Rhenium Nitrido-, Arylimido-, Nitrile, and Carbonyl Complexes with Sterically Hindered Thiolate Ligands

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By the reaction of $[\mathrm{ReNCl_2(PR'_3)}_n]$ ($\mathrm{PR'_3} = \mathrm{PPh_3}$, $n = 2$; or $\mathrm{PMe_2Ph}$, $n = 3$) with the bulky thiol 2,4,6-tri-isopropylbenzenethiol (Htipt) under varying conditions, the nitrido-complexes $[\mathrm{ReN(tipt)_2(PR'_3)_2}]$, $\mathrm{Na_2[ReN(tipt)_4]\cdot 2thf}$ (thf = tetrahydrofuran), and $[\mathrm{PPh_4}][\mathrm{ReN(tipt)_4}]$ have been isolated. The last is a paramagnetic rhenium(VI) complex derived from the aerial oxidation of the rhenium(V) anion $[\mathrm{ReN(tipt)_4}]^{2-}$. The arylimidorhenium(V) complexes $[\mathrm{PPh_4}][\mathrm{Re(NR'')(tipt)_4}]$ ($\mathrm{R''} = \mathrm{Ph}$, $\mathrm{C_6H_4OMe}$-4, or $\mathrm{C_6H_4Me}$-4) can be isolated by the reaction of $[\mathrm{Re(NR'')Cl_3(PPh_3)_2}]$ with Htipt and triethylamine, whereas $\mathrm{N_2}$ loss occurs with $\mathrm{PhS^-}$. The complexes $[\mathrm{Re(tipt)_3(NCR''')_2}]$ ($\mathrm{R'''} = \mathrm{Me}$ or $\mathrm{Bu^t}$) have been prepared by reaction of $\mathrm{K_2[ReCl_6]}$ with Htipt and triethylamine in R'''CN as solvent. These bis(nitrile) complexes have a trigonal-bipyramidal structure with equatorial thiolate ligands. They react with CO to give, sequentially, two isomers of $[\mathrm{Re(tipt)_3(CO)(NCR''')}]$ and then $[\mathrm{Re(tipt)_3(CO)_2}]$ which have analogous structures. Analogues of some of the complexes, containing 2,4,6-trimethylbenzenethiolate or 2,6-di-isopropylbenzenethiolate ligands, are also described.

There is much current interest in developing systems for the reduction of dinitrogen to ammonia and organonitrogen derivatives at molybdenum sites ligated predominantly by sulphur, which are relevant to the biological reduction of dinitrogen and other substrates catalysed by nitrogenase. In parallel with our search for sulphur-ligated metal sites capable of binding dinitrogen, we have sought direct synthetic routes to metal thiolate complexes containing reduced nitrogen ligands. Use of sterically demanding arenethiols such as 2,4,6-tri-isopropylbenzenethiol (Htipt), 2,6-di-isopropylbenzenethiol (Hdipt), and 2,4,6-trimethylbenzenethiol (Htmt) has helped to overcome some of the difficulties inherent in thiolate chemistry (which include a strong bridging tendency and C–S bond cleavage) and has led to synthesis of complex types which (sometimes for incompletely understood reasons) could not be directly prepared with unsubstituted benzenethiolate or alkanethiolate ligands.

This paper describes studies of some reactions of rhenium complexes with the thiols Htipt, Hdipt, and Htmt with a range of co-ligands, carried out in conjunction with similar studies of molybdenum.[1] Thiolate complexes of rhenium have received scant attention in the past, being limited to the square-pyramidal anions $[\mathrm{ReO(SR)_4}]^-$ [SR = ½(dithiolate)[2] or SPh[3]], tetrameric carbonyl species $[\mathrm{Re_4(SR)_4(CO)_{12}}]$,[4] and species with nitrosyl ligands.[5]

Results and Discussion

Nitrido-complexes.—The nitrido-complex $[\mathrm{ReNCl_2(PMe_2Ph)_3}]$ reacts with Htipt in methanol containing triethylamine, rapidly giving a microcrystalline yellow precipitate of $[\mathrm{ReN(tipt)_2(PMe_2Ph)_2}]$. The analogues $[\mathrm{ReN(dipt)_2(PMe_2Ph)_2}]$ and $[\mathrm{ReN(tipt)_2(PPh_3)_2}]$ can be prepared similarly, the latter from $[\mathrm{ReNCl_2(PPh_3)_2}]$. These species have been characterised by i.r., ^{1}H n.m.r., and ^{31}P n.m.r. spectroscopy and molecular-weight determinations. Spectroscopic details are presented in the Table. These results contrast with those of reactions carried out using thiophenol or alkanethiols under similar conditions, which give uncharacterised, nitrogen-free material,[6] and of the reaction of $[\mathrm{ReNCl_2(PPh_3)_2}]$ with sodium benzenethiolate in MeCN under aerobic conditions, which gives the phosphiniminato-complex $[\mathrm{Re(NPPh_3)(SPh)_4}]$.[7] If, however, $[\mathrm{ReNCl_2(PPh_3)_2}]$ is treated with 4 mol of Na(tipt) (generated *in situ* by the reaction of Htipt with sodium metal) in tetrahydrofuran (thf) solution, ligand substitution proceeds further to give the rhenium(V) dianion $[\mathrm{ReN(tipt)_4}]^{2-}$. The reaction proceeds *via* formation of $[\mathrm{ReN(tipt)_2(PPh_3)_2}]$ since this species can be isolated after shorter reaction times. The purified salt $\mathrm{Na_2[ReN(tipt)_4]\cdot 2thf}$ is extremely air-sensitive, being rapidly oxidised to the dark green, paramagnetic rhenium(VI) anion $[\mathrm{ReN(tipt)_4}]^-$, which is isolable from methanol solution as a crystalline tetraphenylphosphonium ($[\mathrm{PPh_4}]^+$) salt. These reactions are summarised in the Scheme.

