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A systematic route to mixed imido complexes of rhenium

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The synthesis and structure of Re(VII) complexes with mixed imido ligands are described.

The imido ligand's ability to stabilise high-oxidation state metals and their utility as ancillary ligands in ring opening metathesis polymerisation (ROMP)[1] has spurred interest in the synthesis and reactivity of complexes containing these ligands.[2] More recently, compounds containing multiple imido ligands have exhibited the ability to take part in C–H bond activation.[3] One of the most important features of the π-donor imido ligand is the ability to vary the size of the alkyl or aryl functional group in the nitrogen. A change in the steric pressures of the imido ligands results in dramatic effects on both the structure and reactivity of their complexes.[4] It is therefore surprising that there are only a few publications that analyse this effect and even less that deal with internal comparisons of imido reactivity.[5] We have recently been investigating the reactivity of rhenium(VII) tris(imido) complexes and in particular how the steric demands of the imido groups influence reactivity both at the metal and at the imido ligand. To evaluate this reactivity in a logical way we have developed a systematic synthetic route to mixed imido complexes.

Mixed imido complexes are rare, with only a handful of reports in the literature.[5,6] In general, the method for preparing bis- and tris-(imido) complexes require that all of the imido ligands be added to the metal during a single reaction. While it is possible to prepare mixed ligand complexes by employing mixtures of imido ligand precursors, this is not always satisfactory.[6] We required a general method for the formation of mixed imido complexes that could be carried out in large scale with minimal purification.

Here, we outline a route that provides a systematic method for forming mixed imido complexes of rhenium. The methodology is based upon chemistry reported by Schrock and Williams.[7] Treatment of ReO_4NH_4 with H_2NAr or H_2NAr' (Ar = 2,6-diisopropylphenyl, Ar′ = 2,6-dimethylphenyl) in the presence of $SiMe_3Cl$ and pyridine gives the bis(imido) complexes $ReCl_3(py)(NAr)_2$ and $ReCl_3(py)(NAr')_2$, respectively. Interestingly, replacing the pyridine with triethylamine results in the formation of tris(imido) complexes. This difference can be attributed to the relative pK_a values of the pyridine and triethylamine. The bis(imido) complexes provide excellent routes to mixed imido complexes.

Treatment of $ReCl_3(py)(NAr)_2$ with an aniline in the presence of triethylamine results in the formation of a mixed tris(imido) complex. Examples of the range of mixed complexes available from this route are shown in Scheme 1. The yields for these reactions are generally good (60–85%), although all are very soluble and crystallisation proves difficult in some cases leading to losses upon purification. The compounds are all red/orange and produce simple NMR spectra consistent with their formulation.† It is possible that ligand exchange can occur for complexes containing smaller ligands. Solutions were generally handled at room temperature and below, and no exchange was observed.

Crystals of $ReCl(NAr)_2(NAr^*)$ (Ar* = 2-*tert*-butylphenyl) were obtained by cooling a pentane solution to −35 °C. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are given in the caption.‡ The metal–nitrogen bond distances 1.744(3) [Re(1)–N(1)], 1.751(3) [Re(1)–N(2)] and 1.757(3) [Re(1)–N(3)] are consistent with bond lengths generally found for arylimido ligands bound to rhenium.[8] The M–N–C angles for the NAr ligands are very similar at 172.4(2)° [Re(1)–N(1)–C(1a)] and 171.2(2)° [Re(1)–N(2)–C(1b)]. In contrast the 2-*tert*-butylphenyl ligand has a Re–N–C angle at 160.8(2)° due to unfavourable steric interactions caused by the

