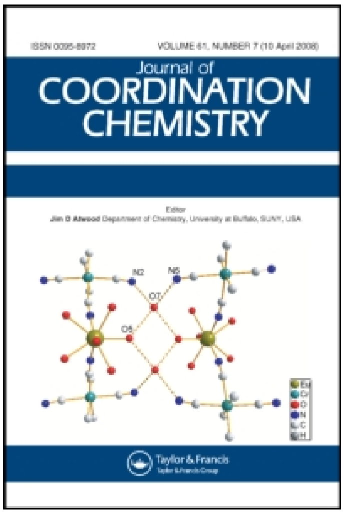


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

An Examination of the Coordination Chemistry of L_2Pt(1,2-DITHIOLENES) Using Atmospheric Pressure Chemical Ionization Mass Spectrometry

Julie M. Hough[a]; Carol A. Haney[a]; Robert D. Bereman[a]; Christopher E. Keefer[a]
[a] Department of Chemistry, North Carolina State University, Raleigh, NC, USA

To cite this Article Hough, Julie M. , Haney, Carol A. , Bereman, Robert D. and Keefer, Christopher E.(2000) 'An Examination of the Coordination Chemistry of L_2Pt(1,2-DITHIOLENES) Using Atmospheric Pressure Chemical Ionization Mass Spectrometry', Journal of Coordination Chemistry, 51: 1, 45 — 54

To link to this Article: DOI: 10.1080/00958970008047077

URL: http://dx.doi.org/10.1080/00958970008047077

J. Coord. Chem., 2000, Vol. 51, pp. 45–54
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

AN EXAMINATION OF THE COORDINATION CHEMISTRY OF L_2Pt(1,2-DITHIOLENES) USING ATMOSPHERIC PRESSURE CHEMICAL IONIZATION MASS SPECTROMETRY

JULIE M. HOUGH, CAROL A. HANEY*,
ROBERT D. BEREMAN* and CHRISTOPHER E. KEEFER

Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204, USA

(Received 5 April 1999; Revised 23 July 1999; In final form 12 November 1999)

Atmospheric pressure chemical ionization mass spectrometry (APCI-MS) has been utilized in the characterization of two series of platinum dithiolene complexes, (COD)Pt(dt) **1**, (COD)-Pt(edt) **2**, (COD)Pt(dmid) **3**, (COD)Pt(mnt) **4**, (COD)Pt(eddo) **5**, (COD)Pt(dddt) **6** and (Ph$_3$P)$_2$Pt(dt) **7**, (Ph$_3$P)$_2$Pt(edt) **8**, (Ph$_3$P)$_2$Pt(dmid) **9**, (Ph$_3$P)$_2$Pt(dmit) **10**, (Ph$_3$P)$_2$Pt(mnt) **11** (where COD = 1,5-cyclooctadiene, dt = ethane-1,2-dithiolate, edt = ethylene-1,2-dithiolate, dmid = 1,3-dithiole-2-oxo-4,5-dithiolate, dmit = 1,3-dithiole-2-thione-4,5-dithiolate, mnt = maleonitrile-1,2-dithiolate, eddo = 4-(ethylene-1′,2′-dithiolate)-1,3-dithiole-2-one, and dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate). The series that contains triphenylphosphine is labile toward the loss of HPPh$_3^+$. In addition, an orthometallated species involving the platinum and triphenylphosphine is identified. A dimer is identified for **2**, which is shown to be a product of the experiment and not present in the parent material. In addition, a 1 : 1 adduct with NH$_4^+$ is identified for **4** and **11** where the NH$_4^+$ originates from the acid hydrolysis of acetonitrile. Finally, a highly unique ion, Pt$^+$, a bare platinum ion, is observed in all COD complexes indicating that a radical mechanism must accompany the decomposition of the COD complexes during the fragmentation process.

Keywords: Dithiolenes; platinum; mass spectrometry; APCI-MS

INTRODUCTION

We have long been interested in the synthesis and coordination chemistry of new organosulfur ligands, especially dithiolenes. New complexes are of

---

* Corresponding authors. Tel.: 919 515 9370. Fax: 919 515 8909.

interest because of wide interest in dithiolenes as charge-transfer complexes, as well as possible precursors to high temperature organic conductors and superconductors. The design of target ligands, the development of synthetic methodology, and the use of appropriate characterization methods for new complexes of this type have remained challenges.[1,2] Recently, we had reason to focus our work on Pt(II) complexes, specifically L_2Pt(1,2-dithiolenes), where L_2 is either 1,5-cyclooctadiene (COD) or L is triphenylphosphine. X-ray crystallography, ^{195}Pt NMR and mass spectrometry were used for characterzation of these compounds.

