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Syntheses and structures of di- and trinuclear heterometallic complexes with nitrido bridges between rhenium and titanium

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Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday.

Abstract

$[TiCl_4(MeCN)]_2$ (**1**) is obtained from a gas phase reaction of $TiCl_4$ and MeCN. It crystallizes in the orthorhombic space group *Cmca* with the cell constants $a = 961.8(2)$, $b = 984.0(5)$, $c = 1637.0(4)$ pm, and $Z = 4$. The symmetry of the dinuclear complex is C_{2h}. The Ti atoms are connected with symmetrical chloro bridges, and the octahedral coordination is completed by one acetonitrile ligand coordinated to each Ti atom. $[TiCl_4(MeCN)]_2$ reacts with $ReNCl_2(PMe_2Ph)_3$ in CH_2Cl_2 to form the dinuclear complex $(Me_2PhP)_3(MeCN)ClRe{\equiv}N–TiCl_5$ (**2**). It crystallizes as $\mathbf{2}{\cdot}CH_2Cl_2$ in the monoclinic space group $P2_1/n$ with the cell constants $a = 982.0(2)$, $b = 1245.3(2)$, $c = 3088.1(5)$ pm, $\beta = 92.44(2)°$, and $Z = 4$. The linear nitrido bridge (Re–N–Ti = 167.7(4)°) is characterized by distances Re–N = 167.6(8) pm and Ti–N = 223.9(9) pm. By using a fourfold excess of $ReNCl_2(PMe_2Ph)_3$ in toluene, the trinuclear complex $[(Me_2PhP)_3Cl_2ReN]_2TiCl_4$ (**3**) is obtained in form of crystals **3**·2 toluene: $P\bar{1}$, $a = 1070.4(2)$, $b = 1283.2(5)$, $c = 1300.0(3)$ pm, $\alpha = 85.21(2)°$, $\beta = 80.57(2)°$, $\gamma = 86.19(3)°$, $Z = 1$. The centrosymmetric complex **3** contains a linear axis Re≡N–Ti–N≡Re with a Re–N distance of 168.5(9) pm and a Ti–N distance of 215.7(9) pm. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Nitrido bridges between rhenium and titanium; Synthesis; Crystal structure

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1. Introduction

Nitrido complexes with a terminal nitrido ligand show Lewis basic behavior and can thus form nitrido bridges to Lewis acidic species. The rhenium (V) complex $ReNCl_2(PMe_2Ph)_3$ [1,2] was found to be of high basicity. Concerning this complex, three different reaction types with Lewis acids are observed. First, the Lewis acids bind to the terminal nitrido ligand, thus forming a nitrido bridge [3–7]. Second, the use of strong Lewis acids causes a separation of ligands of the rhenium complex. The resulting undercoordinated fragments recombine to a multinuclear rhenium complex with the nitrido bridges Re≡N–Re [8]. If the reaction is carried out in a chlorinated solvent like $CHCl_3$ or CH_2Cl_2, the solvent is involved in the reaction. HCl is formed protonating the nitrido ligand, and the Cl^- anion coordinates to the Lewis acid [9].

We report on our attempts to synthesize complexes with a nitrido bridge between Re and Ti by the reaction of $ReNCl_2(PMe_2Ph)_3$ with $TiCl_4$. In this case, $TiCl_4$ acts as a strong Lewis acid, and the formation of a nitrido bridge has not been observed so far. We therefore tried to weaken the acidity of $TiCl_4$ by adding MeCN. The resulting $[TiCl_4(MeCN)]_2$ (**1**) afforded the new complexes $(Me_2PhP)_3(MeCN)ClReNTiCl_5$ (**2**) and $[(Me_2PhP)_3Cl_2ReN]_2TiCl_4$ (**3**) with the nitrido bridges Re≡N–Ti.

2. Results and discussion

2.1. Syntheses and properties of $[TiCl_4(MeCN)]_2$ (1), $(Me_2PhP)_3(MeCN)ClReNTiCl_5$ (2) and $[(Me_2PhP)_3Cl_2ReN]_2TiCl_4$ (3)

The mononuclear complex $TiCl_4{\cdot}2MeCN$ has long been known [10,11]. It is formed by the reaction of

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$TiCl_4$ with an excess of MeCN in the liquid phase. We obtained the new dinuclear complex $[TiCl_4(MeCN)]_2$ (**1**) by a reaction of $TiCl_4$ with MeCN in the gas phase in form of very moisture sensitive, yellow needles. $[TiCl_4(MeCN)]_2$ reacts with $ReNCl_2(PMe_2Ph)_3$ in dichloromethane to give the dinuclear complex $(Me_2PhP)_3(MeCN)ClRe{\equiv}N–TiCl_5$ (**2**), which crystallizes as **2**·CH_2Cl_2 in the form of air sensitive, red violets needles. When a fourfold excess of the rhenium nitrido complex was used in toluene, the centrosymmetrical trinuclear complex $[(Me_2PhP)_3Cl_2Re{\equiv}N]_2TiCl_4$ (**3**) resulted. It forms triclinic brown needles with the composition **3**·2 toluene, which decompose in air within a short time.

