═S) bond[18]. There is no considerable difference in the frequency of (N—H) bond stretching which appears above 3000 cm^{-1} in the IR spectra of the free ligands and their complexes, which indicates no metal-nitrogen bond formation.

TABLE-1
ANALYTICAL DATA OF PLATINUM METAL COMPLEXES

	Complex	Colour	m.p. (°C)	Yield (%)	Found (Calc.) %		
					C	H	N
1.	$[Pd(BPTU)Cl_2]_2$	Brown	160	72	40.3(40.1)	3.4(3.4)	6.9(6.7)
2.	$[Pd(DMPTU)Cl_2 \cdot C_2H_5OH]$	Brown	175	66	32.1(31.5)	3.8(3.5)	7.2(7.3)
3.	$[Pd(PMPTU)_2Cl_2]$	Yellow-orange	122	81	46.7(46.6)	5.4(5.2)	9.0(9.1)
4.	$[Pd(MPTU)_3Cl]Cl \cdot H_2O$	Yellow-orange	190	74	41.8(41.5)	4.5(4.6)	11.8(12.1)
5.	$[Pd(n\text{-}BPTU)_3Cl]Cl$	Orange	140	81	50.1(49.5)	6.1(6.0)	9.6(10.5)
6.	$[Pd(BPTU)_3Cl]Cl$	Brown	100	75	55.9(55.8)	4.7(4.7)	9.4(9.3)
7.	$[Pd(MPTU)_4]Cl_2 \cdot H_2O$	Yellow	200	66	44.4(44.7)	4.8(4.9)	12.7(13.1)
8.	$[Pd(n\text{-}BPTU)_4]Cl_2 \cdot 2H_2O$	Orange	155	82	51.1(50.7)	6.6(6.6)	10.1(10.8)
9.	$[Pd(PPTU)_4]Cl_2$	Yellow	130	74	57.0(57.2)	4.3(4.4)	10.1(10.3)
10.	$[Pd(1\text{-}NPTU)_4]Cl_2$	Orange-brown	155	75	63.0(63.2)	4.2(4.3)	8.5(8.7)
11.	$[Pt(PTU)Cl_2]_2$	Orange	215	68	20.2(20.1)	2.2(1.9)	6.6(6.7)
12.	$[Pt(MPTU)Cl_2]_2$	Yellow	200	62	22.1(22.2)	2.4(2.3)	6.3(6.3)
13.	$[Pt(BPTU)_2Cl_2]$	Yellow	150	74	44.7(44.8)	3.6(3.8)	7.5(7.5)
14.	$[Rh(H_2O)_2Cl_3(CPTU)] \cdot H_2O$	Orange	160	77	30.9(31.4)	4.3(4.8)	5.6(5.6)
15.	$[Rh(CO)_2(DMPTU)_2]Cl \cdot 2H_2O$	Brown	145	81	39.0(40.6)	4.3(4.8)	9.5(9.5)
16.	$[Rh(CO)_2(BPTU)_2]Cl$	Orange	140	84	52.4(53.1)	4.2(4.1)	8.4(8.3)
17.	$[Rh(CO)_2(1\text{-}NPTU)_2]Cl \cdot 2H_2O$	Orange	150	70	55.5(54.9)	4.3(4.1)	7.2(7.1)
18.	$[Rh(CO)_2(PMPTUAT)] \cdot H_2O$	Brown	210	61	42.9(42.3)	4.9(4.3)	7.2(7.1)
19.	$[Ir(H_2O)_2Cl_3(PMPTU)]$	Yellow	220	62	26.4(25.9)	3.7(3.6)	5.0(5.0)
20.	$[Ir(H_2O)_2Cl_3(CPTU)] \cdot 2H_2O$	Yellow	250	75	25.9(25.8)	4.0(4.3)	4.5(4.6)
21.	$[Ir(H_2O)_2Cl_3(PPTU)]$	Yellow	266	73	29.1(27.8)	2.5(2.8)	5.0(5.0)
22.	$[Ir(CO)Cl(MPTU)_2] \cdot 2H_2O$	Yellow	172	64	31.1(30.8)	3.9(3.9)	8.7(9.0)
23.	$[Ir(CO)Cl(CPTU)_2] \cdot 2H_2O$	Yellow	160	61	42.8(42.7)	5.3(4.9)	7.4(7.2)
24.	$[Ir(CO)Cl(BPTU)_2] \cdot 3H_2O$	Yellow	125	68	44.0(43.9)	4.4(4.3)	7.4(7.1)
25.	$[Ir(CO)Cl(DMPTU)_2] \cdot 2H_2O$	Yellow	145	78	34.2(35.0)	3.8(4.3)	8.8(8.6)
26.	$[Ir(CO)Cl(PMPTU)_2] \cdot 3H_2O$	Yellow	177	81	39.6(39.9)	5.2(5.1)	8.0(7.4)
27.	$[Ir(CO)Cl(PTU)_2] \cdot 2H_2O$	Orange	162	60	31.6(30.2)	3.8(3.4)	9.0(9.4)
28.	$[Ir(CO)Cl(PPTU)_2] \cdot 4H_2O$	Yellow	135	77	40.5(41.4)	3.7(4.1)	7.1(7.1)