$$\begin{tikzcd}
{[\mathrm{ReNCl_2(PPh_3)_2}]} \arrow[r, "(i)"] & {[\mathrm{ReN(tipt)_2(PPh_3)_2}]} \arrow[d, "(ii)"] \\
{[\mathrm{ReN(tipt)_4}]^-} & {[\mathrm{ReN(tipt)_4}]^{2-}} \arrow[l, "(iii)"']
\end{tikzcd}$$

Scheme. Reactions of $[\mathrm{ReNCl_2(PPh_3)_2}]$ with Htipt. (*i*) Htipt, $\mathrm{NEt_3}$, MeOH or Na(tipt), thf; (*ii*) Na(tipt), thf; (*iii*) $\mathrm{O_2}$

The i.r. spectra of complexes $[\mathrm{ReN(SR)_2(PR'_3)_2}]$ show the expected thiolate and phosphine bands, and a strong, sharp band at *ca.* 1 060 cm^{-1} assigned to ν(Re≡N). This is a somewhat higher frequency than those assigned for the five-co-ordinate complexes $[\mathrm{ReNCl_2(PEtPh_2)_2}]$ (1 010 cm^{-1}) and $[\mathrm{ReNCl_2(PPr^nPh_2)_2}]$ (1 035 cm^{-1}),[8] but not so much as to suggest a different structural type. A singlet is observed in the ^{31}P-{^{1}H} n.m.r. spectra of all the complexes. The $\mathrm{PMe_2Ph}$ complexes show one doublet integrating as 12 protons assigned to the phosphine methyl groups. This is consistent with a square-pyramidal structure with the thiolate and tertiary phosphine groups arranged *trans* [structure (**A**), Figure 1]. The ^{1}H n.m.r of $[\mathrm{ReN(dipt)_2(PMe_2Ph)_2}]$ shows two equal-intensity heptets assigned to the methine protons of the *ortho*-isopropyl groups. This indicates that there is no plane of symmetry bisecting the thiolate aryl groups. The resonances due to the isopropyl methyl groups are generally broad and

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Table. Rhenium complexes with sterically hindered thiolates; n.d. = not determined

Compound	Colour	I.r. data[a] (cm^{-1})	N.m.r. data[b] (p.p.m.)	Electronic spectral data[c]
(**1**) $[ReN(tipt)_2(PMe_2Ph)_2]$	Yellow	ν(Re≡N) 1 060	δ(^{31}P) −149.0	n.d.
(**2**) $[ReN(dipt)_2(PMe_2Ph)_2]$	Yellow	ν(Re≡N) 1 050	δ(^{31}P) −147.2	n.d.
(**3**) $[ReN(tipt)_2(PPh_3)_2]$	Orange-yellow	ν(Re≡N) 1 067	n.d.	n.d.
(**4**) $Na_2[ReN(tipt)_4]$·2thf	Orange	ν(Re≡N) 1 045	δ(OCH_2) 3.40 (br) δ(OCH$_2$CH_2) 1.72 (br)	n.d.
(**5**) $[PPh_4][ReN(tipt)_4]$	Green	ν(Re≡N) 1 065[d]	Paramagnetic	755 (5 600), 580 (sh), 460 (sh), 397 (sh), 371 (sh), 358 (2 600)
(**6**) $[PPh_4][Re(NPh)(tipt)_4]$	Brown	—		n.d.
(**7**) $[PPh_4][Re(NC_6H_4Me\text{-}4)(tipt)_4]$	Brown	—		n.d.
(**8**) $[PPh_4][Re(NC_6H_4OMe\text{-}4)(tipt)_4]$	Brown	—		n.d.
(**9**) $[Re(tipt)_3(NCMe)_2]$	Violet	ν(C≡N) 2 240	δ(NCCH_3) 2.33, 3.02	760 (220), 700 (220), 539 (1 470)
(**10**) $[Re(dipt)_3(NCMe)_2]$	Violet	ν(C≡N) 2 230	δ(NCCH_3) 2.38, 3.04	n.d.
(**11**) $[Re(tmt)_3(NCMe)_2]$	Violet	ν(C≡N) 2 240	δ(NCCH_3) 2.34, 3.11	760 (22), 710 (22), 540 (1 700)
(**12**) $[Re(tipt)_3(NCBu^t)_2]$	Violet	ν(C≡N) 2 205	δ[NCC(CH_3)$_3$] 0.52, 1.15	760 (260), 690 (300), 539 (1 780)
(**13**) $[Re(tipt)_3(CO)(NCMe)]$				
kinetic isomer	Orange	ν(C≡O) 1 910	δ(NCCH_3) 2.17	424 (sh), 394 (sh), 338 (sh), 311 (3 200)
thermodynamic isomer	Orange		δ(NCCH_3) 1.96	
(**14**) $[Re(tmt)_3(CO)(NCMe)]$				
kinetic isomer	Orange	ν(C≡O) 1 934[d]	δ(NCCH_3) 2.21	n.d
thermodynamic isomer	Orange	ν(C≡O) 1 910[d]	δ(NCCH_3) 2.10	n.d
(**15**) $[Re(tipt)_3(CO)_2]$	Orange	ν(C≡O) 1 963	—	n.d.
(**16**) $[Re(tmt)_3(CO)_2]$	Orange	ν(C≡O) 1 965	—	486 (sh), 432 (sh), 400 (sh), 352 (sh), 327 (*ca.* 30 000)

