Utah State University

DigitalCommons@USU

5-1998

Thermal Decomposition of Cp*Re(CO)(NO)NO2

Kale Allen Swainston
Utah State University

Utah State University
MERRILL-CAZIER LIBRARY

Thermal Decomposition of Cp*Re(CO)(NO)NO$_2$

by

Kale Allen Swainston

Thesis submitted in partial fulfillment
of the requirements for the degree

of

UNIVERSITY HONORS
WITH DEPARTMENTAL HONORS

in

Chemistry

Approved:

_____   _____
Thesis/Project Advisor   Department Honors Advisor

_____
Director of Honors Program

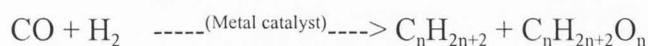UTAH STATE UNIVERSITY
Logan, UT

1998

Abstract

The focus of this work is to examine the thermal reactivity of the $Cp^*Re(CO)(NO)NO_2$ complex. Upon heating with a flame, the orange crystals decompose very rapidly, with a darkening of color and gas production. To investigate this reaction, the decomposition was carefully controlled by heating with N_2 gas, and in heated solution. The products obtained from the heated solution were purified using column chromatography, yielding two new interesting compounds, believed to be Cp^*ReNO dimers with bridging oxygens.

Background

In 1968, E.O. Fischer synthesized $[CpRe(CO)_2NO]^+PF_6^-$. This complex was one of the first group of rhenium complexes synthesized that belongs to the family of "piano stool" complexes. These complexes are called such because of their structure; they have three relatively small ligands (the legs) opposite the large cyclopentadienyl (Cp) ligand (the seat). Interest in these complexes was piqued as Americans endured the fuel shortages of the 1970's. As interest in alternative forms of fuel grew, scientists realized the role that transition metal complexes can play in the synthesis of new fuels (Sum, 1). Two example reactions, the water-gas shift reaction and the Fischer Tropsch catalysis, respectively, are shown below:

$$CO + H_2O \ ----^{(Metal\ catalyst)}---> \ CO_2 + H_2$$

$$CO + H_2 \ ----^{(Metal\ catalyst)}---> C_nH_{2n+2} + C_nH_{2n+2}O_n$$
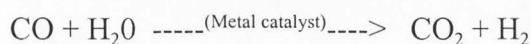
Another key player in the study of these rhenium complexes is J. A. Gladysz. Gladysz has reported the synthesis and structure of many of these Cp and Cp* (pentamethylcyclopentadienyl) compounds, and continues work on them today.

The family of complexes discussed in this paper can serve as models for the catalysis of the reactions above. Even though the world is not in the midst of another fossil fuel shortage, the supply is still finite, and alternatives must be found.

Previous Work

Beginning in the early 1990's, John L. Hubbard and his research group have been studying this type of rhenium chemistry. In 1991, Vivienne Sum wrote her BSc dissertation on $Cp*Re(CO)_2(NO)I$. She studied this compound's behavior with respect to carbonyl substitution products and thermal activity. Her substitution work led to the complex that is the subject of this paper, $Cp*Re(CO)(NO)NO_2$. Sum found that by treating $Cp*Re(CO)(NO)I$ with $AgNO_2$, the nitro group would displace the iodine. This new compound actually exists as two linkage isomers, designated $Cp*Re(CO)(NO)NO_2$ and $Cp*Re(CO)(NO)ONO$. The difference between these isomers is the NO_2 isomer is connected to the metal center by the nitrogen ("N-bound"),

and the ONO isomer is connected by one of the oxygens ("O-bound").

In 1995, another of Dr. Hubbard's graduate students, Radford Perry, wrote a thesis on the thermal decomposition of $Cp*Re(CO)(NO)NO_2$. It was found that the compound quickly darkens and gives off an aerosol upon heating. Perry's work concentrated on the analysis of the gases given off during this reaction. The gases were analyzed using a thermo-gravimetric analyzer (TGA). This piece of equipment is designed to give a graphical representation of the mass of a sample as a function of temperature. The exhaust of the TGA was directed to an FT-IR spectrometer, so that the gases given off by the sample could be constantly monitored. This analysis led to the conclusion that the gases given off consisted mainly of CO_2, N_2O, N_2, and a small amount of NO. This analysis led Perry to propose a mechanism for the decomposition, and a structure of the products. To confirm his ideas, a study of the solid decomposition products and the effect that the linkage isomers have on the products would need to be done.