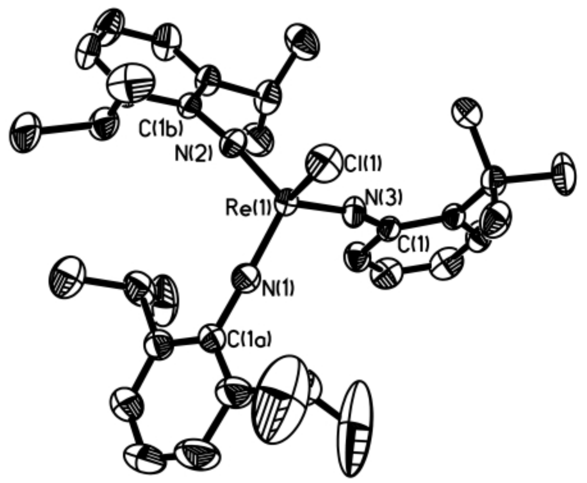
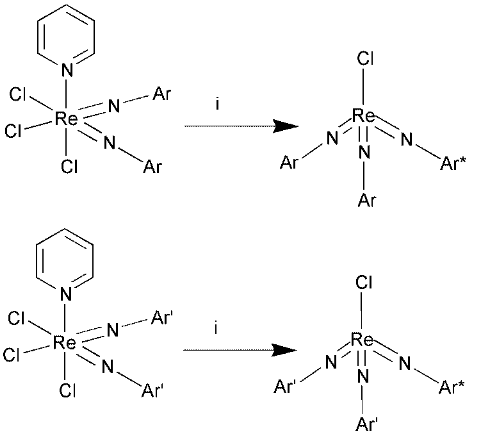


Fig. 1 Molecular structure of $ReCl(NAr)_2(NAr^*)$ (Ar* = 2-*tert*-butylphenyl). H atoms are omitted and thermal ellipsoids are plotted at the 50% level. Selected dimensions (Å and °): Re(1)–N(1) 1.744(3), Re(1)–N(2) 1.751(3), Re(1)–N(3) 1.757(3), Re(1)–Cl(1) 2.2990(8); N(1)–Re(1)–N(2) 111.46(13), N(1)–Re(1)–N(3) 110.56(13), N(2)–Re(1)–N(3) 111.62(12), N(1)–Re(1)–Cl(1) 107.54(9), N(2)–Re(1)–Cl(1) 107.37(8), N(3)–Re(1)–Cl(1) 108.10(9).



Scheme 1 Reagents and conditions: i, H_2NAr^*, $3NEt_3$, benzene, room temp, 30 min (Ar* = 2,6-dimethylphenyl, 2,6-diisopropylphenyl, *p*-tolyphenyl, *p*-nitrophenyl, 2-*tert*-butylphenyl, 2-chlorophenyl, 3-chlorophenyl, 4-fluorophenyl).

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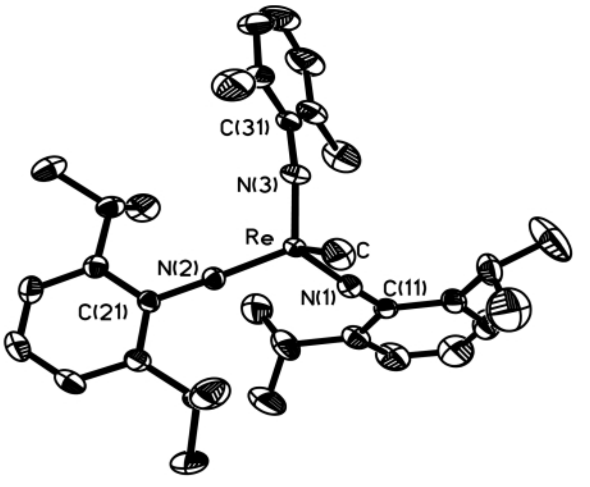
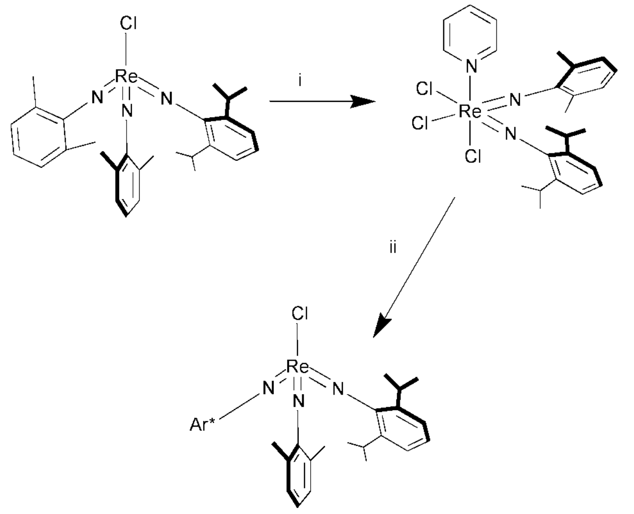