[a] Nujol mull. [b] In CD_2Cl_2 solution. [c] In CH_2Cl_2 solution, 10^{-4} mol dm^{-3}; ε/dm^3 mol^{-1} cm^{-1} given in parentheses. [d] In CH_2Cl_2 solution.

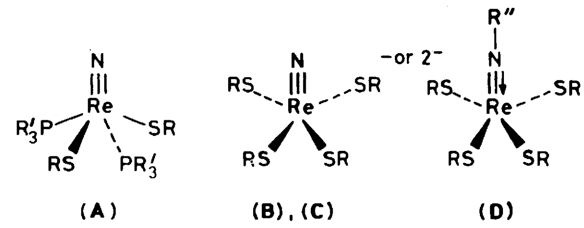


Figure 1. Structural types found for thiolato-complexes with nitrido- and arylimido-ligands

unresolved and this may be due to rotation of the methyls about the arene–CH bond. Rotation about the Re–S and S–C bonds is ruled out as this would render the *ortho*-isopropyl groups equivalent. In contrast, the spectrum of $[ReN(tipt)_2(PPh_3)_2]$ is fully resolved, showing four sharp, well spaced doublets for the *ortho*-methyl groups. It may be that here the increased steric hindrance of the triphenylphosphine ligands introduces a greater degree of inequivalence. A plausible structure, based on these spectra, space-filling models, and the known structures of other five-co-ordinate rhenium nitrido-complexes $[ReNCl_2(PPh_3)_2]$[9] and $[ReN(SCH_2CH_2SCH_2CH_2S)(PMe_2Ph)]$[10] is represented by (**A**) (Figure 1).