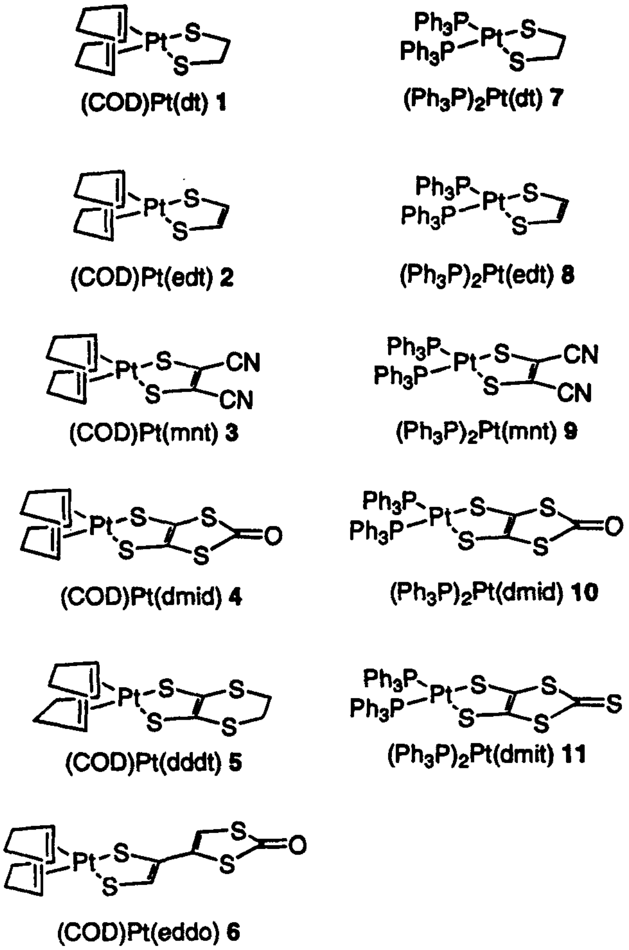
APCI-MS is a soft-ionization technique that is useful for the characterization of small, non-polar to moderately polar molecules. APCI-MS does not require preformed ions in solution; therefore, additives to the mobile phase, which can interfere with the ionization process, can be kept to the minimum needed for good chromatographic separation. The ionization process occurs at atmospheric pressure, resulting in an interface compatible with high performance liquid chromatography (HPLC) as well as with mass spectrometry. The mobile phase is used as the reagent gas for the chemical ionization process, and supplies the protons to make $(M+H)^+$, or scavenges the protons to make $(M-H)^-$.

Structural information can be obtained from a soft-ionization technique such as APCI-MS using collision-induced dissociation (CID) of the analyte to create fragmentation. For a single quadrupole instrument, the CID occurs in the transport region of the source (*e.g.* between the capillary exit and the skimmer). As the potential of the capillary exit voltage is increased, the ions gain translational energy, increasing the energy of each collision with the nitrogen (the drying gas used in the APCI-MS system). This results in the collision-induced decomposition of the ions entering the system. At higher energies, the collisions are more energetic, therefore producing more fragments.[3] These fragments can then be used to ascertain structural and chemical properties of the analyte.

In the present paper, we report the results of applying APCI-MS to the study of the coordination chemistry of L_2Pt(1,2-dithiolene) complexes. Figure 1 depicts the Lewis structures for all of the complexes in this study.

EXPERIMENTAL

Acetonitrile and water (Fisher Scientific) were HPLC grade and used with no modification. All L_2Pt(1,2-dithiolenes) were synthesized in our lab according to reported literature preparations.[1,2,4]



(COD)Pt(dt) **1**

(Ph$_3$P)$_2$Pt(dt) **7**

(COD)Pt(edt) **2**

(Ph$_3$P)$_2$Pt(edt) **8**

(COD)Pt(mnt) **3**

(Ph$_3$P)$_2$Pt(mnt) **9**

(COD)Pt(dmid) **4**

(Ph$_3$P)$_2$Pt(dmid) **10**

(COD)Pt(dddt) **5**

(Ph$_3$P)$_2$Pt(dmit) **11**

(COD)Pt(eddo) **6**

FIGURE 1 Platinum dithiolene compounds included in this study, where dt = ethane-1,2-dithiolate, edt = ethylene-1,2-dithiolate, dmid = 1,3-dithiole-2-oxo-4,5-dithiolate, dmit = 1,3-dithiole-2-thione-4,5-dithiolate, mnt = maleonitrile-1,2-dithiolate, eddo = 4-(ethylene-1′,2′-dithiolate)-1,3-dithiole-2-one, and dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate.