Current Work

The work that I have done picks up where Perry's left off. The goal of my work is to control the thermal decomposition of $Cp*Re(CO)(NO)NO_2$ and to analyze the solid products of the decomposition reaction.
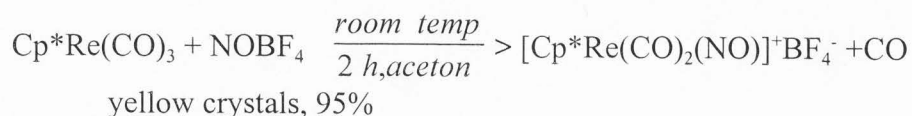
The time that I have spent as an undergraduate research assistant has been spent mastering the synthesis of $Cp*Re(CO)(NO)NO_2$, and examining different ways of controlling and monitoring the decomposition process.
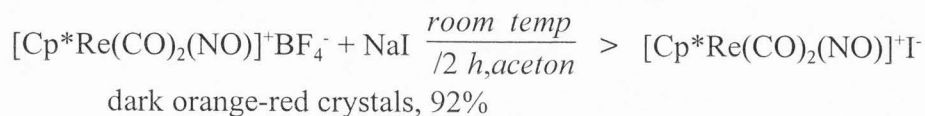
Synthesis

The synthesis of $Cp*Re(CO)(NO)NO_2$ is a multi-reaction process. The starting materials are rhenium carbonyl and pentamethylcyclopentadiene. The reaction liberates CO and adds the Cp* ligand to the metal.

$$Re_2(CO)_{10} + 2Cp* \xrightarrow[hour]{210C} 2Cp*Re(CO)_3 + 4CO \qquad \text{white crystals, 95\%}$$

The $Cp*Re(CO)_3$ is then treated with Nitrosyltetrafluoroborate, then recrystallized. A carbonyl ligand is displaced by a nitrosyl ligand, liberating CO. The BF_4 remains as a counterion.

$$Cp*Re(CO)_3 + NOBF_4 \xrightarrow[2\ h,aceton]{room\ temp} [Cp*Re(CO)_2(NO)]^+BF_4^- + CO$$
$$\text{yellow crystals, 95\%}$$

The BF_4 salt is then treated with sodium iodide. The BF_4 is displaced by iodine.

$$[Cp*Re(CO)_2(NO)]^+BF_4^- + NaI \xrightarrow[/2\ h,aceton]{room\ temp} [Cp*Re(CO)_2(NO)]^+I^-$$
$$\text{dark orange-red crystals, 92\%}$$

The iodine salt is then heated. This causes a carbonyl ligand to be ejected, and the iodine takes its place. This generates a neutral complex.

$$[Cp*Re(CO)_2(NO)]^+I^- \xrightarrow[DME]{130C,1\ hour} Cp*Re(CO)_2(NO)I + CO$$
$$\text{dark red crystals, 99\%}$$
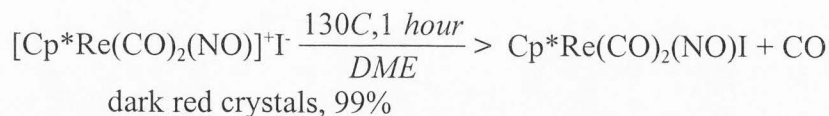
Finally, the neutral iodine complex is treated with silver nitrite. The iodine is displaced by the nitro group, and the silver iodide precipitates out.

$$Cp^*Re(CO)_2(NO)I + AgNO_2 \xrightarrow[acetone]{overnight} Cp^*Re(CO)_2(NO)NO_2 + AgI$$