The complex dianion $[ReN(tipt)_4]^{2-}$ is formed from $[ReNCl_2(PPh_3)_2]$ more readily in thf solution probably because the solubility of the intermediates, including $[ReN(tipt)_2(PPh_3)_2]$, is greater in this solvent. The proposed formula [(**B**), Figure 1] is based on microanalysis, the ^{1}H n.m.r. spectrum, and on the ready conversion by oxygen into the more fully characterised rhenium(VI) species $[ReN(tipt)_4]^-$. The presence of 2 mol of thf in the crystalline disodium salt $Na_2[ReN(tipt)_4]$·2thf is inferred from bands in the ^{1}H n.m.r. spectrum at δ = 3.40 and 1.72 p.p.m. (*vs.* $SiMe_4$) assigned to (OCH$_2$) and (OCH$_2$CH_2) protons respectively, and a broad resonance at *ca.* 880 cm^{-1} associated with a C–O–C stretching mode. It is not known whether the thf is co-ordinated, although this is thought to be unlikely in view of the known behaviour of the iso-electronic species $[ReO(SR)_4]^-$.[2,3,6] Pure crystalline $Na_2[ReN(tipt)_4]$·2thf is pale orange, and extremely air-sensitive. Its i.r. spectrum shows a band due to ν(Re≡N) at 1 045 cm^{-1}, consistent with the dianionic charge which is expected to weaken N→Re π bonding. The presence of five very strongly electron-donating ligands, and the dianionic charge, probably contribute to the ease of oxidation from Re^V to Re^{VI}. This aerial oxidation can be carried out either on the crude thf reaction solution containing $[ReN(tipt)_4]^{2-}$ or on the isolated salt dissolved in methanol. Addition of $[PPh_4]Br$ to the green, oxidised methanol solution gives crystalline $[PPh_4][ReN(tipt)_4]$. The presence of the nitrido-ligand in this complex was confirmed by identification of ν(Re≡N) in the i.r. spectrum. This could only be accomplished by isotopic labelling of the nitrogen because of interference from ligand and counter-ion bands. A shoulder at 1 065 cm^{-1} for $[PPh_4][Re^{14}N(tipt)_4]$ is shifted, appearing as a new peak at 1 031 cm^{-1} for $[PPh_4][Re^{15}N(tipt)_4]$, a shift of 34 cm^{-1} which is the expected magnitude. Thus we see a shift in ν(Re≡N) from 1 045 to 1 065 cm^{-1} on oxidation from Re^V to Re^{VI}. The value for $[PPh_4][ReN(tipt)_4]$ is significantly lower than that for $[AsPh_4][ReNCl_4]$ (1 084 cm^{-1}) consistent with a stronger electronating ability of the thiolate ligands, which weakens N→Re σ and π bonding. The electronic properties support a square-pyramidal structure (**C**) (Figure 1) for the anion $[ReN(tipt)_4]^-$. The e.s.r. spectrum is similar to that of $[ReOCl_4]^-$, consistent with a d^1 axially symmetric species,[11] and the visible spectrum shows an intense absorption at 755 nm (ε = 5 600 dm^3 mol^{-1} cm^{-1}). By analogy with the isoelectronic $[MoO(SPh)_4]^-$ ion, which has a very similar spectrum including a band at 593 nm (6 600 dm^3 mol^{-1} cm^{-1}), this is probably S(3*p*) to Re($5d_{xy}$) charge transfer in origin.[12] A square-pyramidal geometry similar to that of $[ReO(dipt)_4]^-$ [13] is proposed on this basis [(C), Figure 1].

Arylimido-complexes.—Previous attempts to synthesise complexes of the type $[Re(NR'')(SR)_4]^-$ by metathesis of $[ReO(SR)_4]^-$ with reagents such as $R''NH_2$ and $R''N(SiMe_3)_2$ have been unsuccessful, and reaction of $[Re(NR'')Cl_3(PPh_3)_2]$ complexes with thiophenolate in methanol leads to high yields of salts of $[ReO(SPh)_4]^-$. By contrast, $[Re(NPh)Cl_3(PPh_3)_2]$ reacts smoothly with Htipt and triethylamine in methanol–dichloromethane (1:1) to give the anion $[Re(NPh)(tipt)_4]^-$, isolable as a tetraphenylphosphonium salt; $[Re(NC_6H_4Me\text{-}4)Cl_3(PPh_3)_2]$ and $[Re(NC_6H_4OMe\text{-}4)Cl_3(PPh_3)]$ react analogously. I.r. absorptions due to ν(Re=N) are not unambiguously assignable for these complexes without recourse to isotope studies, as is often found with similar complexes.[14] The expected ^{1}H n.m.r. resonances for the imido-ligands are present, however, and the methyl and methine resonances of the thiolate ligands are indicative of four equivalent thiolates. This is consistent with a square-pyramidal geometry with a linear, axial arylimido-ligand, analogous to the structure of $[ReO(dipt)_4]^-$.[13]

Nitrile and Carbonyl Complexes.—The reaction of potassium hexachlororhenate(IV) with Htipt and triethylamine has been studied, initially in attempts to synthesis thiolato-complexes containing reactive halide ligands. Experiments with various solvents showed that the reaction proceeds only in nitrile or alcohol solvent. In methanol, salts of $[ReO(tipt)_4]^-$ are obtained in high yield. In scrupulously dry refluxing acetonitrile, $[Re(tipt)_3(NCMe)_2]$ is formed, but the presence of traces of moisture causes formation of varying amounts of $[ReO(tipt)_4]^-$ as a co-product. Analogous behaviour is shown by the reactions with Hdipt and Htmt. Using trimethylacetonitrile as solvent, $[Re(tipt)_3(NCBu^t)_2]$ can be obtained. The reaction proceeds with reduction of Re^{IV} to Re^{III}, according to equation (1) (SR = tipt, dipt, or tmt; R''' = Me or Bu^t). The disulphides RSSR have been isolated from the reaction mixture and characterised by melting-point measurements.

$$K_2[ReCl_6] + 4HSR + 4NEt_3 \xrightarrow[\text{Heat}]{R'''CN} [Re(SR)_3(NCR''')_2] + 2KCl + 4[NHEt_3]Cl + \tfrac{1}{2}RSSR \quad (1)$$

