$[Cl_3Ga-NReCl_2(PMe_2Ph)_3]$ and $[Cl_3Ga-NReCl(PMe_2Ph)_3(NCMe)][GaCl_4]$: the First Complexes with Nitrido Bridges between Main Group and Transition Metals

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Almost linear nitrogen bridges between rhenium and gallium are formed during the reaction of rhenium(v) complexes containing terminal 'N^{3-}' ligands with gallium trichloride.

The nitrido ligand is one of the strongest π-donor ligands and stabilises transition metals in high formal oxidation states. The ligand 'N^{3-}' can coordinate terminally or bridging, forming either symmetric and asymmetric linear bridges, bent bridges with M–N–M angles as low as 91.3° or as a μ_3-ligand.[1–3] Nitrido bridges have been observed between a number of transition metals[3,4] as well as between transition-metal centres and Lewis acids as BX_3 (X = Cl, Br, F, Ph).[1–3,5] To our knowledge there is no report on covalent nitrogen bridges between transition and main group metals.

We investigated the ability of terminal nitrido ligands to undergo reactions with Lewis-acidic compounds. Here we report the synthesis and structural characterization of the first complexes with a Re–N–Ga core.

Gallium trichloride reacts with $[ReNCl_2(PMe_2Ph)_3]$ in CH_2Cl_2 by attack of the nucleophilic nitrido ligand. Two complexes with nitrogen bridges between rhenium and gallium could be isolated from the reaction mixture: the purple $[Cl_3Ga-NReCl_2(PMe_2Ph)_3]$ **1** and the dark red, cationic $[Cl_3Ga-NReCl(PMe_2Ph)_3(NCMe)]^+$ **2** which crystallizes as a tetrachlorogallate. The yields of the individual products can be controlled by the amount of $GaCl_3$ used during the reaction. Both complexes are stable as solids. Solutions of **1** in dichloromethane, however, slowly turn red, indicating a slow decomposition and the formation of considerable amounts of **2**.

Elemental analyses and ^1H NMR spectra of the products are consistent with the given formulations. Their infrared spectra show intense absorptions of the ReN multiple bonds at 1109 cm^{-1} (**1**) and 1104 cm^{-1} (**2**), respectively. They are shifted to higher wavenumbers with respect to the Re≡N frequency in the starting complex $[ReNCl_2(PMe_2Ph)_3]$ (1061 cm^{-1}). This is in accordance with previous results for BX_3 adducts (X = Cl, Br) of nitrido ligands[2–4,6,7] and can be understood in terms of a coupling between the Re–N and N–Ga vibrations and is not a consequence of an increase of the Re–N bond order. The coordinated acetonitrile in **2** can be detected by a weak absorption at 2300 cm^{-1}. Mass spectrometric studies (including FAB^+ and FD^+ ionization techniques) gives evidence for the molecular ions at *m/z* 859 (**1**) and 867 (**2**). Fragmentation occurs mainly by abstraction of complete ligands.

Air-stable, purple crystals of $[Cl_3Ga-NReCl_2(PMe_2Ph)_3]$ suitable for X-ray diffraction were obtained from CH_2Cl_2–*n*-hexane. An ORTEP representation[7] of the structure is given in Fig. 1.† The nitrido bridge between the metals is almost linear. The formation of the Ga–N bond results in an only slight increase of the Re–N bond with respect to $[NReCl_2(PMe_2Ph)_3]$ (1.68 *vs.* 1.66 Å).[8] However, a significant loss of the structural *trans* influence due to the multiply bonded nitrogen ligand can be observed, which is evident from the Re–Cl(2) distance which decreases by 0.15 Å with respect to the corresponding value in $[NReCl_2(PMe_2Ph)_3]$.[8]

The complex $[Cl_3Ga-NReCl(PMe_2Ph)_3(NCMe)][GaCl_4]$ is formed as a red oily product during the same reaction and can be recrystallized from CH_2Cl_2 by slow diffusion of *n*-hexane into a CH_2Cl_2 solution and dark red crystals of X-ray quality were obtained. The structure of the complex cation is shown in Fig. 2.† The tetrachlorogallate anion shows no unusual structural features and is not further discussed. The bonding situation in the nitrido bridge is similar to that in **1**. The Ga–N bond lengths of *ca.* 1.95 Å are comparable with covalent gallium–nitrogen single bonds which have been found for numerous gallium