bright orange crystals, 85%
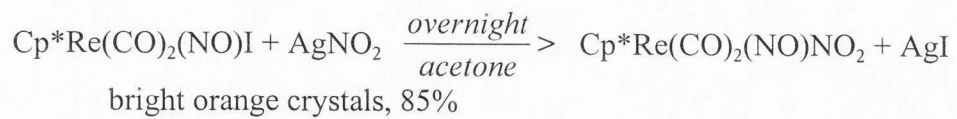
The product has been found to be relatively air stable, but the crystals will tend to darken if not kept in the freezer.
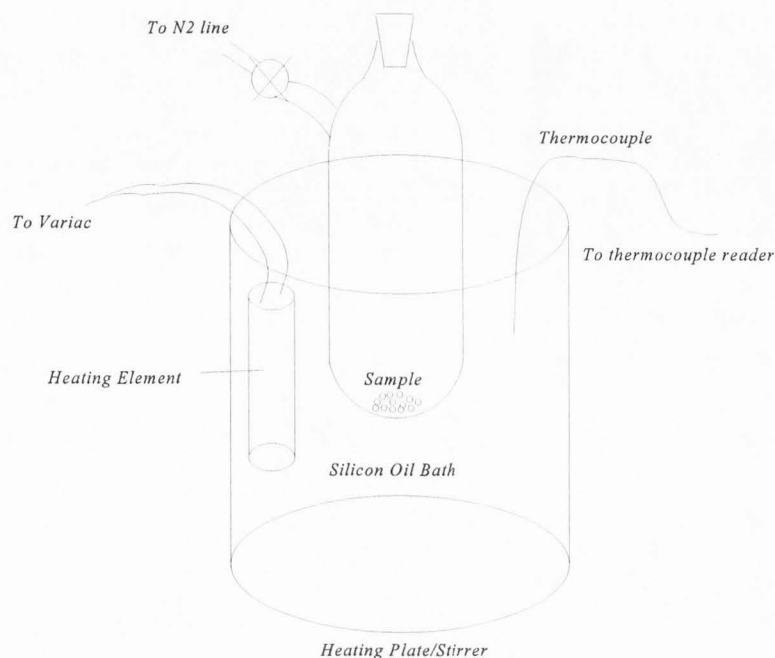
Decomposition Methods

This brings us to the decomposition of the complex. Different methods of controlling and monitoring the reaction were tried. The first method involved placing a sample of the complex in the bottom of a Schlenk tube, and submerging the Schlenk tube in a silicon oil bath. The oil bath was heated by a resistive heating element controlled by a variac. The setup is sketched:

To N2 line

Thermocouple

To Variac

To thermocouple reader

Heating Element   *Sample*

Silicon Oil Bath

Heating Plate/Stirrer

This setup allowed good heating of the sample, but the temperature control was not very precise, and had a lot of lag time when adjusted. Spectroscopically monitoring the reaction was also difficult because the Schlenk would have to be opened and a sample withdrawn.

The next setup allowed the reaction to be monitored by IR as it proceeded. The compound was placed on a KBr pellet (thin film). The pellet holder was modified with a thermocouple and a gas inlet. Nitrogen gas was heated with a resistive heating element, and passed over the sample. The setup looked like this:

Outlet

Sample

To thermocouple reader

To resistive element heater/ N2 inlet

IR sample holder
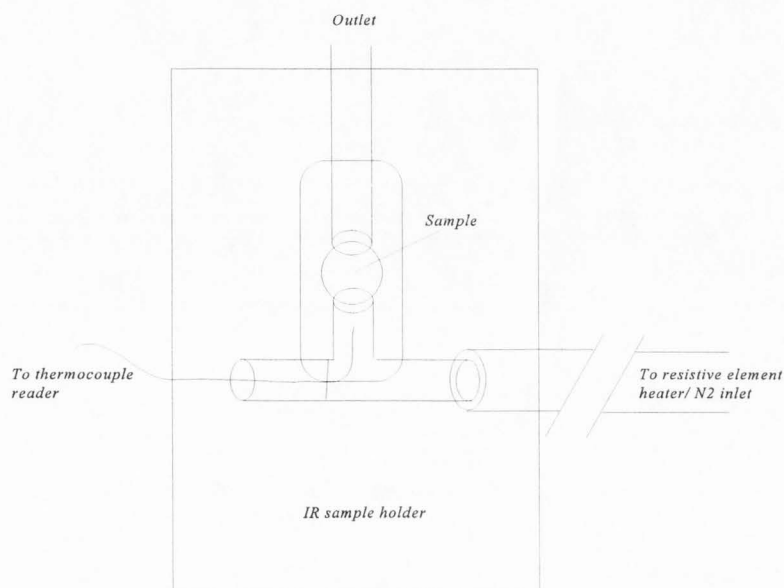
This setup allowed fairly precise temperature control, and an easy way to monitor the reaction by IR. The spectra obtained from this setup were rather indeterminate, probably because the products on the thin film were not separated from each other. This lead to the third setup.