The complexes $[Re(SR)_3(NCR''')_2]$ are bright violet, crystalline, diamagnetic materials, highly soluble in hydrocarbon solvents as a consequence of the lipophilicity of the thiolate substituents. They have been shown to be monomeric by cryoscopic measurements in benzene. They each exhibit a single i.r. band due to ν(C≡N) in the range 2 205—2 240 cm^{-1}, consistent with mutually *trans*-co-ordinated nitrile ligands. This suggests a trigonal-bipyramidal geometry with equatorial thiolates and axial nitrile ligands. Further structural resolution is possible from the ^{1}H n.m.r. spectra. The most clearly defined spectrum shows the presence of two sharp singlets assigned to the MeCN methyl protons, indicating non-equivalent axial ligands in spite of the *trans* structure. This eliminates structures (E) and (F) from the list of possible trigonal-bipyramidal arrangements shown in Figure 2. The methine signals appear as a set of multiplets, which although overlapping are readily identifiable as three heptets of equal intensity. Since structure (G) would contain no more than two types of *ortho*-methine protons, this is also eliminated. The thiolate methyl resonances, although less clearly resolved, do not contradict this conclusion.

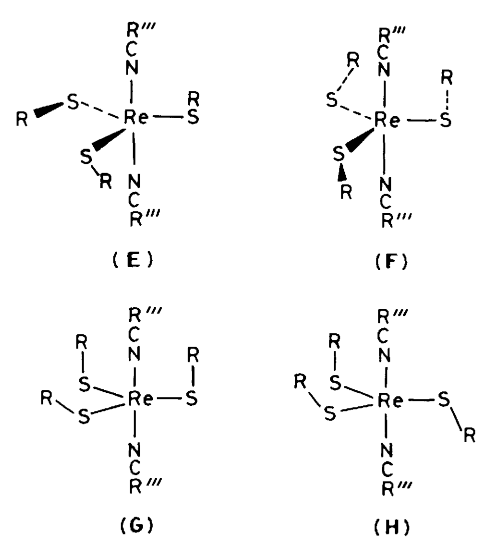
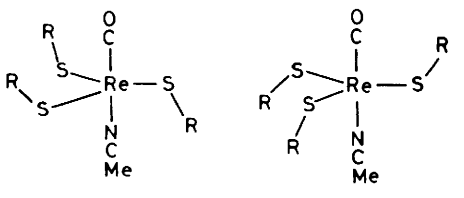


Figure 2. Possible arrangements for aryl groups in thiolato-complexes $[Re(SR)_3(NCR''')_2]$

Therefore the most likely structure to account for the observed i.r. and n.m.r. spectra is (H), showing a preference for orientation of the S–C bonds parallel to the approximate C_3 axis of the ReS_3N_2 core, rather than perpendicular as in (E) and (F), while minimising steric interactions. This observation is in agreement with the known structure of the isoelectronic ion $[Mo(tipt)_3(CO)_2]^-$ [15] which contains axial carbonyl ligands and has an overall structure corresponding to (H). This preference for orientation of S–C bonds parallel to the axial ligands is interpreted as maximising S→Re π-bonding interactions in the complexes $[Re(SR)_4(NO)]$,[5] and is in agreement with theoretical predictions for such d^4 systems.[16] Other related trigonal-bipyramidal d^4 complexes, although maintaining the parallel S–C vector arrangements, have the structure (G). These include $[W(SPh)_3Cl(NO)]^-$,[17] perhaps to avoid unfavourable interactions between S(3*p*) lone pairs and the W–N–O systems, and $[Re(SPh)_3(NCMe)(PPh_3)]$[7] in which steric crowding between the thiolate phenyl groups and the bulky phosphine ligand is minimised.

Violet solutions of $[Re(tipt)_3(NCMe)_2]$ in dichloromethane rapidly turn orange on purging with carbon monoxide for a few seconds. The resulting solutions contain mixtures of two compounds, separable by fractional crystallisation after addition of methanol. The first compound to crystallise is orange $[Re(tipt)_3(CO)_2]$, which shows only tipt resonances in its ^{1}H n.m.r. spectrum and has a single ν(CO) band at 1 963 cm^{-1}, corresponding to mutually *trans* CO ligands. This complex appears to be similar structurally and electronically to $[Mo(tipt)_3(CO)_2]^-$.[15] Subsequent fractions have an additional ν(CO) at 1 910 cm^{-1}, and show ^{1}H n.m.r. evidence for the presence of co-ordinated MeCN. There is no i.r. band corresponding to ν(C≡N), but microanalysis indicates the presence of nitrogen in variable amounts. This evidence is consistent with the more soluble fractions containing $[Re(tipt)_3(CO)(NCMe)]$. This compound can be prepared pure by the reaction of $K_2[ReCl_6]$ with thiol and triethylamine in MeCN under an atmosphere of CO. The reaction of $[Re(tmt)_3(NCMe)_2]$ with CO proceeds in a similar manner. The i.r. and n.m.r. spectra of $[Re(tmt)_3(CO)(NCMe)]$ and $[Re(tipt)_3(CO)(NCMe)]$ show evidence of isomerisations in solution. Freshly precipitated $[Re(tipt)_3(CO)(NCMe)]$ {from brief treatment of $[Re(tipt)_3(NCMe)_2]$ with CO} in CD_2Cl_2 solution shows two methyl resonances for co-ordinated MeCN at 2.17 and 1.96 p.p.m.