TABLE-2

CHARACERISTIC IR BANDS^{a} (cm^{-1}) OF COMPLEXES AND LIGANDS AND THE MOLAR CONDUCTIVITY (ohm^{-1} cm^{2} mol^{-1}) VALUES OF COMPLEXES

Compounds No. and ligands	ν(C=S)	ν(CO)	ν(M—Cl)^{a}	ν(M—S)	$(\Lambda_m)^{b}$
1.	965m, 735m	—	355s^{t}, 260w^{b}	420w	29.4
2.	1020w, 740m	—	350m^{t}, 300w^{b}	390m	30.6
3.	1015m, 750s	—	330w	380m	25.3
4.	1030m, 740w	—	340w	400w	46.2
5.	1030w, 740w	—	375m	380m	69.5
6.	965m, 755m	—	—	410w	58.8
7.	1005w, 730m	—	—	430w	46.6
8.	1030m, 750w	—	—	400w	44.6
9.	1010m, 700m	—	—	410w	45.3
10.	1020m, 750w	—	—	370m	30.9
11.	1030w, 745m	—	235w^{b}, 370m^{t}	410w	23.3
12.	1040m, 740w	—	270w^{b}, 370m^{t}	450w	20.9
13.	965w, 740s	—	366m	430w	50.5
14.	970m, 740m	—	300b	330w	17.6
15.	1000m, 730w	1985s, 2060s	—	350b	27.6
16.	965w, 750s	1995s, 2065s	—	350b	35.8
17.	1010m, 765s	1985s, 2066s	—	340m	33.5
18.	900w, 740m	1975s, 2050s	—	355m	16.8
19.	1020m, 765s	—	350m	380s	7.5
20.	970w, 745w	—	340m	370m	2.3
21.	990w, 735m	—	320m	370m	12.4
22.	990m, 740m	2030s	330m	370m	12.4
23.	985m, 740s	2025s	320m	370m	12.2
24.	960w, 710m	2030s	320m	370m	18.8
25.	1000m, 750m	2050s	305m	350m	13.8
26.	1010m, 755m	2050s	300m	345m	18.1
27.	1030w, 740w	2040s	330m	380m	11.6
28.	1000w, 755w	2060s	330m	370m	19.2
DMPTU	1020s, 760m				
PMPTU	1030s, 755m				
CPTU	980s, 740s				
BPTU	970s, 740s				
1-NPTU	1020s, 745s				
PPTU	1000m, 750s				
PTU	1050s, 755s				
n-BPTU	1030s, 730s				
MPTU	1040s, 750s				

a. ( )^{t} stands for terminal and ( )^{b} for bridging.

b. Λ_m : molar conductivity of 1×10^{-3} M solution at 25°C in DMF.

However, it was observed that the band due to N—H bond stretching is sharper and stronger in the infrared spectra of the free ligands which may be due to hydrogen bonding in the complexes[12].