Fig. 2 Molecular structure of $Re(Me)(NAr)_2(NAr')$. H atoms are omitted and thermal ellipsoids are plotted at the 50% level. Selected dimensions (Å and °): Re–N(1) 1.763(4), Re–N(2) 1.757(3), Re–N(3) 1.753(4), Re–C 2.113(5); N(3)–Re–N(2) 115.63(17), N(3)–Re–N(1) 115.23(18), N(2)–Re–N(1) 114.75(17), N(3)–Re–C 102.81(19), N(2)–Re–C 101.85(19), N(1)–Re–C 103.9(2).



Scheme 2 Reagents and conditions: i, 2pyHCl, THF, room temp, 30 min. ii, H_2NAr^*, $3NEt_3$, benzene, room temp, 30 min ($Ar^* = p$-tolyphenyl, *p*-nitrophenyl, 2-*tert*-butylphenyl).

tert-butyl group. In all other respects the structure is similar to previously reported rhenium tris(imido) complexes.[8]

Reaction of the mixed imido complexes with Grignard reagents (MeMgBr, p-$CH_3C_6H_4MgBr$) results in clean conversion to the respective organometallic complex. Thus treatment of $ReCl(NAr)_2(NAr')$ with one equivalent of MeMgBr, produces the methyl complex $Re(Me)(NAr)_2(NAr')$.† Crystals of $Re(Me)(NAr)_2(NAr')$ were obtained by cooling a pentane solution to −35 °C. The molecular structure is shown in Fig. 2 and selected bond lengths and angles are given in the caption.‡ As with $ReCl(NAr)_2(NAr^*)$ (Ar^* = 2-*tert*-butylphenyl) the metal–nitrogen bond distances 1.763(4) [Re–N(1)], 1.757(3) [Re–N(2)] and 1.753(4) [Re–N(3)] are consistent with bond lengths generally found for arylimido ligands bound to rhenium. The M–N–C angles for all of the imido ligands are very similar at 169.1(3)° [Re–N(1)–C(11)] and 171.2(3)° [Re–N(2)–C(21)] and 168.5(3)° [Re–N(3)–C(31)], indicating that the steric effects are less pronounced when the smaller NAr′ ligand is present.

We envisioned that the nitrogen atoms of the smaller imido ligands would be selectively protonated in preference to those of the larger imido ligands. Indeed, we found that in all cases the nitrogen of the least sterically demanding ligand is protonated upon treating the mixed imido complex with 2 equivalents of pyHCl. In particular, the reaction of $ReCl(NAr')_2(NAr)$ gives $ReCl_3(NAr')(NAr)(py)$ in 70% yield. The synthesis and reactions of this new mixed bis(imido) complex are shown in Scheme 2. This complex provides a clean specific route to a tris(mixed imido) complex. Treatment of $ReCl_3(NAr')(NAr)(py)$ with H_2NAr^* (Ar^* = 2-*tert*-butylphenyl) in the presence of triethylamine results in the formation of a racemic mixture of $ReCl(NAr')(NAr)(NAr^*)$ enantiomers. The chemistry of technetium and rhenium tris(imido) complexes with the formula $XRe({=}NR)_3$ (R = *tert*-butyl, 2,6-dimethylphenyl and 2,6-diisopropylphenyl) have been investigated in some detail and both reactivity and structure in these complexes is influenced by the size of the imido ligands.[9] The methodologies reported here provide access to a π-loaded rhenium(VII) core where the steric demands at the metal can be tuned in a systematic and well defined fashion, hopefully providing control over the reactivity both at the metal centre and at the ligands.