(I) (J)

Figure 3. Possible isomers for $[Re(SR)_3(CO)(NCMe)]$

{neither of which corresponds to those of $[Re(tipt)_3(NCMe)_2]$}. On standing for a few hours, the peak at 2.17 p.p.m. diminishes to zero intensity while that at 1.96 p.p.m. gains intensity at the same rate. Identical behaviour is exhibited by $[Re(tmt)_3(CO)(NCMe)]$. The process can also be followed by i.r. spectroscopy. A band at 1 934 cm^{-1} for $[Re(tmt)_3(CO)(NCMe)]$ (dichloromethane solution) is diminished and one at 1 910 cm^{-1} gains intensity on standing. A similar change is noticeable but less clear-cut in the i.r. spectrum of $[Re(tipt)_3(CO)(NCMe)]$ because the bands overlap considerably. A probable origin of this isomerism is the asymmetric disposition of the thiolate substituents. Thus, there can be two isomers (**I**) and (**J**) (Figure 3). Presumably one of these is kinetically favoured, the other thermodynamically, while their interconversion is slow at room temperature.

This chemistry is complementary to that previously described for the system $[Mo(tipt)_3(CO)L]^-$,[1] and the range of complexes of Mo, W, and Re of this type now characterised demonstrates the flexibility of the d^4 $[M(SR)_3]^n$ core in its ligand-binding properties and suggests applications in activation of small molecules and generation of new metal thiolate species. These possibilities are being investigated.

Experimental

The thiols Htmt, Htipt, and Hdipt were prepared as described in ref. 5. The complexes $[ReOCl_3(PPh_3)_2]$,[18] $[ReNCl_2(PPh_3)_2]$,[8] $[ReNCl_2(PMe_2Ph)_3]$,[8] $K_2[ReCl_6]$,[19] and $[Re(NR'')Cl_3(PPh_3)_2]$[20] were prepared by literature methods. The complex $[Re^{15}NCl_2(PPh_3)_2]$ was prepared by stirring $[ReOCl_3(PPh_3)_2]$ (0.5 g) with $^{15}N_2H_4{\cdot}H_2SO_4$ (0.1 g) and triphenylphosphine (0.5 g) in wet ethanol overnight at reflux temperature and filtering off the product (50% yield).

All reactions were carried out under dinitrogen using conventional Schlenk techniques with solvents freshly distilled from drying agents under dinitrogen. Spectroscopic measurements and elemental analyses were performed as described previously.[2,5] The numbers used in parentheses refer to the Table.

Bis(dimethylphenylphosphine)nitridobis(2,4,6-*tri-isopropylbenzenethiolato*)*rhenium*(V), $[ReN(tipt)_2(PMe_2Ph)_2]$, (**1**).—This preparation was carried out in air. To a stirred suspension of $[ReNCl_2(PMe_2Ph)_3]$ (0.4 g, 0.48 mmol) in methanol (5 cm^3) were added Htipt (0.60 cm^3, 2.80 mmol) and triethylamine (0.38 cm^3, 2.80 mmol). The solid rapidly dissolved to give an orange solution, and a lemon-yellow microcrystalline solid then precipitated which was collected, washed with methanol, and recrystallised from dichloromethane–methanol. Yield 0.42 g, 76% (Found: C, 58.4; H, 7.6; N, 1.8%; *M* 962. $C_{46}H_{68}NP_2ReS_2$ requires C, 58.3; H, 6.6; N, 1.5%; *M* 946).

Bis(2,6-di-isopropylbenzenethiolato)bis(dimethylphenylphosphine)nitridorhenium(V), $[ReN(dipt)_2(PMe_2Ph)_2]$, (**2**), was prepared analogously to the complex above in similar yield (Found: C, 55.7; H, 6.9; N, 1.7. $C_{40}H_{56}NP_2ReS_2$ requires C, 55.7; H, 6.5; N, 1.6%).

Nitridobis(2,4,6-*tri-isopropylbenzenethiolato*)*bis*(*triphenylphosphine*)*rhenium*(V), $[ReN(tipt)_2(PPh_3)_2]$, (**3**).—Thin strips of sodium metal, washed with thf, were suspended in thf (30 cm^3) and Htipt (0.34 cm^3, 1.57 mmol) was added. The suspension was heated to 40 °C for 1 h with stirring, making provision for escape of H_2 evolved. After this time the solution was filtered to remove excess of sodium, and to the filtrate was added $[ReNCl_2(PPh_3)_2]$ (0.5 g, 0.63 mmol) and the suspension stirred until all of the complex had dissolved (*ca.* 2 h) to give a yellow solution, which was then filtered through Celite to remove NaCl and evaporated to dryness. The residue was stirred with methanol to give a yellow-orange powder which was collected and washed with methanol. Yield of crude complex 0.4 g, 53% (Found: C, 63.9; H, 6.3; N, 1.4. $C_{66}H_{76}NP_2ReS_2$ requires C, 66.3; H, 6.4; N, 1.2%). After recrystallisation from dichloromethane–methanol the product is still visibly contaminated with white solid.