The third method of decomposing the complex turned out to be the most advantageous for the solid product analysis. This method involved placing a sample of $Cp^*Re(CO)(NO)NO_2$ in a Schlenk tube and dissolving it in toluene. The Schlenk was placed in the silicon oil bath, and heated at 110 degrees C overnight. When cooled, all of the $Cp^*Re(CO)(NO)NO_2$ had decomposed, as determined by IR. The toluene was then removed *in vacuo*, and the products separated by column chromatography. This separation yielded 5 bands, with some products left on the column. Two of the bands yielded very interesting crystals. These two compounds, when crystallized, were very similar, yet distinct, in color (KSII, light red, KSIV, cherry red). The are

also very similar in density, combustion analysis, infra-red, and X-ray crystal analysis (see data section). The X-ray structures of these crystals show that they are probably Re dimers, as Perry's paper proposed.
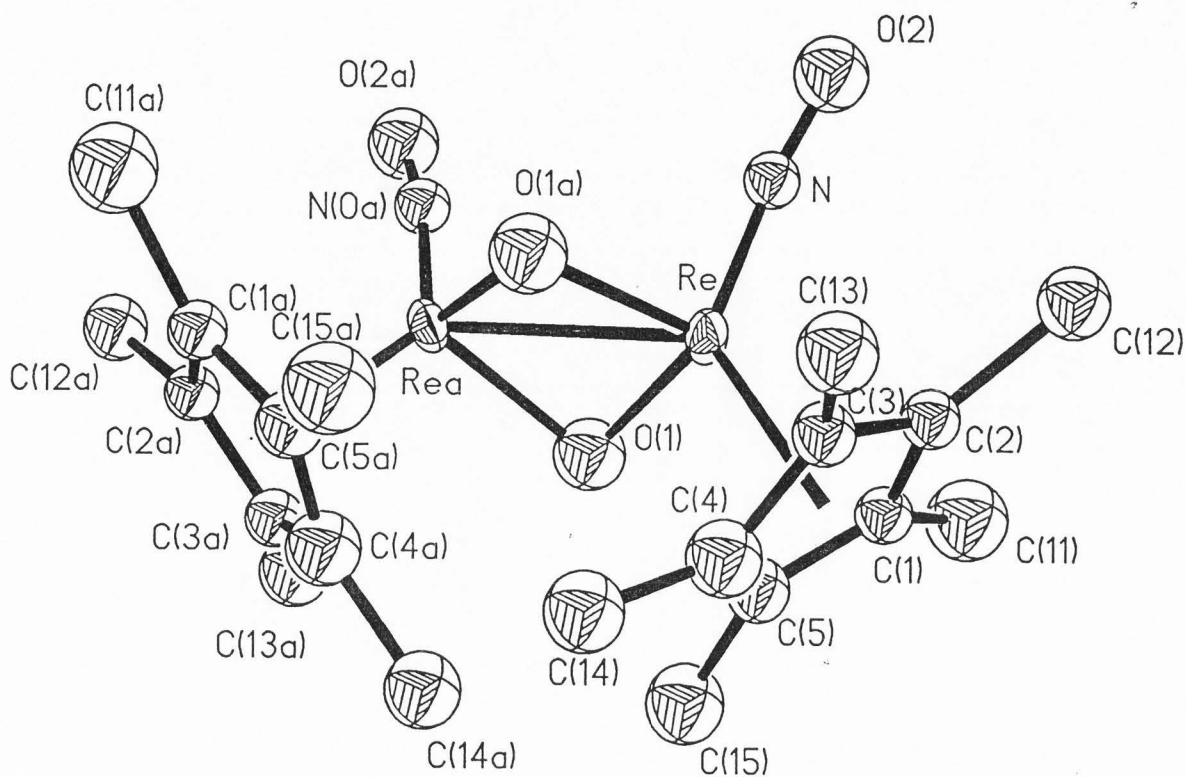
Unfortunately, not enough of the compounds were obtained for a more thorough analysis.

Future Work

Work is currently being done to make more decomposition products. The synthesis underway is using the Cp^ ligand, instead of the Cp*. The Cp^ ligand is a tetramethyl ethyl version of the pentamethyl ligand. This will give the Cp^Re(CO)(NO)NO$_2$ complex a more informative NMR spectrum, as there will be more than one chemically equivalent proton environment.