The samples were prepared on the day of analysis by dissolving ~ 1 mg of solid into 5 mL of 80% acetonitrile and 20% water. In all cases, this produced a saturated solution of the analyte. A small amount of the solution was centrifuged for 2 min at 9000 rpm to remove any remaining particulate material before analysis. This solution was transferred to a sample vial, capped, and placed in the autosampler.

A Hewlett Packard 1100 series liquid chromatograph, consisting of a degas unit, a binary pump with high pressure mixing, an autosampler,

TABLE I Summary of instrument parameters

Corona current	3 μA
Capillary voltage	3000 V
Fragmentor voltage	60–300 V, steps of 60 V
Vaporizer temperature	275°C
Nebulizer pressure	60 psig
Ionization source pressure	Atmospheric

a multicolumn switching compartment, and a UV–Vis diode array detector, was used. A Hewlett Packard 1100 MSD single quadrupole mass spectrometer, which was equipped with an APCI source (Palo Alto, CA), was used for this study. The mass spectrometer conditions are listed in Table I.

The autosampler injected 10 μL of sample. The flow rate was 1.0 mL/min of 80% acetonitrile and 20% water. Chromatography was performed on a Phenomenex IB-SIL 5 C_1 column that was 150 × 4.6 mm. This separated any impurities present in the sample such as salts that could interfere with the MS detection. A Hewlett Packard Vectra XA Pentium computer running HP ChemStation software (rev. 6.01) collected the spectra. Data were analyzed using the same system and software.

Fragments were formed in the high pressure region of the mass spectrometer beyond the transfer capillary. The potential drop between the exit of the transfer capillary and the first skimmer controlled the energy of the ions. For the 1100 MSD, this potential drop is called the fragmentor voltage. At low fragmentor voltages, the collisions that occur are not energetic, resulting in few or no fragments. As the fragmentor voltage is increased, the collisions become more energetic, therefore more fragments are seen.

RESULTS AND DISCUSSION

Figures 2 and 3 show representative spectra of a $(Ph_3P)_2Pt$(1,2-dithiolene) and a (COD)Pt(1,2-dithiolene) at various fragmentor voltages. Each sample was analyzed at five different fragmentor voltages, which correspond to increasing collision energy. This allowed the fragmentation processes of the analyte to be observed at various energies to obtain maximum structural and bonding information. Low collision energies tend to give only parent ions, while higher collision energies tend to give more structural information.

Characterization of the platinum dithiolenes is aided by the diagnostic isotope pattern resulting from the presence of both platinum and sulfur; *e.g.* the theoretical isotope pattern for protonated $(Ph_3P)_2Pt$(edt) is shown in Figure 4(a) and the observed pattern is shown in Figure 4(b).

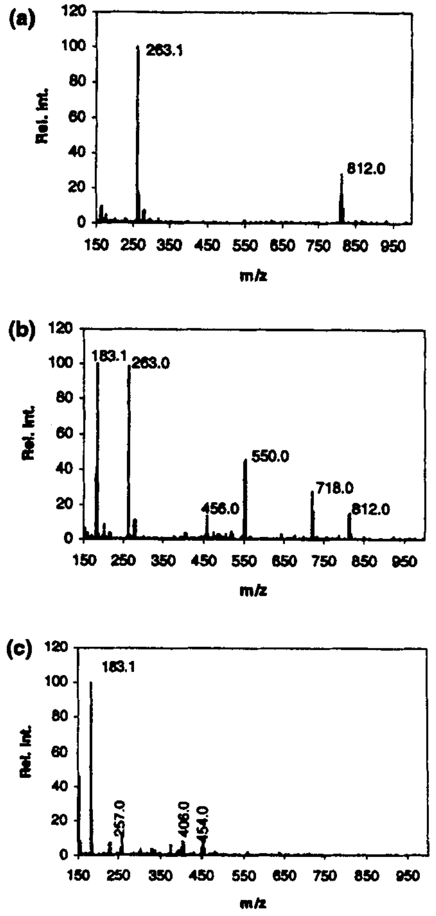


FIGURE 2 Spectra of $(Ph_3P)_2Pt(dt)$ at fragmentor energies of (a) 60 V, (b) 180 V, and (c) 300 V.