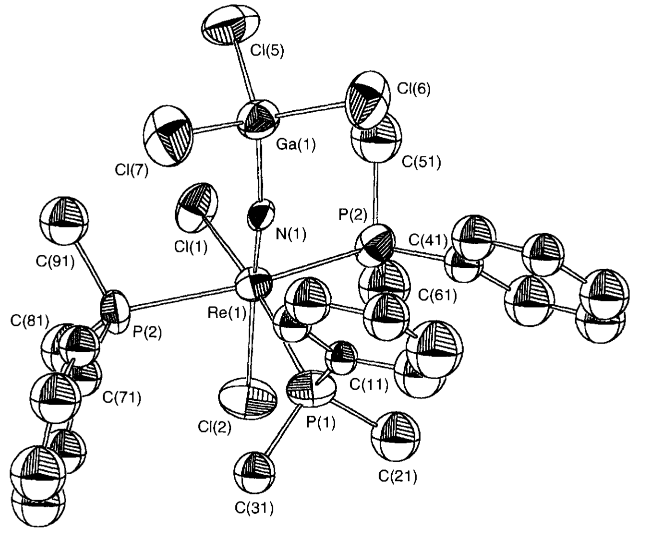

Fig. 1 ORTEP plot[7] of one of the virtually identical molecules of $[Cl_3Ga-NReCl_2(PMe_2Ph)_3]$ (thermal ellipsoids at 50% probability level). Selected bond lengths (Å) and angles (°): Re(1)–N(1) 1.67(1), Re(1)–Cl(1) 2.421(5), Re(1)–Cl(2) 2.477(5), Re(1)–P(1) 2.452(6), Re(1)–P(2) 2.461(10), Re(1)–P(3) 2.481(10), Ga(1)–N(1) 1.97(1); Re(1)–N(1)–Ga(1) 167.8(8), N(1)–Re(1)–Cl(1) 101.1(5), N(1)–Re(1)–Cl(2) 172.3(4), N(1)–Re(1)–P(1) 95.5(5), N(1)–Re(1)–P(2) 94.0(8), N(1)–Re(1)–P(3) 95.5(8).

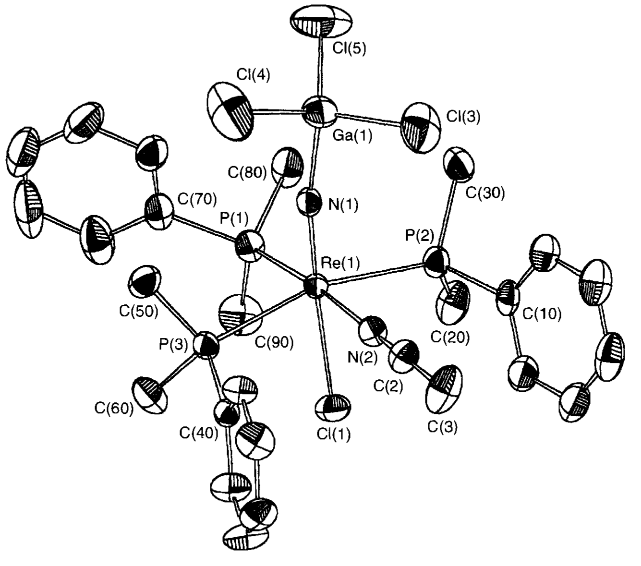

Fig. 2 ORTEP plot[7] of $[Cl_3Ga-NReCl(PMe_2Ph)_3(NCMe)]^+$ (thermal ellipsoids at 50% probability level). Selected bond lengths (Å) and angles (°): Re–N(1) 1.679(3), Ga(1)–N(1) 1.959(4), Re–Cl(1) 2.419(1), Re–P(1) 2.439(2), Re–P(2) 2.492(2), Re–P(3) 2.489(2), Re–N(2) 2.118(4), N(2)–C(2) 1.130(5), C(2)–C(3) 1.446(6); Re–N(1)–Ga(1) 167.1(2), N(1)–Re–Cl(1) 176.3(1), N(1)–Re–P(1) 93.1(1), N(1)–Re–P(2) 94.6(1), N(1)–Re–P(3) 99.6(1), N(1)–Re–N(2) 93.1(1), Re–N(2)–C(2) 178.3(3), N(1)–C(2)–C(3) 178.9(5).

