π-Loaded Rhenium Complexes

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This is dedicated to my life long companion,
Jacqueline Marie

Abstract

A range of rhenium(VII) tris(imido) complexes, $XRe(NR)_3$ (X=Me_3SiO, R=Ar'; X=Cl, R=Ar', mes, Ar), have been synthesized either from $[ReO_4]^-$, RNH_2 (R=Ar', mes, Ar), Et_3N and Me_3SiCl or $Re(NR)_2Cl_3(py)$, RNH_2 (R=Ar', Ar) and Et_3N. An X-ray crystal structure of $Me_3SiORe(NAr')_3$ and $ClRe(NAr)_3$ showed a slightly bent Re-N-C angle (158.8(5)° and 168.8(7)° respectively) and short Re-N distances (1.749(6)Å and 1.758(7)Å). Mixed tris(imido) complexes, $ClRe(NR)_2(NR')$ (R=Ar, R'=Ar, *p*-tol; R=Ar, R'=Ar, *p*-FC_6H_4, *p*-$NO_2C_6H_4$, *p*-tol, AMP, *o*-ClC_6H_4, *m*-ClC_6H_4, *o*-$^tBuC_6H_4$) have been synthesized from $Re(NR)_2Cl_3(py)$ (R=Ar', Ar), $R'NH_2$ (R'= Ar, *p*-tol, Ar', *p*-FC_6H_4, *p*-$NO_2C_6H_4$, AMP, *o*-ClC_6H_4, *m*-ClC_6H_4, *o*-$^tBuC_6H_4$) and Et_3N. An X-ray crystal structure of $ClRe(NAr)_2(NAr')$ showed near linear Re-N-C angles (165(2)-172.5(19)°) and short Re-N distances (1.70(2)-1.766(19)Å). The crystal structure of $ClRe(NAr)_2(N\text{-}o\text{-}^tBu)$ showed 2 near linear Re-N-Ar angles (172.4(2)° and 171.2(2)°) and one bent Re-N-*o*-^{t}Bu angle (160.8(2)°). 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, $ClRe(NAr')(NAr)(N\text{-}o\text{-}^tBu)$, was synthesized from $Re(NAr')(NAr)Cl_3(py)$, *o*-$^tBuC_6H_4NH_2$ and Et_3N. Alkyl/aryl derivatives of the mixed tris(imido) complexes, $R''Re(NR)_2(NR')$ (R=Ar', Ar, R'=Ar', Ar, R"=Me, *p*-tol, CH_2Ph), have been synthesized from $ClRe(NR)_2(NR')$ (R=Ar, R'=Ar'; R=Ar', R'=Ar) and the Grignard, R"MgX (R"=Me, *p*-tol, X=Br; R"=CH_2Ph, X=Cl). An X-ray crystal structure of $MeRe(NAr)_2(NAr')$ showed near linear Re-N-C angles (168.5(3)-171.2(3)°) and short Re-N lengths (1.753(4)-1.763(4)Å). The Re-N-Ar' angle was found to be ~10° larger than those found for tris(Ar'-imido) Re(VII) tetrahedral complexes. An oxo-bridging species, $[Re(NAr)_2(p\text{-tol})(\mu\text{-}O)]_2$, was isolated presumably from the hydrolysis of *p*-$tolRe(NAr)_3$. The crystal structure of $[Re(NAr)_2(p\text{-tol})(\mu\text{-}O)]_2$ 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)Å). Bis(imido) complexes, $Re(NR)(NR')Cl_3(py)$ (R=Ar', R'=Ar', Ar; R=R'=Ar), were synthesized from $ClRe(NR)_2(NR')$ (R=Ar', R'=Ar', Ar; R=Ar, R'=Ar', Ar) and pyHCl. An X-ray crystal structure of $Re(NAr')_2Cl_3(py)$ showed near linear Re-N-C angles (171.8(12) and 174.4(3)°) and short Re-N distances (1.734(18) and 1.760(14)Å). 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)°. Amido complexes, *p*-$tolNHRe(NR)(NR')(NR")$, have been synthesized from $ClRe(NR)(NR')(NR")$

(R=R'=Ar, R"=Ar, *o*-^{t}Bu; R=Ar, R'=Ar', R"=*o*-^{t}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*-^{t}Bu), have been synthesized from $XRe(NR)_2(NR')$ (X=Me_3SiO, 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 $ClSnMe_3$ and $ClAuPPh_3$ to form Re-Sn ($Me_3SnRe(NAr)_2(NR)$, R=Ar', Ar, *o*-^{t}Bu) and Re-Au ($Ph_3PAuRe(NR)_2(NR')$, R=R'=Ar'; R=Ar, R'=Ar', Ar) complexes respectively. The crystal structure of $Me_3SnRe(NAr)_3$ and $Me_3SnRe(NAr)_2(NAr')$ 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*-^{t}Bu) and ferrocenium, $[Cp_2Fe]^+$. Both $Re_2(NAr')_6$ and $Re_2(NAr)_4(NAr')_2$ contain bridging imido ligands, while $Re_2(NAr)_6$ and $Re_2(NAr)_4(N\text{-}o\text{-}^tBu)_2$ contain only terminal imido ligands, as indicated by proton NMR. An X-ray crystal structure of $[Re(NAr')_2(\mu\text{-}NAr')]_2$ 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 $Re_2(NAr)_6$ 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 S_6 axis. A Re(VII) cation, $[Re(NAr)_3]^+$, is implicated on the basis of formation of a ferrocene complex, $(C_5H_5)Fe(C_5H_4)Re(NAr)_3$.

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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
m-Cl	*m*-chlorophenyl
Me	methyl
mes	2,4,6-trimethylphenyl
^{n}Bu	butyl
NMR	nuclear magnetic resonance
Np	neopentyl (CH_2CMe_3)
o-Cl	*o*-chlorophenyl
o-^{t}Bu	*o-tert*-butylphenyl
OTf	triflate ($OSO_2CF_3^-$)
o-tol	*o*-methylphenyl
p-F	*p*-fluorophenyl
Ph	phenyl
p-NO_2	*p*-nitrophenyl
PPN	$[Ph_3P{=}N{=}PPh_3]^+$
p-tol	*p*-methylphenyl

py	pyridine
R	organic group
s	singlet
Si*	Si^tBu_3
t	triplet
^{t}Bu	*tert*-butyl
thf	tetrahydrofuran
TM	transition metal
tmed	N,N,N',N'-tetramethylethylenediamine
TMS	trimethylsiloxy
VB	valance bond
X	anionic ligand