Disodium Nitridotetrakis(2,4,6-*tri-isopropylbenzenethiolato*)*rhenate*(V)*–Tetrahydrofuran*(1/2), $Na_2[ReN(tipt)_4]{\cdot}2thf$, (**4**).—A thf solution of Na(tipt) was prepared [as described for (**3**)] from Htipt (0.82 cm^3, 3.15 mmol) and excess of sodium metal. To the filtered solution was added $[ReNCl_2(PPh_3)_2]$ (0.5 g, 0.63 mmol) and the suspension stirred for 24 h, giving a yellow solution. This was evaporated to near-dryness *in vacuo* and the yellow oily residue extracted with pentane. The yellow pentane solution was filtered through Celite and stirred until a pale orange microcrystalline precipitate had formed. This was collected and washed with pentane (Found: C, 60.9; H, 8.4; N, 1.0. $C_{68}H_{108}NNa_2O_2ReS_4$ requires C, 61.3; H, 8.1; N, 1.0%).

Tetraphenylphosphonium Nitridotetrakis(2,4,6-*tri-isopropylbenzenethiolato*)*rhenate*(VI), $[PPh_4][ReN(tipt)_4]$, (**5**).—The yellow thf solution was obtained as described for (**4**). This was evaporated to dryness and the residue extracted with methanol. The solution was filtered, in air, on a fluted paper, during which time the solution turned green. After stirring the filtrate in air for 0.5 h, tetraphenylphosphonium bromide (1 g) was added, affording a green solid. This was recrystallised from dichloromethane–methanol (Found: C, 68.3; H, 7.9; N, 1.1. $C_{84}H_{112}NPReS_4$ requires C, 68.1; H, 7.6; N, 0.9%). The ^{15}N analogue $[PPh_4][Re^{15}N(tipt)_4]$ was prepared in the same way from $[Re^{15}NCl_2(PPh_3)_2]$.

Tetraphenylphosphonium Phenylimidotetrakis(2,4,6-*tri-isopropylbenzenethiolato*)*rhenate*(V), $[PPh_4][Re(NPh)(tipt)_4]$, (**6**).—The complex $[Re(NPh)Cl_3(PPh_3)_2]$ (0.1 g, 0.11 mmol) was suspended in dichloromethane–methanol (1:1). Then Htipt (0.15 cm^3, 0.70 mmol) and triethylamine (0.1 cm^3, 0.70 mmol) were added. After stirring for 0.5 h a green-brown solution resulted. Addition of tetraphenylphosphonium bromide yielded, after partial evaporation to remove dichloromethane, a brown microcrystalline solid which was recrystallised from dichloromethane–methanol (Found: C, 68.7; H, 7.4; N, 0.6. $C_{90}H_{117}NPReS_4$ requires C, 69.4; H, 7.5; N, 0.9%).

Tetraphenylphosphonium 4-tolylimidotetrakis(2,4,6-tri-isopropylbenzenethiolato)rhenate(V), $[PPh_4][Re(NC_6H_4Me\text{-}4)(tipt)_4]$, (**7**), was prepared in the same way as (**6**), from $[Re(NC_6H_4Me\text{-}4)Cl_3(PPh_3)_2]$ (Found: C, 69.7; H, 7.9; N, 0.8. $C_{91}H_{119}NPReS_4$ requires C, 69.5; H, 7.6; N, 0.9%), as was tetraphenylphosphonium 4-methoxyphenylimidotetrakis(2,4,6-tri-isopropylbenzenethiolato)rhenate(V), $[PPh_4][Re(NC_6H_4OMe\text{-}4)(tipt)_4]$, (**8**) from $[Re(NC_6H_4OMe\text{-}4)Cl_3(PPh_3)_2]$

(Found: C, 69.0; H, 7.4; N, 1.0. $C_{91}H_{119}NOPReS_4$ requires C, 68.8; H, 7.5; N, 0.9%).