The valence vibration $\nu(ReN) = 1061\ cm^{-1}$ of the educt $ReNCl_2(PMe_2Ph)_3$ [1] is only slightly shifted to lower wave numbers of $1041\ cm^{-1}$ for **2** and $1018\ cm^{-1}$ for **3** by coordinating $TiCl_5^-$ or $TiCl_4$ to the terminal nitrido ligand.

In the mass spectra of **2** and **3** only fragments of the rhenium complex are observed showing that the Ti–N bond is easily cleft.

The complexes **2** and **3** are diamagnetic with $\chi_{Mol} = -2.04 \times 10^{-4}$ emu mol^{-1} for **2** and $\chi_{Mol} = -7.74 \times 10^{-4}$ emu mol^{-1} for **3** at room temperature. Thus, the two d-electrons of Re(V) are paired as in the educt $ReNCl_2(PMe_2Ph)_3$.

2.2. Crystal structures of $[TiCl_4(MeCN)]_2$ (1), $(Me_2PhP)_3(MeCN)ClReNTiCl_5$ (2) and $[(Me_2PhP)_3Cl_2ReN]_2TiCl_4$ (3)

$[TiCl_4(MeCN)]_2$ forms orthorhombic crystals in the space group *Cmca* (Table 1). The dinuclear complex has the crystallographic symmetry C_{2h}. The two Ti atoms are connected by two symmetrical chloro bridges, and the octahedral coordination is completed by an acetonitrile ligand coordinated to each Ti atom (Fig. 1). The distances from the Ti atom to the terminal chloro ligands are 221 pm and correspond to covalent single bonds. The distances to the bridging Cl atoms of 248 pm are slightly longer due to their bridging function. For the distance of Ti–N = 219 pm, a coordinative single bond can be assumed.

Table 1
Crystal data and structure refinement for **1**, **2** and **3**

	1	**2**·CH_2Cl_2	**3**·$2C_7H_8$
Molecular formula	$C_4H_6Cl_8N_2Ti_2$	$C_{27}H_{38}Cl_8N_2P_3ReTi$	$C_{62}H_{82}Cl_8N_2P_6Re_2Ti$
Formula weight	461.51	1001.20	1745.02
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Cmca*	$P2_1/n$	$P\bar{1}$
a (pm)	959.8(2)	982.0(2)	1070.4(2)
b (pm)	982.2(2)	1245.3(2)	1283.2(5)
c (pm)	1637.5(2)	3088.1(5)	1300.0(3)
α (°)	90	90	85.21(2)
β (°)	90	92.44(2)	80.57(2)
γ (°)	90	90	86.19(3)
V (nm^3)	1.5437(5)	3.773(1)	1.753(1)
Z	4	4	1
Temperature (K)	293(2)	293(2)	208(2)
$D_{calc.}$ ($g\ cm^{-3}$)	1.986	1.762	1.653
Absorption coefficient (mm^{-1})	2.392	4.133	4.036
F(000)	896	1968	866
Color, habit	Yellow block	Violet needle	Brown needle
Crystal size (mm)	0.25 × 0.25 × 0.10	0.25 × 0.15 × 0.10	0.20 × 0.10 × 0.05
Theta range for data collection (°), method	3.22–30.97 ω-scans	3.11–26.97 ω-scans	3.12–27.00 ω-scans
Index ranges	$-13 \leq h \leq 11$, $-14 \leq k \leq 11$, $-23 \leq l \leq 23$	$-12 \leq h \leq 12$, $0 \leq k \leq 15$, $-1 \leq l \leq 39$	$-13 \leq h \leq 13$, $-16 \leq k \leq 16$, $-1 \leq l \leq 16$
Reflections collected	6412	8661	8675
Independent reflections	1292 [$R_{int} = 0.0754$]	8205 [$R_{int} = 0.0721$	7650 [$R_{int} = 0.060$]
Reflections with $I > 2\sigma(I)$	1090	4330	5320
Absorption correction	ψ-scans	ψ-scans	ψ-scans
Max/min transmission	0.9339/0.8694	0.9667/0.9345	0.9534/0.6338
Refined parameters	52	379	367
Goodness-of-fit on F^2	1.064	0.974	1.013
Weighting scheme	$w1/[\sigma^2(F_o^2)+(0.1000P)^2]$ $P = (F_o^2+2F_c^2)/3$	$w1/[\sigma^2(F_o^2)+(0.0406P)^2]$ $P = (F_o^2+2F_c^2)/3$	$w1/[\sigma^2(F_o^2)+(0.0822P)^2]$ $P = (F_o^2+2F_c^2)/3$
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0467$, $wR_2 = 0.1317$	$R_1 = 0.0567$, $wR_2 = 0.0945$	$R_1 = 0.0657$, $wR_2 = 0.1404$
R indices (all data)	$R_1 = 0.0572$, $wR_2 = 0.1388$	$R_1 = 0.1491$, $wR_2 = 0.1164$	$R_1 = 0.1230$, $wR_2 = 0.1614$
Depository number	CCDC 126011	CCDC 126012	CCDC 126013