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Notes and references

† Data for $ReCl(NAr)_2(NAr')$: ^1H NMR (C_6D_6): δ 7.10 (d, 4, J = 7.1, Ar), 6.96 (t, 2, J = 7.1, Ar), 6.88 (d, 2, J = 7.1, Ar′), 6.72 (t, 1, J = 7.1, Ar′), 3.84 (sept, 4, J = 6.8, $C\mathit{H}Me_2$), 2.32 (s, 6, CH_3), 1.13 (d, 24, J = 7.0, $CHC\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.8 (Ar), 152.7 (Ar′), 143.0 (Ar), 142.5 (Ar′), 132.1 (Ar), 127.1 (Ar′), 122.5 (Ar), 122.4 (Ar′), 28.1 ($\mathit{C}HCH_3$), 23.5 ($CH\mathit{C}H_3$), 17.9 (CH_3). Found: C 55.97; H 6.12; N 5.96. Calc: C 55.59; H 6.27; N 6.08%.

Data for $ReCl(NAr')_2(NAr)$: ^1H NMR (C_6D_6): δ 7.03 (d, 2, J = 7.1, Ar), 6.89 (t, 1, J = 7.1, Ar), 6.79 (d, 4, J = 7.1, Ar′), 6.65 (t, 2, J = 7.1, Ar′), 3.79 (sept, 2, J = 6.7, $C\mathit{H}Me_2$), 2.25 (s, 12, CH_3), 1.10 (d, 12, J = 7.0, $CHC\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 159.2 (Ar), 152.2 (Ar′), 142.9 (Ar), 142.6 (Ar′), 132.2 (Ar), 126.9 (Ar′), 121.9 (Ar), 121.8 (Ar′), 28.1 ($\mathit{C}HCH_3$), 23.0 ($CH\mathit{C}H_3$), 17.8 (CH_3). Found: C 52.67; H 5.85; N 6.33. Calc: C 52.95; H 5.55; N 6.61%.

Data for $ReCl(NAr)_2(NAr^*)$ (Ar^* = 2-*tert*-butylphenyl): ^1H NMR (C_6D_6): 7.19 (d, 1, J = 7.2, Ar*), 7.01 (d, 4, J = 7.0, Ar), 6.64–6.91 (m, 5, Ar/Ar*), 3.72 (sept, 4, J = 6.8, $C\mathit{H}Me_2$), 1.48 (s, 9, *tert*-butyl), 1.04 (d, 24, J = 7.0, $CHC\mathit{H}_3$). ^{13}C NMR (C_6D_6): δ 155.2 (Ar), 151.9 ($\mathit{C}_6H_5C(CH_3)_3$), 143.0 (Ar), 142.9 ($\mathit{C}_6H_5C(CH_3)_3$), 128.6 ($\mathit{C}_6H_5C(CH_3)_3$), 125.4 (Ar), 125.1 ($\mathit{C}_6H_5C(CH_3)_3$), 125.0 ($\mathit{C}_6H_5C(CH_3)_3$), 124.8 ($\mathit{C}_6H_5C(CH_3)_3$), 122.6 (Ar), 35.2 ($C_6H_5\mathit{C}(CH_3)_3$), 30.6 ($C_6H_5C(\mathit{C}H_3)_3$), 27.6 ($\mathit{C}CH_3$), 23.1 ($C\mathit{C}H_3$). Found: C 57.06; H 6.78; N 6.50. Calc: C 56.76; H 6.58; N 5.84%.

Data for $Re(Me)(NAr)_2(NAr')$: ^1H NMR (C_6D_6): δ 7.11 (d, 4, J = 7.1, Ar), 7.02 (t, 2, J = 7.1, Ar), 6.96 (d, 2, J = 7.1, Ar′), 6.81 (t, 1, J = 7.1, Ar′), 3.82 (sept, 4, J = 6.8, $C\mathit{H}Me_2$), 2.68 (s, 3, CH_3), 2.29 (s, 6, Ar′-CH_3), 1.08 (d, 24, J = 7.0, $CHC\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 156.2 (Ar), 152.9 (Ar′), 141.9 (Ar), 141.7 (Ar′), 129.5 (Ar), 125.6 (Ar′), 123.1 (Ar), 122.8 (Ar′), 28.8 ($\mathit{C}HCH_3$), 23.1 ($CH\mathit{C}H_3$), 18.6 (Ar′CH_3), 7.6 ($ReCH_3$). Found: C, 58.96; H, 6.77; N, 6.51. Calc: C 59.07; H 6.91; N 6.26%.