For the triphenylphosphine compounds, at low collision energy, the protonated molecular ion was seen for all compounds (Figure 2(a)). A base peak for all triphenylphosphine compounds at *m/z* 263 was also seen which we assigned to a protonated triphenylphosphine ($HPPh_3^+$). We believe that this fragment ion results from the facile cleavage of the platinum–phosphorus bond (Scheme 1). This fragmentation results from protonation of the parent compound and occurs without collision-induced dissociation. The fragment likely results from electrophilic attack of a proton or protonated species on the metal yielding the protonated fragment through a 1,1-reductive elimination-like mechanism. It is also evident that several different sites on the

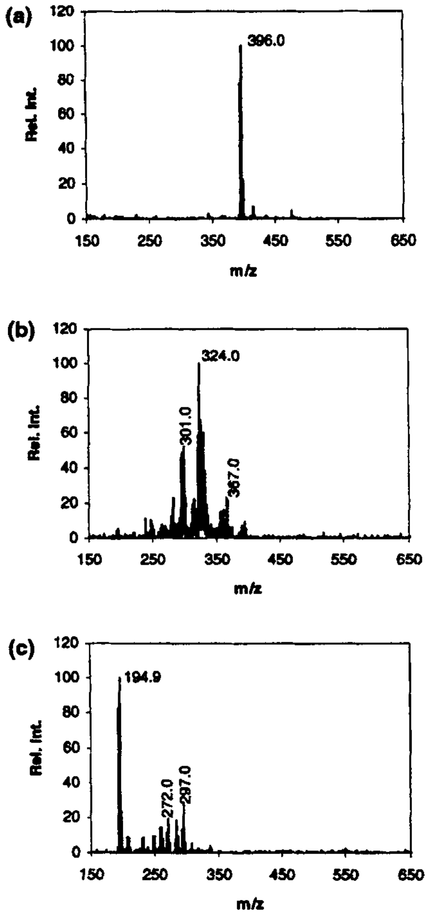


FIGURE 3 Spectra of (COD)Pt(dt) at fragmentor energies of (a) 60 V, (b) 180 V, and (c) 300 V.

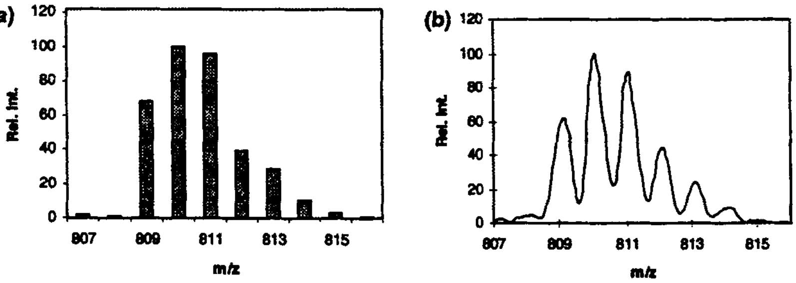
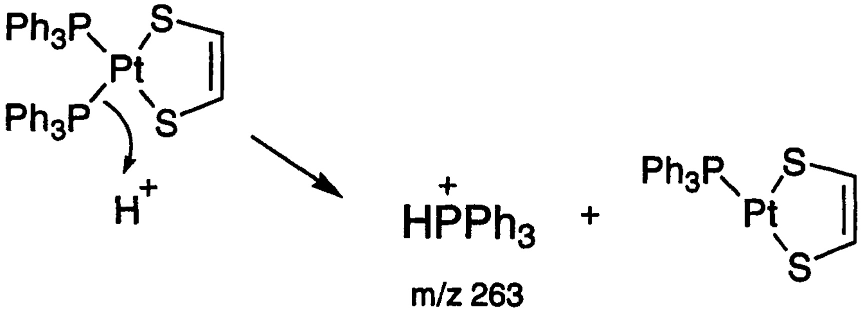


FIGURE 4 (a) Theoretical isotope pattern and (b) actual isotope pattern for the $(M+H)^+$ ion of $(Ph_3P)_2Pt(edt)$.



SCHEME 1 Proposed fragmentation mechanism of the (Ph$_3$P)$_2$Pt(dithiolenes) to produce the protonated triphenylphosphine ion at *m/z* 263.

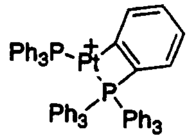


FIGURE 5 Proposed structure of the orthometallated species seen at *m/z* 718 for the triphenylphosphine complexes.

parent molecule can be protonated since a parent ion is seen. A dominant ionization process occurs as shown by the intensity of the HPPh$_3^+$.