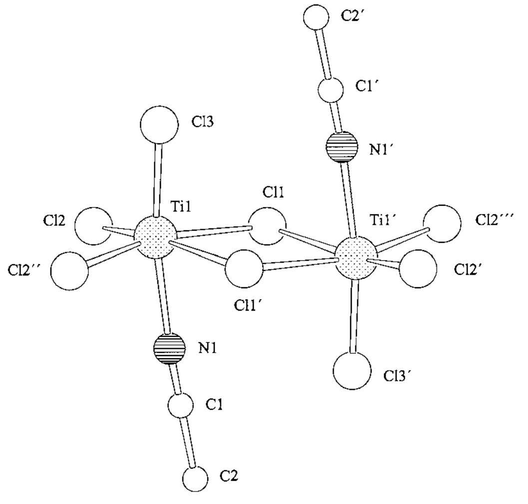

Fig. 1. Structure of **1**, showing the atom numbering scheme [20]. Selected bond lengths (pm) and angles (°): Ti–Cl(1) = 248.32(8); Ti–Cl(2) = 220.96(9); Ti–Cl(3) = 220.9(1); Ti–N = 218.9(3); Ti–Cl(1)–Ti′ = 100.81(4).

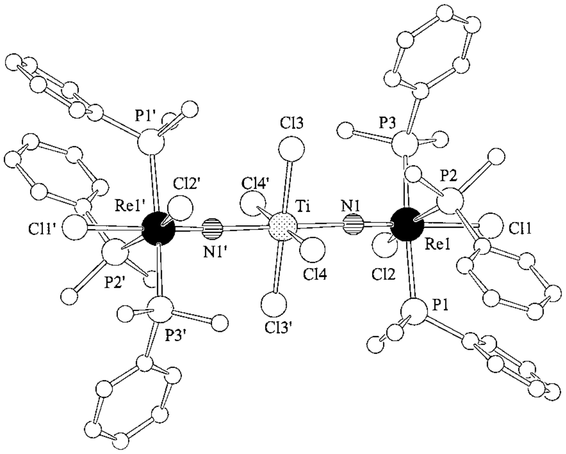

Fig. 3. Structure of **3**, showing the atom numbering scheme [20]. The toluene solvent molecules have been omitted for clarity. Selected bond lengths (pm) and angles (°): Re–N(1) = 168.5(9); Re–Cl(1) = 248.5(3); Re–Cl(2) = 243.1(3); Re–P(1) = 248.3(3); Re–P(2) = 243.5(3); Re–P(3) = 249.3(3); Ti–N(1) = 215.7(9); Ti–Cl(3) = 228.9(3); Ti–Cl(4) = 228.7(3); Re–N(1)–Ti = 175.4(5).

In the dinuclear complex **2** (Fig. 2) the anion $[TiCl_5]^-$ is coordinated to the nitrido ligand of the cationic Re(V) complex $[ReNCl(MeCN)(PMe_2Ph)_3]^+$ to form a linear nitrido bridge Re≡N–Ti (Re–N–Ti = 167.7(4)°, Re–N = 167.6(8) pm and Ti–N = 223.9(9) pm). The Re–N distance lies within the range of triple bonds [12,13], and is only marginally longer than the Re–N distance in the educt $ReNCl_2(PMe_2Ph)_3$ (166 pm [14]). The Ti–N distance is, however, considerably longer than expected for a covalent single bond (207 pm [15]). It is also longer than the distances of 219 pm in **1** and 216 pm in **3**. In agreement to the weak Ti–N bond in **2**, the distance Ti–Cl(3) of 228 pm in *trans* position is shorter than the distances in the *cis* positions, which range from 229 to 232 pm.