Molar conductivity values of the neutral complexes fall in the range usually assigned for neutral species. However, the obtained values of molar conductance for ionic complexes are less than those expected. This decrease might be caused by intramolecular hydrogen bonding or ion-dipole interaction of chloride ion with coordinated ligand and this leads to a decrease in the dissociation ability of the complex in DMF solvent. Similar results were obtained previously for some complexes of platinum and palladium with thiourea derivatives[19]. As a support for this is the X-ray structure of some thiourea complexes where hydrogen bonding between coordination thiourea derivative and the chloride ion was established[11, 12, 20].

Rhodium and iridium complexes: Few number of rhodium[21–23] and iridium[24] complexes have been reported in the literature. The complexes we have prepared are obtained by reaction of thiourea derivative with either MCl_3 or $[M(CO)_2Cl_2]^-$ (M = Rh, Ir). In many cases reaction with the salts produced compounds that were difficult to characterize which might be due to formation of mixtures with similar solubilities and therefore difficult to separate.

The complexes that are formulated as $[M(H_2O)_2Cl_3(RNHCSNHPh)]$ (M = Rh, R = cyclohexyl; M = Ir, R = phenyl, cyclohexyl, $(CH_2)_5$) were obtained from reaction of thiourea derivative with the trichloride salt.

Infrared spectra of the above complexes show broad bands in the range 290–230 cm^{-1} and 250–230 cm^{-1} which could be assigned for (Rh—Cl) and (Rh—S) bonds, respectively. The bands that appear in the range 350–320 cm^{-1} is attributed to (Ir—Cl) bond but the band that appears in the range 380–365 cm^{-1} is due to (Ir—S) bond.

Moreover, the band at 980 cm^{-1} which appears in the IR spectra of the free ligand CPTU, appears as a weak band at 970 cm^{-1} in the spectrum of the complex. However, the strong band that appears in the range of 1020–980 cm^{-1} in the infrared spectra of the thiourea derivatives that form complexes to iridium is also weakened which indicates formation of metal-sulfur bond[12, 17, 18]. Moreover, the strong band which is responsible for (N—C—N) antisymmetric stretching which appears in the range 1530–1510 cm^{-1} in free ligands is shifted to higher frequencies (1580–1550 cm^{-1}) which is also an evidence for M—S bond formation[17, 18].

Coordinated water is indicated by appearance of a broad band in the range 3520–3120 cm^{-1} due to O—H bond stretching. However, coordinated water is not easy to assign since the vibration frequencies of coordinated water are expected to appear in the range of 1000–600 cm^{-1} where usually several bands due to thiourea derivatives appear.

The complexes which were formulated as $[Rh(CO)_2L_2]Cl$ and $[Ir(CO)ClL_2]$ where L is N,N-dimethyl-N′-phenylthiourea, N-benzyl-N′-ethylthiourea, N-1-naphthyl-N′-phenylthiourea, N-methyl-N′-phenylthiourea, N,N′-diphenylthiourea, N-cyclohexyl-N′-phenylthiourea, N,N-pentamethylene-N-phenylthiourea were obtained upon reaction of the dichlorocarbonyl anion with the thiourea derivative. It seems that in these reactions two molecules of thiourea derivative substitute two chloride ions in the square planar $[M(CO)_2Cl_2]^-$ to produce tetracoordinate ionic dicarbonyl rhodium complexes and neutral monocarbonyl iridium complexes.