As the fragmentor voltage was increased, the collision energy increased, thus creating additional structurally important ions that were observed (Figure 2(b)). The intensity of the protonated molecular ion and the protonated triphenylphosphine ion decreased. A new peak at *m/z* 718 appeared which can be attributed to an orthometallated triphenylphosphine ligand to the platinum (Figure 5).[5–8] The loss of neutral triphenylphosphine from the protonated molecular ion was also seen. Interestingly, only one ligand, the dmid^{2-}, shows any evidence of fragmentation of the dithiolene species itself.

At high collision energies, corresponding to the 240 and 300 V settings for the fragmentor, the spectra became similar (Figure 2(c)). The protonated molecular species was no longer present, indicating that it has dissociated completely into fragment components. The protonated triphenylphosphine ligand was seen, but with considerably reduced intensity. Also, the peak at *m/z* 718 was present for most compounds, disappearing only at the highest collision energy.

From the similarity of all peaks in the triphenylphosphine compounds, it can be concluded that the triphenylphosphine ligand and the platinum tends to drive the fragmentation. The dithiolene ligand plays little to no part in the fragmentation at higher energies except perhaps to be a neutral leaving group. This is due to the stability of the dithiolene unit. This is reasonable, since it would be difficult to imagine a positively charged dithiolene ligand coming from the protonated parent complex.

The mass spectral results for the COD compounds were much harder to interpret, due to extensive overlap of peaks that are close together and contain platinum isotope patterns. The extensive fragmentation of the COD compounds appears to be driven by cleavage of the COD–Pt π-bond. Unlike the triphenylphosphine, the COD can act as either a weak σ donor or as a strong π acceptor.[2] In this series of compounds, the COD is acting as a π acceptor. At low collision energy, the protonated molecular ion was seen for all compounds (Figure 3(a)). This was the base peak for all of these compounds.

As the collision energy was increased, the COD began to form fragments, as expected of an organic moiety under high collision energy conditions (Figure 3(b)). Unfortunately, the platinum isotopes complicated the spectra. In addition, the platinum isotope patterns overlap due to losses of H_2 from the COD, making determination of the correct mass of the peaks difficult.

At very high collision energies, the spectra for all of the species appear similar, showing a high degree of fragmentation (Figure 3(c)). With the COD compounds, similar to the triphenylphosphine compounds, the COD ligand and the platinum rather than the dithiolene are directing the fragmentation.

A unique and interesting feature of the (COD)Pt(1,2-dithiolenes) was that at high collision energy, a peak at *m/z* 195 was present, indicating a Pt^+ species (Figure 3(c)). The platinum, which was originally Pt(II), picked up an electron and became a positively charged Pt(I) species that was detectable by the mass spectrometer. This was not seen for the triphenylphosphine compounds. This indicates that the Pt–COD bond fragments *via* a single electron process and, with enough energy input into the molecule, the Pt is left bare in the (COD)Pt(1,2-dithiolenes).

We observed a dimer in the spectrum of (COD)Pt(edt) **2** (Figure 6). In order to determine if the dimer was present as a covalent species in solution or if it was a product of the ionization, five different concentrations were analyzed. If the dimer were present as a covalent species in solution, then the ratio of dimer present to molecular ion present would have remained constant. The experiments showed that the dimer to monomer ratio changed considerably with decreasing concentration proving the dimer is a product of ion–molecule reactions in the mass spectrometer. However, it is still possible for a non-covalent dimer to be present in solution. Using fast-atom bombardment (FAB) mass spectrometry on the same sample further

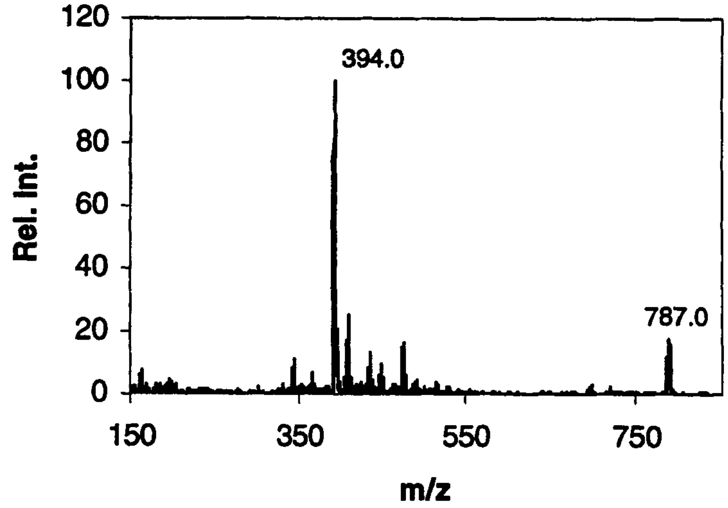


FIGURE 6 Spectrum of (COD)Pt(edt) 2 at a fragmentor energy of 60 V, showing the protonated dimer.