Data for $ReCl(NAr)(NAr')(NAr^*)$ (Ar^* = 2-*tert*-butylphenyl): ^1H NMR (C_6D_6): δ 7.21 (d, 1, J = 7.2, *tert*-butyl), 7.02 (d, 2, J = 7.0, Ar), 6.61–6.92 (m, 7, Ar/*tert*-butyl/Ar′), 3.78 (sept, 2, J = 7.0, $C\mathit{H}Me_2$), 2.29 (s, 6, CH_3), 1.48 (s, 9, *tert*-butyl), 1.05 (d, 12, J = 7.0, $CHC\mathit{H}_3$). ^{13}C NMR (C_6D_6): δ 155.8 (Ar), 154.6 (Ar′), 152.1 ($\mathit{C}_6H_4CMe_3$), 143.2 (Ar), 143.0 ($\mathit{C}_6H_4CMe_3$), 142.4 (Ar′), 133.2 (Ar), 129.9 (Ar′), 128.0 ($\mathit{C}_6H_4CMe_3$), 127.4 ($\mathit{C}_6H_4CMe_3$), 126.4 ($\mathit{C}_6H_4CMe_3$), 126.2 ($\mathit{C}_6H_4CMe_3$), 125.4 (Ar), 122.8 (Ar′), 35.4 ($\mathit{C}Me_3$), 30.2 ($C(\mathit{C}H_3)_3$), 28.6 ($\mathit{C}HMe_2$), 23.0 ($CH(\mathit{C}H_3)_2$), 18.2 (CH_3). Found: C, 54.26; H, 5.87; N, 6.58. Calc: C, 54.32; H, 5.93; N, 6.33%.

‡ Crystal data for $ReCl(NAr)_2(NAr^*)$ (Ar^* = 2-*tert*-butylphenyl): $C_{34}H_{47}ClN_3Re$, M = 719.40; crystal size 0.38 × 0.17 × 0.06 mm, triclinic, $P\bar{1}$, a = 10.6026(2), b = 10.6126(2), c = 15.93340(10) Å, α = 80.3510(10), β = 72.8540(10), γ = 81.98°, V = 1681.19(5) Å^3, Z = 2, D_c = 1.421 Mg m^{-3}, $F(000)$ = 728, μ(Mo-Kα) = 3.718 mm^{-1}, λ = 0.71073 Å, 16481 reflections were collected (7301 unique, R_{int} = 0.0205), $R(f)$ = 0.0214 [$I > 2\sigma(I)$] and $wR(F^2)$ = 0.0707.

Crystal data for $Re(Me)(NAr)_2(NAr')$: $C_{33}H_{46}N_3Re$, M = 670.93; crystal size 0.53 × 0.40 × 0.26 mm, monoclinic, $P2(1)/c$, a = 9.3838(3), b = 39.3038(11), c = 9.1197(2) Å, β = 107.789(1), V = 3202.7(15) Å^3, Z = 4, D_c = 1.391 Mg m^{-3}, $F(000)$ = 1360, μ(Mo-Kα) = 3.818 mm^{-1}, λ = 0.71073 Å, data were collected at 203 K on a Siemens SMART

CCD area-detector. 19520 reflections were collected (7073 unique, $R_{\mathrm{int}} = 0.0279$), $R(F) = 0.0361$ [$I > 2\sigma(I)$] and $wR(F^2) = 0.0812$. CCDC reference number 186/2063. See http://www.rsc.org/suppdata/dt/b0/b004938g/ for crystallographic files in .cif format.

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