Bis(*acetonitrile*)*tris*(2,4,6-*trimethylbenzenethiolato*)-*rhenium*(III), [Re(tmt)$_3$(NCMe)$_2$] (**11**).—Finely ground $K_2[ReCl_6]$ (0.2 g, 0.42 mmol) was suspended in acetonitrile (20 cm^3). Then Htmt (0.24 cm^3, 1.6 mmol) and triethylamine (0.23 cm^3, 1.6 mmol) were added and the solution stirred under reflux for 2.5 h. The resulting violet solution was filtered while hot and allowed to cool, whereupon a bright violet solid crystallised. This was collected, washed with water and methanol, and dried *in vacuo* at 60 °C. Yield 0.14 g, 45% (Found: C, 51.8; H, 5.7; N, 3.8%; *M* 745. $C_{31}H_{39}N_2ReS_3$ requires C, 51.6; H, 5.4; N, 3.9%; *M* 721).

Prepared similarly were: bis(acetonitrile)tris(2,4,6-tri-isopropylbenzenethiolato)rhenium(III), [Re(tipt)$_3$(NCMe)$_2$], (**9**), using Htipt, in similar yield (Found: C, 60.7; H, 7.6; N, 3.1. $C_{49}H_{75}N_2ReS_3$ requires C, 60.4; H, 7.7; N, 2.9%); bis(acetonitrile)tris(2,6-di-isopropylbenzenethiolato)rhenium(III), [Re(dipt)$_3$(NCMe)$_2$], (**10**), using Hdipt, in *ca.* 55% yield (Found: C, 56.1; H, 6.8; N, 3.3. $C_{40}H_{57}N_2ReS_3$ requires C, 56.7; H, 6.7; N, 3.3%); and tris(2,4,6-tri-isopropylbenzenethiolato)-bis(trimethylacetonitrile)rhenium(III), [Re(tipt)$_3$(NCBu^t)$_2$], (**12**), using Htipt in trimethylacetonitrile as solvent (dried and distilled from calcium hydride), yield 0.27 g, 60% (Found: C, 62.8; H, 8.1; N, 2.4. $C_{55}H_{87}N_2ReS_3$ requires C, 62.4; H, 8.2; N, 2.7%).

Acetronitrilecarbonyltris(2,4,6-*trimethylbenzenethiolato*)-*rhenium*(III), [Re(tmt)$_3$(CO)(NCMe)], (**14**).—Complex (**11**) (0.1 g) was dissolved in dichloromethane (10 cm^3). The purple solution was purged with carbon monoxide for 0.25 h. Methanol (10 cm^3) was added and the volume reduced by pumping off dichloromethane, yielding an orange solid. This was collected and fractionally recrystallised from dichloromethane–methanol. The first crop of crystals were pure complex (**14**); subsequent crops were mixtures of (**14**) and (**16**) [Found: C, 50.6; H, 4.6; N, 0.80. $C_{30}H_{36}NOReS_3$ requires C, 50.8; H, 5.1; N, 2.0. $C_{29}H_{33}O_2ReS_3$, (**16**), requires C, 50.1; H, 4.7; N, 0.0%].

Dicarbonyltris(2,4,6-trimethylbenzenethiolato)rhenium(III), [Re(tmt)$_3$(CO)$_2$], (**16**) was prepared similarly (Found: C, 49.9; H, 4.9; N, 0.0%).

Acetonitrilecarbonyltris(2,4,6-*tri-isopropylbenzenethiolato*)-*rhenium*(III), [Re(tipt)$_3$(CO)(NCMe)], (**13**).—*Method* (*i*). This cannot be used to prepare pure (**13**). Complex (**9**) was treated analogously to the preparation of (**14**).

Method (*ii*). A suspension of $K_2[ReCl_6]$ in acetonitrile was treated as in the preparation of (**9**), but under an atmosphere of carbon monoxide. The orange solution resulting was filtered and evaporated to low volume, whereupon orange microcrystals formed which were collected and dried *in vacuo* (Found: C, 60.1; H, 8.0; N, 1.7. $C_{48}H_{72}NOReS_3$ requires C, 60.0; H, 7.5; N, 1.5%).

Dicarbonyltris(2,4,6-tri-isopropylbenzenethiolato)-rhenium(III), [Re(tipt)$_3$(CO)$_2$], (**15**) was not prepared pure but identified in admixture with (**13**) [method (*ii*) for (**13**)].

Acetonitriletris(2,4,6-*tri-isopropylbenzenethiolato*)(*triphenylphosphine*)*rhenium*(III), [Re(tipt)$_3$(NCMe)(PPh$_3$)].—The complex [ReCl$_3$(NCMe)(PPh$_3$)$_2$] (0.5 g, 0.58 mmol), Htipt (0.76 cm^3, 2.9 mmol), and triethylamine (0.40 cm^3, 2.9 mmol) were heated in acetonitrile for 2.5 h at reflux temperature, giving a dark green solution. Reduction of the volume *in vacuo* gave dark green microcrystals, which were collected and washed with acetonitrile and methanol. Yield 0.24 g (35%) (Found: C, 64.8; H, 7.3; N, 1.7. $C_{65}H_{87}NPReS_3$ requires C, 65.3; H, 7.3; N, 1.2%).

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