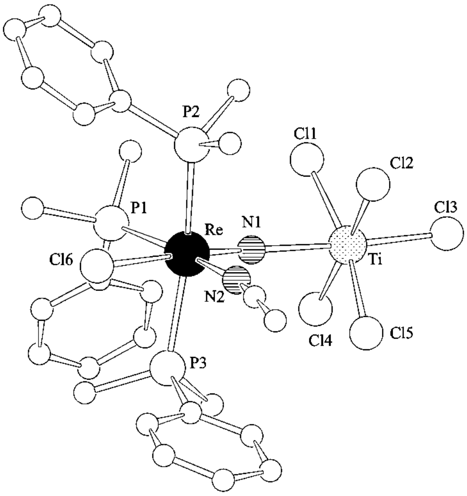

Fig. 2. Structure of **2**, showing the atom numbering scheme [20]. The dichloromethane solvent molecule has been omitted for clarity. Selected bond lengths (pm) and angles (°): Re–N(1) = 167.6(8); Re–N(2) = 211.2(8); Re–Cl(6) = 248.8(3); Re–P(1) = 244.7(2); Re–P(2) = 249.7(3); Re–P(3) = 247.7(3); Ti–N(1) = 223.9(9); Ti–Cl(1) = 231.8(3); Ti–Cl(2) = 230.0(3); Ti–Cl(3) = 227.9(3); Ti–Cl(4) = 229.3(3); Ti–Cl(5) = 231.6(4); Re–N(1)–Ti = 167.7(4).

It is interesting that despite the *trans* effect of the nitrido ligand, the *cis* Cl atom of the educt $ReNCl_2(PMe_2Ph)_3$ is substituted by an acetonitrile molecule, and is then bound to the Ti atom. The reason for this phenomenon is that, after the coordination of the Ti atom to the nitrido ligand, the closer Cl atom in *cis* position is probably substituted more easily. In addition, the *trans* effect is weakened by the coordination of a Lewis acid. This weakening of the *trans* effect is also confirmed by the reduction of the Re–Cl(*trans*) distance from 263.3(2) pm in the educt [14] to 248.8(3) pm in **2**. It has almost the same value as Re–Cl(*cis*) = 244.2(2) pm in $ReNCl_2(PMe_2Ph)_3$.

The trinuclear nitrido complex **3** crystallizes in the triclinic space group $P\bar{1}$ with one centrosymmetrical complex and two toluene molecules in the unit cell. It is isotypic to the recently found compound $[(Me_2PhP)_3Cl_2ReN]2NbCl_4{\cdot}2C_7H_8$ [16]. Other comparable three nuclear complexes are $[(Me_2PhP)_3Cl_2ReN]_2VOCl_2$ [9] and $[\{(Me_2PhP)_3(EtCN)ClReN\}_2MoCl_4]^{2+}$ [7]. In the latter case, the *cis* chloro ligand of the educt $ReNCl_2(PMe_2Ph)_3$ is also substituted by a nitrile molecule as in **2**.

The trinuclear complex **3** is centrosymmetrical with the Ti atom occupying the center of symmetry. Unlike in **2**, the coordination geometry of the two rhenium complex fragments remains unchanged in comparison to the structure of the educt complex $ReNCl_2(PMe_2Ph)_3$. By coordinating the nitrido ligands to the central, square-planar moiety $TiCl_4$, a linear skeleton Cl–Re≡N–Ti–N≡Re–Cl is formed (Fig. 3).

The Re–N distances of 168.5(9) pm agree with the observation in **2**, and they are only slightly longer than in $ReNCl_2(PMe_2Ph)_3$ [14]. The Ti–N distances are considerably shorter than in **2**. A comparison of the Re–Cl distances of 243.1(3) and 248.5(3) pm in *cis* and *trans* position to the nitrido ligand shows that its *trans* influence is almost negligible, as it is usually found when a Lewis acid is coordinated to the nitrido ligand.

As it is expected, the different lengths of the Re–P distances in **2** as well as in **3** show that the phosphine ligands cause a slightly stronger *trans* influence than the acetonitrile or chloro ligands.

3. Experimental

3.1. General techniques

All syntheses were carried out under dry nitrogen with dehydrated solvents. $ReNCl_2(PMe_2Ph)_3$ was synthesized as described in [2]. $TiCl_4$ was distilled before use.

