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π -Loaded Rhenium Complexes

A thesis presented in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

in

Chemistry

at Massey University, Palmerston North, New Zealand

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2000

This is dedicated to my life long companion,
Jacqueline Marie

Abstract

A range of rhenium(VII) tris(imido) complexes, $X\text{Re}(\text{NR})_3$ ($X=\text{Me}_3\text{SiO}$, $\text{R}=\text{Ar}'$; $X=\text{Cl}$, $\text{R}=\text{Ar}'$, *mes*, *Ar*), have been synthesized either from $[\text{ReO}_4]^-$, RNH_2 ($\text{R}=\text{Ar}'$, *mes*, *Ar*), Et_3N and Me_3SiCl or $\text{Re}(\text{NR})_2\text{Cl}_3(\text{py})$, RNH_2 ($\text{R}=\text{Ar}'$, *Ar*) and Et_3N . An X-ray crystal structure of $\text{Me}_3\text{SiORe}(\text{NAr}')_3$ and $\text{ClRe}(\text{NAr}')_3$ showed a slightly bent Re-N-C angle ($158.8(5)^\circ$ and $168.8(7)^\circ$ respectively) and short Re-N distances ($1.749(6)\text{\AA}$ and $1.758(7)\text{\AA}$). Mixed tris(imido) complexes, $\text{ClRe}(\text{NR})_2(\text{NR}')$ ($\text{R}=\text{Ar}$, $\text{R}'=\text{Ar}$, *p-tol*; $\text{R}=\text{Ar}$, $\text{R}'=\text{Ar}$, *p-FC}_6\text{H}_4*, *p-NO}_2\text{C}_6\text{H}_4*, *p-tol*, *AMP*, *o-ClC}_6\text{H}_4*, *m-ClC}_6\text{H}_4*, *o-t-BuC}_6\text{H}_4*) have been synthesized from $\text{Re}(\text{NR})_2\text{Cl}_3(\text{py})$ ($\text{R}=\text{Ar}'$, *Ar*), $\text{R}'\text{NH}_2$ ($\text{R}'=\text{Ar}$, *p-tol*, *Ar'*, *p-FC}_6\text{H}_4*, *p-NO}_2\text{C}_6\text{H}_4*, *AMP*, *o-ClC}_6\text{H}_4*, *m-ClC}_6\text{H}_4*, *o-t-BuC}_6\text{H}_4*) and Et_3N . An X-ray crystal structure of $\text{ClRe}(\text{NAr}')_2(\text{NAr}')$ showed near linear Re-N-C angles ($165(2)$ - $172.5(19)^\circ$) and short Re-N distances ($1.70(2)$ - $1.766(19)\text{\AA}$). The crystal structure of $\text{ClRe}(\text{NAr}')_2(\text{N-}o\text{-}t\text{-Bu})$ showed 2 near linear Re-N-Ar angles ($172.4(2)^\circ$ and $171.2(2)^\circ$) and one bent Re-N-*o-t-Bu* angle ($160.8(2)^\circ$). Intermolecular imido ligand exchange was shown to occur slowly at room temperature between NAr' and Nmes . However, exchange between NAr' and NAr required heating to 60°C for exchange to occur. A chiral tetrahedral complex, $\text{ClRe}(\text{NAr}')(\text{NAr})(\text{N-}o\text{-}t\text{-Bu})$, was synthesized from $\text{Re}(\text{NAr}')(\text{NAr})\text{Cl}_3(\text{py})$, *o-t-BuC}_6\text{H}_4\text{NH}_2 and Et_3N . Alkyl/aryl derivatives of the mixed tris(imido) complexes, $\text{R}''\text{Re}(\text{NR})_2(\text{NR}')$ ($\text{R}=\text{Ar}'$, *Ar*, $\text{R}'=\text{Ar}'$, *Ar*, $\text{R}''=\text{Me}$, *p-tol*, CH_2Ph), have been synthesized from $\text{ClRe}(\text{NR})_2(\text{NR}')$ ($\text{R}=\text{Ar}$, $\text{R}'=\text{Ar}'$; $\text{R}=\text{Ar}'$, $\text{R}'=\text{Ar}$) and the Grignard, $\text{R}''\text{MgX}$ ($\text{R}''=\text{Me}$, *p-tol*, $\text{X}=\text{Br}$; $\text{R}''=\text{CH}_2\text{Ph}$, $\text{X}=\text{Cl}$). An X-ray crystal structure of $\text{MeRe}(\text{NAr}')_2(\text{NAr}')$ showed near linear Re-N-C angles ($168.5(3)$ - $171.2(3)^\circ$) and short Re-N lengths ($1.753(4)$ - $1.763(4)\text{\AA}$). The Re-N-Ar' angle was found to be $\sim 10^\circ$ larger than those found for tris(Ar'-imido) Re(VII) tetrahedral complexes. An oxo-bridging species, $[\text{Re}(\text{NAr}')_2(\text{p-tol})(\mu\text{-O})]_2$, was isolated presumably from the hydrolysis of *p-tolRe}(\text{NAr}')_3. The crystal structure of $[\text{Re}(\text{NAr}')_2(\text{p-tol})(\mu\text{-O})]_2$ showed the rhenium atoms to be in a distorted square pyramidal geometry, as indicated by the Re-O bond distances ($1.948(2)$ and $1.985(3)\text{\AA}$). Bis(imido) complexes, $\text{Re}(\text{NR})(\text{NR}')\text{Cl}_3(\text{py})$ ($\text{R}=\text{Ar}'$, $\text{R}'=\text{Ar}'$, *Ar*; $\text{R}=\text{R}'=\text{Ar}$), were synthesized from $\text{ClRe}(\text{NR})_2(\text{NR}')$ ($\text{R}=\text{Ar}'$, $\text{R}'=\text{Ar}'$, *Ar*; $\text{R}=\text{Ar}$, $\text{R}'=\text{Ar}'$, *Ar*) and pyHCl . An X-ray crystal structure of $\text{Re}(\text{NAr}')_2\text{Cl}_3(\text{py})$ showed near linear Re-N-C angles ($171.8(12)$ and $174.4(3)^\circ$) and short Re-N distances ($1.734(18)$ and $1.760(14)\text{\AA}$). The Cl ligands in the *cis* positions to the imido ligands are bent away from the imido ligands at an angle of $166.10(19)^\circ$. Amido complexes, *p-tolNHRe}(\text{NR})(\text{NR}')(\text{NR}''), have been synthesized from $\text{ClRe}(\text{NR})(\text{NR}')(\text{NR}'')$***