ks7
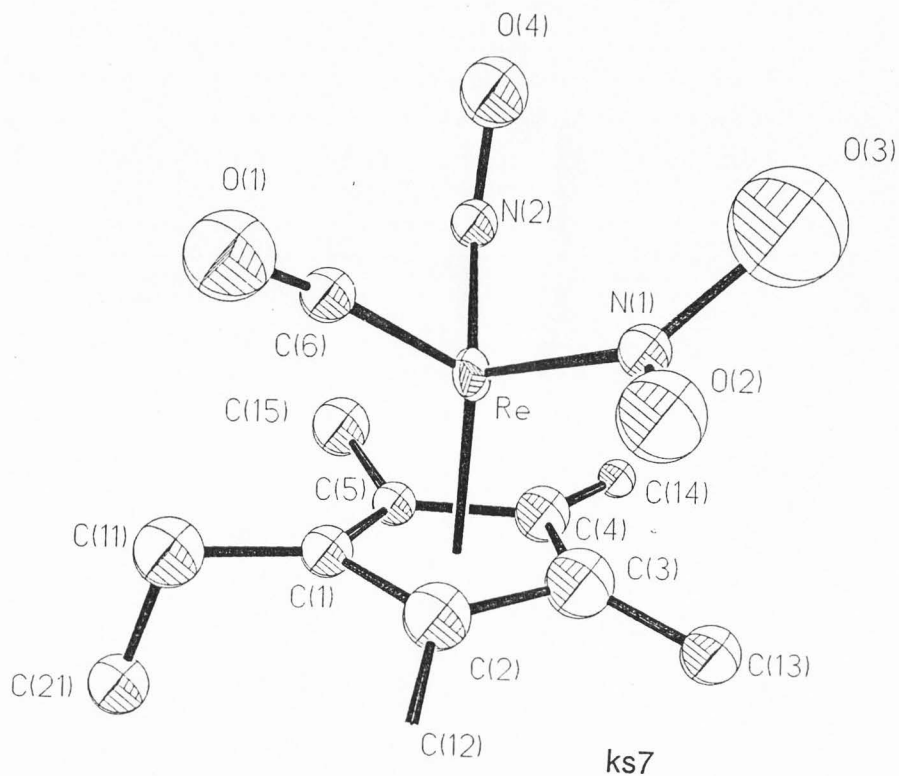
Future decomposition reactions will concentrate on the relative ratio of nitro/nitrito isomers in the complex. Some degree of control of this ratio may be exerted by placing the complex in different solvents. Any change in the composition of the products with a change in the ratio of the isomers will provide more information for proposing a mechanism.

Finally, a gentler column support that will not bind the products must be found. With a better chromatography separation, a better yield of products will be obtained.

Experimental

For all preparations, standard Schlenk techniques were used. The following preparations were also used with the Cp^ ligand, with similar yields.

Preparation of Cp*Re(CO)$_3$. A 100-mL round-bottom flask was charged with pentamethylcyclopentadiene and Re$_2$(CO)$_{10}$ (3.3:1 Cp*:Re$_2$(CO)$_{10}$ molar ratio) with a reflux condenser and a bubbler. The flask was placed in a silicone oil bath on a stirrer/ hotplate. The reaction was stirred and heated. The rhenium carbonyl crystals dissolved, and gas was evolved. The reaction was heated at 150° C for .5 h, then heated to 180° C for 2-5 h. At this time, gas evolution had ceased. The contents crystallized as the flask reached room temperature. The contents were chilled in the freezer, and washed over a Hirsch funnel with cold hexanes. This gave white crystals, 95% yield.

Preparation of [Cp*Re(CO)$_2$]$^+$BF$_4^-$. A Schlenk flask was charged with freshly degassed acetone and Cp*Re(CO)$_3$ (27 mL acetone per gram of solid). The reaction was stirred to dissolve the solid. NO$^+$BF$_4^-$ was added (1:1.5 Cp*Re(CO)$_3$:NO$^+$BF$_4^-$ molar ratio) slowly in portions. The solution darkened and began to evolve gas. After all NO$^+$BF$_4^-$ was added, the reaction stirred for 2h. The solution was then chilled and poured into diethyl ether (147 mL ether per gram of Cp*Re(CO)$_3$), giving a yellow precipitate. The precipitate was separated by filtration, dissolved in dichloromethane, filtered, and layered with ether. Crystals formed upon standing overnight in the freezer, 95% yield.

Preparation of [Cp*Re(CO)$_2$(NO)]I. A solution of [Cp*Re(CO)$_2$]$^+$BF$_4^-$ in acetone was treated with NaI (1:1.5 [Cp*Re(CO)$_2$]$^+$BF$_4^-$:NaI molar ratio). This produced a color change from yellow to dark orange-red. After 0.5 h of stirring, the solvent was removed *in vacuo*, yielding orange-red crystals, 92%.

Preparation of Cp*Re(CO)(NO)I. [Cp*Re(CO)$_2$(NO)]I was dissolved in DME and heated at 130° C for 0.5 h. The solvent was then removed *in vacuo*, yielding dark red crystals, 99%.