3.2. $[TiCl_4(MeCN)]_2$

The reaction of gas mixtures of 11% $TiCl_4$ and 11% MeCN in dry argon at 65°C results quantitatively in yellow needlelike crystals of $[TiCl_4(MeCN)]_2$. When the product is sublimated at 65°C and 1 atm. of argon, yellow blocks suitable for the X-ray experiments can be obtained.

Anal. Found: C, 12.40; H, 1.35; N, 7.24 $C_2H_3NCl_4Ti$. Anal. Calc.: C, 10.40; H, 1.31; N, 6.06%.

IR (KBr): cm^{-1} 2926 w (CH_3), 2311 vs (C≡N), 2282 vs (C≡N), 1402 w (CH_3), 1357 m (CH_3), 942 s (C–C), 381 vs (TiCl). MS (EI 20 eV): m/z (%) 345 (5) (Ti_2Cl_47), 190 (50) ($TiCl_4$), 153 (70) ($TiCl_3$), 118 (15) ($TiCl_2$), 83 (25) (TiCl), 48 (15) (Ti), 41 (100) (MeCN).

3.3. $(Me_2PhP)_3(MeCN)ClReNTiCl_5$

$[TiCl_4(MeCN)]_2$ (0.1 g, 0.216 mmol) is dissolved in 15 ml CH_2Cl_2. $ReNCl_2(PMe_2Ph)_3$ (0.3 g, 0.438 mmol) is slowly added to this solution. The initial yellow solution changes to deep red. It is stirred at room temperature for one more hour. Under reduced pressure, the solution is concentrated to 50% of its original volume and covered with a layer of 25 ml *n*-hexane. Within 24 h, red violet needles of **2**·CH_2Cl_2 are obtained (0.4 g = 91%).

Anal. Found: C, 33.7; H, 3.3; N, 1.9; Cl, 26.44 $C_{27}H_{38}Cl_8N_2P_3ReTi$. Anal. Calc.: C, 32.36; H 3.80; N, 2.80; Cl, 28.37%.

IR(KBr): cm^{-1} 2919 w, 2327 w, 2299 w, 1482 w, 1436 s, 1287 w, 1105 m, 1041 vs, 945 s, 915 vs, 749 s, 713 m, 694 m, 491 s, 423 w, 350 vs, 289 w. MS (FAB^+): m/z (%) 650 (40) ($(Me_2PhP)_3ReNCl$), 547 (80) ($(Me_2PhP)_2ReNCl_2$), 512 (100) ($(Me_2PhP)_2ReNCl$), 408 (50) ($(Me_2PhP)ReNCl_2$).

3.4. $[(Me_2PhP)_3Cl_2ReN]_2TiCl_4$

$[TiCl_4(MeCN)]_2$ (0.1 g, 0.216 mmol) is dissolved in 25 ml toluene. Subsequently, 0.7 g (1.0 mmol) $ReNCl_2(PMe_2Ph)_3$ are added slowly. Afterwards, the reaction mixture is stirred for 24 h. Under reduced pressure, the volume is reduced to about 50%. The concentrated solution is now covered with a layer of 25 ml *n*-hexane. After 3 weeks brown crystals of **3**·$2C_7H_8$ are obtained in a yield of 60%.

Anal. Found: C, 34.7; H, 4.4; N, 1.3; Cl, 23.2 $C_{48}H_{66}Cl_8N_2P_6Re_2Ti$. Anal. Calc.: C, 36.9; H, 4.2; N, 1.8; Cl, 18.2%.

IR (KBr): cm^{-1} 2917 m, 1435 s, 1413 w, 1282 w, 1261 w, 1104 m, 1018 vs, 945 s, 916 vs, 742 s, 695 s, 489 s, 370 m. MS (FAB^+): m/z (%) 685 (10) ($(Me_2PhP)_3ReNCl_2$), 650 (80) ($(Me_2PhP)_3ReNCl$), 547 (95) ($(Me_2PhP)_2ReNCl_2$), 512 (100) ($(Me_2PhP)_2ReNCl$), 408 (30) ($(Me_2PhP)ReNCl_2$).

3.5. Crystal structure determinations

The crystallographic data (Table 1) were collected by an Enraf-Nonius CAD4 diffractometer with monochromatized Mo–K_α radiation. The unit cell parameters were determined from 25 carefully centered reflections. Intensity data were measured via ω-scans, and an empirical absorption correction, based on ψ-scans, was applied [17]. The structures were solved by direct methods (SHELXS-97 [18]) and refined by a full matrix least-squares procedure using F^2 (SHELXL-97 [19]). All non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were calculated at idealized positions.

4. Supplementary material

Further details of the crystal structure investigations are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, on quoting the depository number and the full journal citation.

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