Infrared spectra of these complexes show bands characteristic of the carbonyl groups. The appearance of two strong bands in the range 2060–2025 and 1995–1985 cm^{-1} in case of rhodium complexes and one strong band in the range 2060–2025 cm^{-1} in case of the iridium complexes is an evidence that these carbonyl groups are terminal[16]. The band in the range 1530–1525 cm^{-1} which appears in the free ligands is shifted to the range 1555–1545 cm^{-1} in the infrared spectra of the rhodium complexes and to the range 1565–1540 cm^{-1} in the infrared spectra of the iridium complexes. In addition, the band that appears in the range 1050–980 cm^{-1} in the infrared spectra of the free ligands is weakend in some complexes and disappears in others which as discussed earlier is an evidence for metal-sulfur bond formation[12, 17]. The band that appears in the range of 380–345 cm^{-1} of the infrared spectra of the complexes could be attributed to (M—S) bond, whereas the band that appears in the infrared spectra of the iridium complexes in the range 330–300 cm^{-1} could be attributed to terminal (Ir—Cl) bond[17]. The strong band which is attributed to (N—H) bond stretching in the infrared spectra of the free ligands appears broad and medium or weak in their complexes which might be due to presence of inter or intramolecular hydrogen bonding[12].

Molar conductivity values of the rhodium complexes in DMF solvent fall in the range of 27.6–35.8 ohm^{-1} cm^2 mol^{-1} which is less than the expected values for ionic complexes. As stated earlier this might be due to hydrogen bonding or ion-dipole interaction of the chloride ion with the coordinated ligands which causes a decrease in the dissociation of the complexes[19].

One of the obtained rhodium complexes, $[(CO)_2Rh(CH_2)_5C(S)NPh]$, was prepared by mixing of the rhodium dicarbonyldichloro anion with N-pentamethylene-N′-phenylthiourea in presence of triethylamine. The added base abstracts a proton making the ligand negatively charged and bonds to the metal as bidentate through N and S atoms. Infrared spectrum of the compound shows the characteristic bands of terminal carbonyl groups at 2050 and 1975 cm^{-1} and bands due to (Rh—S) and (Rh—N) bonds at 355 and 530 cm^{-1}, respectively. Complexes of this formula $[Rh(CO)_2L]$ where L is a thiourea derivative have been reported previously which were formed by reaction of the dimer $[Rh(CO)_2Cl_2]_2$ and some thiourea derivatives in presence of triethylamine[22].

EXPERIMENTAL

Infrared spectra were recorded on a Pye-Unicam SP3-300 spectrophotometer in the 4000–200 cm^{-1} range using CsI discs. Elemental analyses were carried out by M.H.W. laboratories, Phoenix, Arizona, USA. Conductivity measurements were made on 10^{-3} M solutions of the complexes at ambient temperature using a Cole-Parmer 01481-61 conductivity meter in 10^{-3} M dimethylformamide solutions.

Electronic absorption spectra were recorded on a DMS spectrophotometer in dimethylformamide. Melting points were taken on an electrothermal melting point apparatus.

Sulfuric acid, formic acid, Rh(III) chloride trihydrate, dimethylformamide, methylamine, dimethylamine, *n*-butylamine, cyclohexylamine, piperidine, triethylamine and phenylisothiocyanate were purchased from BDH, England. Iridium(III) chloride trihydrate and iridium(IV) chloride trihydrate were purchased from Koch-Light Limited. K_2PtCl_4 was from Aldrich Chemical Company. K_2PdCl_4, N,N′-diphenylthiourea and phenylthiourea were from Fluka.

The N,N′-disubstituted thioureas, $RNC(S)NHC_6H_5$, where R = methyl, benzyl, *n*-butyl, cyclohexyl, 1-naphthyl and of the formula $R_2NC(S)NHC_6H_5$ where $R_2 = (CH_3)_2$ and $(CH_2)_5$ were prepared by using the following standard method[2].

Equimolar quantities of the amino compound (RNH_2) and the corresponding isothiocyanate (RNCS) were dissolved in EtOH. The mixture was heated under reflux for 10 to 90 min. The solution thus formed was kept in ice-cold water for ~ 30 min, giving a white precipitate. This was recrystallized from EtOH and dried *in vacuo* for several hours. The prepared thiourea derivatives were phenylthiourea (PTU), N,N′-diphenylthiourea (PPTU), N-methyl-N′-phenylthiourea (MPTU), N,N-pentamethylene-N′-phenylthiourea (PMPTU), N-benzyl-N′-phenylthiourea (BPTU), N-(1-naphthyl)-N′-phenyl-thiourea (1-NPTU), N-(*n*-butyl)-N′-phenylthiourea (*n*-BPTU), N-cyclohexyl-N′-phenylthiourea (CPTU) and N,N-dimethyl-N′-phenylthiourea (DMPTU).