complexes with nitrogen donor ligands,[9,10] but is much shorter than the shortest hitherto reported distances between 'N^{3-}' ligands and main group metals [*e.g.* the Ba–N distance of 2.735 Å in $Ba(ZrN_2)$].[11]

The acetonitrile ligand in **2** is formed during the reaction between CH_2Cl_2 and coordinated nitrido ligands. The driving forces of this unusual reaction obviously are the high tendency of $GaCl_3$ to form the tetrachlorogallate anion and the ability of terminal nitrido ligands to accept intermedially formed carbonium ions. This has recently been shown by the reaction of a rhenium nitrido complex with the condensation product of acetone which gives $[ReN\{CMe_2CH_2C(O)Me\}X_3(PMe_2Ph)_3]$ complexes[12,13] (X = Cl or Br) or the coupling of a Mo–N centre with the methyl ester of iodoacetic acid which forms functionalized imido complexes.[14] In the reaction under study intermediately formed ClH_2C^+ cations attack the nitrido ligand to give a cationic imido species which has an incipient carbanion character and is able to realize a carbon–carbon bond to a second ClH_2C^+ fragment. The electron-withdrawing capabilities of the chloro substituents may be responsible for a metallo-nitrogen ylide-like structure of the intermediate (see also ref. 14) which is transformed into coordinated acetonitrile upon loss of the chloro substituents (most probably by the formation of $GaCl_4^-$ anions). The shift of the hydrogen atom from the α- to the β-carbon atom may be an important step in the acetonitrile formation since no acetonitrile can be detected when the reaction is performed in CD_2Cl_2.

The formed MeCN is abstracted from the oxidized rhenium centre and is able to coordinate to the complex with the $ReNGaCl_3$ moiety. In this compound the acetonitrile ligand is finally situated *cis* to the nitrido ligand which is unusual with respect to the strong structural *trans* effect of 'N^{3-}' in the starting material. Obviously, the ligand exchange Cl^- *vs.* MeCN takes place in a second step following the formation of the nitrido bridge between the metals which results in a significant decreasing of the *trans* labilizing ability of the nitride. Therefore, the position *trans* to PMe_2Ph is the most labile one in the molecule and is exchanged.

It should be mentioned that the observed activation of organic molecules by nitrido moieties is strongly dependent on the individual nitrido complex and the activating agent (in our case $GaCl_3$). We have studied a number of similar rhenium(v) nitrido compounds with halide, phosphine and organic ligands with sulfur or sulfur/nitrogen donor atoms. However, the conversion of CH_2Cl_2 discussed above could only be observed with $[ReNCl_2(PMe_2Ph)_3]$. The same has been observed earlier for the formation of functionalized imido complexes from nitrido compounds, acetone and HCl or $(Ph_3C)BF_4$.[12,13,15] Thus, the sequence given above may explain the formation of acetonitrile from dichloromethane and a coordinated nitrido ligand, but does not serve as a general mechanism for this type of reaction. To set up a more detailed pattern we are currently studying the mechanisms of similar reactions in different solvents and by isotopic labelling.

In conclusion, nitrido-bridged bimetallic rhenium–gallium complexes can be synthesized by the reaction of gallium trichloride with $[ReNCl_2(PMe_2Ph)_3]$. The products may act as synthons for further ligand-exchange reactions on both metals. It is noteworthy that in the course of the reaction activated organic species are formed which finally form acetonitrile from the solvent CH_2Cl_2.

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Footnote

† *Crystal data* for $[Cl_3Ga–NReCl_2(PMe_2Ph)_3]$: monoclinic, space group $P2_1/c$, a = 17.885(5), b = 20.452(2), c = 17.964(2) Å, β = 82.82(1)°. V = 6529(2) $Å^3$, $F(000)$ = 3360, Z = 8, D_c = 1.756 g cm^{-3}, wR_2 = 0.0843, R_1 = 0.0567. For $[Cl_3Ga–NReCl(PMe_2Ph)_3(NCMe)][GaCl_4]\cdot CH_2Cl_2$: monoclinic, space group $P2_1/c$, a = 14.461(9), b = 13.968(5), c = 21.446(12) Å, β = 92.87(3)°. V = 4327(4) $Å^3$, $F(000)$ = 2264, Z = 4, D_c = 1.786 g cm^{-3}, wR_2 = 0.0668, R_1 = 0.0306.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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