supported the hypothesis that the dimer was either a product of the mass spectrometer or a non-covalent dimer. In the FAB spectrum, no dimer was seen. In addition, the APCI experiment utilized a short column separation. It is not likely that a covalent dimer and a monomer would elute at the same time in the liquid chromatographic separation; however, it is interesting that a protonated dimer is stable and forms in the gas phase.

In the spectra of $(Ph_3P)_2Pt(mnt)$ and (COD)Pt(mnt) several solvent adduct species are present. One of the most interesting is the one corresponding to $(M+18)^+$. Typically, when the vaporizer temperature in APCI-MS is increased, solvent adducts disappear (due to more efficient drying of solvent clusters in the vaporizer). When this experiment was carried out, surprisingly, the $(M+18)^+$ ion, at *m/z* 877 and *m/z* 461 for the $(Ph_3P)_2Pt(mnt)$ and (COD)Pt(mnt), respectively, increased in intensity, eventually becoming more intense than the protonated molecular ion. This was not expected; however, it is known that ammonium ions can be produced by acid hydrolysis of a nitrile.[9] Furthermore, this reaction, which occurs in several steps, is endothermic and would therefore be more likely to occur at higher temperatures. In this environment, the mass spectral difference of 18 is definitive for ammonium. We assign this solvent adduct to an $(M+NH_4)^+$ adduct.

It is curious that diagnostic ions for the dithiolene ligands are absent, especially with the different modes of bonding present in the two types of complexes. In the triphenylphosphine species, we know that the triphenylphosphine is predominately σ-bonded to the platinum, and therefore, due to symmetry, the dithiolene ligand is acting as a weak π-acceptor. Conversely, in the cases of the COD complexes, the COD is acting as a strong π-acceptor, and the dithiolene acts as a π-donor.[2] It is clear that the "extra" stability associated with the resonance structure of dithiolenes is quite important and regardless of the bonding type, the inherent stability of the dithiolenes is dominant.

CONCLUSIONS

In our study of Pt dithiolenes, the need for additional diagnostic physical characterization techniques led us to investigate LC-APCI-MS. We were able to observe several different reactions of these complexes not previously observed. In addition, we were able to show that new complexes as well as a dimer are stable and can be prepared in the conditions of the mass spectral experiment.

Acknowledgments

The authors wish to thank Hewlett Packard for the loan of the HP 1100 Series MSD and LC, without which this work could not have been completed.

References

[1] C.E. Keefer, S.T. Purrington, R.D. Bereman, B.W. Knight, D.R. Bedgood and P.D. Boyle, *Inorg. Chim. Acta*, **282**, 200 (1998).
[2] C.E. Keefer, R.D. Bereman, S.T. Purrington, B.W. Knight and P.D. Boyle, *Inorg. Chem.*, **38**, 2294 (1999).
[3] R.D. Voyksner and T. Pack, *Rapid Commun. Mass Spectrom.*, **5**, 263 (1991).
[4] C.E. Keefer, S.T. Purrington, R.D. Bereman and P.D. Boyle, *Inorg. Chem.*, **38**, 5437 (1999).
[5] J. Fawcett, W. Henderson, R.D.W. Kemmitt, D.R. Russell and A. Upreti, *J. Chem. Soc., Dalton Trans.*, 1897 (1996).
[6] W. Henderson and B.K. Nicholson, *Polyhedron*, **15**, 4015 (1996).
[7] J.M. Law, W. Henderson and B.K. Nicholson, *J. Chem. Soc., Dalton Trans.*, 4587 (1997).
[8] L.J. McCaffrey, W. Henderson, B.K. Nicholson, J.E. Mackay and M.B. Dinger, *J. Chem. Soc., Dalton Trans.*, 2577 (1997).
[9] E.C. Kendall and B. McKenzie, *Org. Syn. Coll.* Vol. 3, p. 25 (1923). Hans Chacher Clarke (Ed.), New York, Wiley and Sons, Inc.