(R=R'=Ar, R''=Ar, *o*-'Bu; R=Ar, R'=Ar', R''=*o*-'Bu) and LiNH*p*-tol. An X-ray crystal structure of *p*-tolNHRe(NAr)₃ showed a bent Re-NH-C angle (129.6(3)°) typical of amido nitrogens. A range of Re(V) tris(imido) complexes, [Re(NR)₂(NR')] (R=R'=Ar'; R=Ar, R'=Ar', Ar, *o*-'Bu), have been synthesized from XRe(NR)₂(NR') (X=Me₃SiO, Cl) and elemental sodium. These anions were found to be very sensitive both in solution and as solids. An X-ray crystal structure of [Re(NAr')₃]⁻ showed the complex to possess a 2-fold axis of symmetry through one of the imido ligands. The counter ion was found to be Na⁺ with 6 coordinated molecules of thf. The anions were found to react with ClSnMe₃ and ClAuPPh₃ to form Re-Sn (Me₃SnRe(NAr)₂(NR), R=Ar', Ar, *o*-'Bu) and Re-Au (Ph₃PAuRe(NR)₂(NR'), R=R'=Ar'; R=Ar, R'=Ar', Ar) complexes respectively. The crystal structure of Me₃SnRe(NAr)₃ and Me₃SnRe(NAr)₂(NAr') showed near linear Re-N-C angles (170.2(5)-172.9(2)°) and short Re-N distances (1.752(6)-1.779(3)Å). Rhenium(VI) dimeric complexes were synthesized from the anion, [Re(NR)₂(NR')] (R=R'=Ar'; R=Ar, R'=Ar', Ar, *o*-'Bu) and ferrocenium, [Cp₂Fe]⁺. Both Re₂(NAr')₆ and Re₂(NAr)₄(NAr')₂ contain bridging imido ligands, while Re₂(NAr)₆ and Re₂(NAr)₄(*N*-*o*-'Bu)₂ contain only terminal imido ligands, as indicated by proton NMR. An X-ray crystal structure of [Re(NAr')₂(μ-NAr')]₂ showed slightly bent terminal imido angles (156.2(3) to 168.8(3)°), short Re-N(terminal) distances (1.750(4) to 1.763(3)Å) and typical Re-N(bridging) distances of 1.951-1.959(4)Å. The average Re-Re distance of 2.735(4)Å indicates a weak metal-metal interaction. The crystal structure of Re₂(NAr)₆ showed the complex adopts an ethane-like geometry with the imido ligands arranged in a staggered orientation. The Re-Re bond lies on a crystallographic S₆ axis. A Re(VII) cation, [Re(NAr)₃]⁺, is implicated on the basis of formation of a ferrocene complex, (C₅H₅)Fe(C₅H₄)Re(NAr)₃.