Prepration of the complexes

$[MLCl_2]_2$ *(M = Pd, L = BPTU, DMPTU; M = Pt, L = PTU, MPTU),* $[ML_2Cl_2]$ *(M = Pd, L = PMPTU; M = Pt, L = BPTU,),* $[PdL_3Cl]Cl$ *(L = MPTU, n-BPTU, BPTU) and* $[PdL_4]Cl_2$ *(L = MPTU, n-BPTU, PPTU, 1-NPTU).*

The complexes $[Pd(BPTU)Cl_2]_2$, $[Pd(MPTU)_3Cl]Cl{\cdot}H_2O$ and [Pd(*n*-MPTU)$_3$ Cl]Cl were prepared by adding an aqueous solution (3 mL) containing (0.31 mmol) of K_2PdCl_4 to an ethanolic solution (5 mL) containing an equimolar quantity of thiourea derivative. The mixture was stirred for about 3 h at room temperature where a precipitate was formed. The precipitate was filtered, washed with water, ethanol then ether and finally was dried overnight at room temperature *in vacuo*.

The complexes $[Pd(DMPTU)Cl_2]_2{\cdot}C_2H_5OH$, $[Pd(PMPTU)_2Cl_2]$, $[Pd(BPTU)_3 Cl]$ and $[PdL_4]Cl_2$ were prepared by the same method described above except the molar ratio of metal to ligand was 1 : 2.

The complexes $[Pt(PTU)Cl_2]_2$ and $[Pt(MPTU)Cl_2]_2$ were prepared by the same method mentioned for the palladium complexes except that K_2PtCl_4 was the metal salt used and metal to ligand molar ratio was 1 : 1.

Rhodium complexes

$[RhCl_3(H_2O)_2L]{\cdot}H_2O$ *where L = N-cyclohexyl, N′-phenylthiourea*

This complex was prepared by mixing 0.10 g of $RhCl_3{\cdot}3H_2O$ (0.38 mmol) and 0.2 g of N-cyclohexyl-N′-phenylthiourea (1.14 mmol) in 10 ml ethanol and the suspension was refluxed for 1 h until a colour change from red to orange was observed. The resulted solution was cooled and *n*-pentane was slowly added until precipitation started. The precipitate was filtered, washed with *n*-pentane, ether and dried at room temperature *in vacuo.*

$[Rh(CO)_2L_2]Cl$ *where L = DMPTU, BPTU and 1-NPTU and* $[Rh(CO)_2]$ *(PMPTUAT)*

Complexes of the general formula $[Rh(CO)_2L_2]Cl$ were prepared by mixing an equimolar quantity of the ligand dissolved in ethanol (5 mL) with an ethanolic solution containing the anion, $[Rh(CO)_2Cl_2]^-$ which was prepared according to the method reported by Chatt[16]. The solution was refluxed for 1 h until a color change was observed. The solution was cooled, then *n*-pentane was gradually added until precipitation started. The precipitate was collected by filtration, washed with *n*-pentane, ether and dried at room temperature *in vacuo.* The complex $Rh(CO)_2$(PMPTUAT) where PMPTUAT is N,N-pentamethylene-N′-phenylthioureate anion was prepared by the same method described above except that an excess amount of triethylamine was added to the mixture at the beginning of the reaction.