Preparation of Cp*Re(CO)(NO)(NO$_2$). A Schlenk flask was charged with Cp*Re(CO)(NO)I, acetone, and freshly prepared (still wet with H$_2$0) AgNO$_2$ (1:1.5 Cp*Re(CO)(NO)I:AgNO$_2$ molar ratio), and stirred overnight. The mixture was then filtered to remove AgI and extracted with dichloromethane, and dried with MgSO$_4$. This resulted in bright orange crystals, 85%.

Column Chromatography. A water-cooled 3" by 1cm ø column packed with silica gel in hexanes was used. Bands were eluted with progressively more polar solvents. A yellow band eluted with toluene, a brown band eluted with toluene and dichloromethane, a brown column eluted with a dichloromethane and diethyl ether mix, an orange/red column eluted with straight diethyl ether, and a dark brown column eluted with acetone.

Data

Density Measurements. The KSII and KSIV samples were measured by adjusting the density of a mixture of 1,3 diiodopropane and carbon tetrachloride until the crystals obtained neutral buoyancy. The densities of KSII and KSIV are 2.20 and 2.21 g/mL, respectively.

Combustion Analysis. Two of the decomposition products were sent to Atlantic Microlab, Inc. for combustion analysis of C, H, and N.

KSII

Element	Calculated	Found
C	32.7	33.76, 33.74
H	4.12	4.07, 4.09
N	3.81	3.75, 3.70

KSIV

Element	Calculated	Found
C	32.7	33.42
H	4.12	4.09
N	3.81	4.41

X-ray crystallography. Crystals were submitted to Dr. John L. Hubbard for X-ray crytallographic analysis. Graphics and data were generated by him.

KSII   (light red)

	A	B	C	Alpha	Beta	Gamma	Volume
Cell dimensions:	8.2652	9.5990	15.6782	90.000	113.948	90.000	1136.79
Error:	0.0016	0.0026	0.0036	0.000	0.016	0.000	0.45

	alpha	alpha1	alpha2
Wavelengths:	0.71073	0.70930	0.71359

KSIV   (dark red)

	A	B	C	Alpha	Beta	Gamma	Volume
Cell dimensions:	8.2583	9.6183	15.6300	90.000	113.726	90.000	1136.55
Error:	0.0020	0.0010	0.0028	0.000	0.015	0.000	0.35

	alpha	alpha1	alpha2
Wavelengths:	0.71073	0.70930	0.71359

KSV   (repeat of KSIV at -100)

	A	B	C	Alpha	Beta	Gamma	Volume
Cell dimensions:	15.4866	9.6085	8.1810	90.022	113.749	90.030	1114.27
Error:	0.0042	0.0030	0.0024	0.024	0.020	0.024	0.55

	alpha	alpha1	alpha2
Wavelengths:	0.71073	0.70930	0.71359

KSVII   ($Cp^\wedge Re(CO)(NO)(NO_2)$, room temp, decomposed on beam)

	A	B	C	Alpha	Beta	Gamma	Volume
Cell dimensions:	12.5880	7.8941	15.4017	90.000	106.959	90.000	1463.93
Error:	0.0026	0.0014	0.0034	0.000	0.016	0.000	0.50

	alpha	alpha1	alpha2
Wavelengths:	0.71073	0.70930	0.71359

References

Hubbard, John L., Kirk L. Kimball, Robert M. Burns, and Vivienne Sum. Halide Nucleophilic
  Attack on the $[(\eta^5\text{-}C_5R_5)Re(CO)_2(NO)]^+$ Cations: $(\eta^5\text{-}C_5R_5)Re(CO)_2(NO)X$ and $[fac\text{-}$
  $X_3Re(CO)_2(NO)]^-$ Formation through Competitive Loss of CO and $(\eta^5\text{-}C_5R_5)$ (R=H,
  CH_3). Inorganic Chemistry, 31, 4224-4230, 1992.

Perry, Radford. Evolved Gas Analysis of the thermal Decomposition of the
  $Cp^*Re(CO)(NO)(NO_2)$ Complex. Thesis, Master of Science in Chemistry. Utah State
  University. 1995.

Sum, Vivienne. Synthesis and Characterization of the tight-ion complex $(\eta^5\text{-}$
  $C_5Me_5)Re(CO)_2(NO)I$ and its Reactivity Leading to Carbonyl Substitution Products.
  Dissertation, BSc (Hons)CNAA Applied Chemistry. Nottingham Polytechnic. May-
  June 1991.