Acknowledgements

During the course of this work, a number of people have provided contributions, whom I would like to acknowledge. First, I thank my supervisor Prof. Tony Burrell for his guidance and dedication for this research. Second, I would like to thank the people of B403/B406 especially Warwick Belcher (use of Sky TV) and Gavin Collis for their advice. Third, I would like to thank John Allen and his team at the Hort Research Mass Spectrometry Facility and the people of the microanalytical lab at Otago University for elemental analysis data.

A special thanks goes to Steven Kennedy, who provided the much needed distractions over the past few years.

Finally, I would like to thank the Marsden Fund for providing financial support.

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Abbreviations

ada	.	.	.	adamantyl
AMP	.	.	.	2-amino,6-methylpyridine
Ar	.	.	.	2,6-diisopropylphenyl
Ar'	.	.	.	2,6-dimethylphenyl
Ar*	.	.	.	2,6-dichlorophenyl
bipy	.	.	.	2,2'-bipyridine
br	.	.	.	broad
Bu	.	.	.	butyl
Cat	.	.	.	catecholate ($C_6H_4O_2^{2-}$)
Cp	.	.	.	cyclopentadienyl
Cp*	.	.	.	pentamethylcyclopentadienyl
d	.	.	.	doublet
DME	.	.	.	1,2-dimethoxyethane
Et	.	.	.	ethyl
hep	.	.	.	heptet
J	.	.	.	coupling constant in Hz
L	.	.	.	ligand
L_n	.	.	.	n number of ligands
M	.	.	.	metal
m	.	.	.	multiplet
<i>m</i> -Cl	.	.	.	<i>m</i> -chlorophenyl
Me	.	.	.	methyl
mes	.	.	.	2,4,6-trimethylphenyl
ⁿ Bu	.	.	.	butyl
NMR	.	.	.	nuclear magnetic resonance
Np	.	.	.	neopentyl (CH_2CMe_3)
<i>o</i> -Cl	.	.	.	<i>o</i> -chlorophenyl
<i>o</i> - ^t Bu	.	.	.	<i>o</i> - <i>tert</i> -butylphenyl
OTf	.	.	.	triflate ($OSO_2CF_3^-$)
<i>o</i> -tol	.	.	.	<i>o</i> -methylphenyl
<i>p</i> -F	.	.	.	<i>p</i> -fluorophenyl
Ph	.	.	.	phenyl
<i>p</i> -NO ₂	.	.	.	<i>p</i> -nitrophenyl
PPN	.	.	.	$[Ph_3P=N=PPh_3]^+$
<i>p</i> -tol	.	.	.	<i>p</i> -methylphenyl

py	pyridine
R	organic group
s	singlet
Si*	Si ^t Bu ₃
t	triplet
^t Bu	<i>tert</i> -butyl
thf	tetrahydrofuran
TM	transition metal
tmed	N,N,N',N'-tetramethylethylenediamine
TMS	trimethylsiloxy
VB	valance bond
X	anionic ligand