Iridium complexes

$[Ir(H_2O)_2Cl_3L]$ *where L = PMPTU, CPTU and PPTU*

These complexes were prepared by mixing an ethanolic solution (10 mL) containing 0.10 g of $IrCl_3\cdot 3H_2O$ with an excess amount of the ligand dissolved in ethanol in 1 : 3 molar ratio. The mixture was refluxed for 1 h until a color change was observed. Cooling the solution and addition of *n*-pentane caused precipitate formation. The precipitate was collected by filtration, washed with *n*-pentane, ether and dried at room temperature *in vacuo.*

$[Ir(CO)ClL_2]$ *where L = MPTU, CPTU, BPTU, DMPTU, PMPTU, PTU, PPTU*

These were prepared by refluxing for 1 h a solution containing the anion $[Ir(CO)_2Cl_2]^-$ and the ligand dissolved in ethanol in 1 : 3 molar ratio. The complex was isolated and dried by the same method described above for the iridium aquo complexes.

ACKNOWLEDGEMENT

Support of Yarmouk University for this project is gratefully acknowledged.

REFERENCES

1. Yu.N. Kukushkin, V.V. Sibirskaya, T.K. Mihhalcheko, L.V. Konovalov, Yu.V. Fadeev and O.I. Artkanglskaya, *Zh. Obshch. Khim.*, **44**, 1912 (1974); *Chem. Abstr.*, **81**, 144842w (1974).
2. T.A.K. Al-Allaf, T.A. Mustafa and S.E. Mukhtar, *Trans. Met. Chem.*, **18**, 1 (1993).
3. F.R. Hartely, The Chemistry of Platinum and Palladium, Applied Science Ltd., London, 1973.
4. A. Yamaguchi, R.B. Penland, S. Mizushima, C. Curran and J.V. Quagliano, *J. Am. Chem. Soc.*, **79**, 527 (1958).
5. F.D. Rochon, J. Bariyanga and P.C. Kong, *Can. J. Chem.*, **63**, 2425 (1985).

6. R.K. Gosavi, U. Agarwala and C.N. Rao, *J. Am. Chem. Soc.*, **89**, 235 (1967).
7. T.J. Lane, A. Yamaguchi, J.V. Quagliano, J.A. Rayan and S. Mizushima, *J. Am. Chem. Soc.*, **81**, 3824 (1959).
8. M. Schafer and C. Curran, *Inorg. Chem.*, **5**, 265 (1996).
9. E.A. Griffith, W.A. Spofford and E.L. Amma, *Inorg. Chem.*, **17**, 1913 (1978).
10. J. Cernak, J. Chomic and P. Kutschy, *Inorg. Chim. Acta*, **181**, 85 (1991).
11. A.C. Fabretti, A. Giusti and W. Malavasi, *J. Chem. Soc. Dalton Trans*, 3091 (1990).
12. A. Sirigu, *Inorg. Chem.*, **9**, 2245 (1970).
13. D.A. Berta, W.A. Spofford, P. Boldrini and E.L. Amma, *Inorg. Chem.*, **9**, 136 (1970).
14. U. Belluco, Organometallic and Coordination Chemistry of Platinum, Academic Press (AP) (1974).
15. C.S. Prasad and S.K. Banerji, *J. Inorg. Nucl. Chem.*, **38**, 1387 (1976).
16. F.T. Esmadi and A. Al-Hamid, *Trans. Met. Chem.*, **19**, 571 (1994).
17. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd edn, Wiley, New York (1978).
18. M. Bret, P. Castan, G. Commenges, J. Lauent and D. Muller, *J. Chem. Soc. Chem. Comm.*, 1273 (1983).
19. Yu. N. Kukushkin and V.V. Sibirskaya, *Zh. Obshch. Khim.*, **53**, 888 (1983); *Chem. Abstr.*, **98**, 222811c (1983).
20. M.S. Weininger, J.E. Connor and E.L. Amma, *Inorg. Chem.*, **8**, 129 (1969).
21. D.H. Thewissen and J.G. Noltes, *Inorg. Chim. Acta*, **59**, 181 (1982).
22. ———, *Inorg. Chim. Acta*, **51**, 135 (1981).
23. D.H. Thewissen, *J. Organomet. Chem.*, **188**, 211 (1980).
24. J. Chatt, B.L. Shaw and A.E. Field, *J. Chem. Soc. (A)*, 78 (1966).

(*Received*: 26 July 2000; *Accepted*: 18 October 2000) AJC-2140