



ELSEVIER

Isocyanide–Group 5 complexes and metal-centred C–C coupling

Dieter Rehder *, Christian Böttcher, César Collazo, Ronald Hedelt, Hauke Schmidt

Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

Received 26 February 1999; received in revised form 24 April 1999

Abstract

The Nb^I complexes [XNb(CO)₂(CNR)₄] (X = I, Br; R = *t*Bu, *c*Hex, 2,6-Me₂C₆H₃) (**4**) have been identified as intermediates in the system [Nb(CO)₆][−]/CNR/X₂, which generates the Nb^{III} complexes [I₂Nb(CNR)₆]I (**1**) and [X₃Nb(CNR)₃] (**2**) or, on addition of toluene, [I₂Nb(CN*t*Bu)₃tolane]I (**3**). In the presence of small amounts of water, the aminoalkyne–Nb^{III} complexes [X₂Nb(CNR)₄RHNC≡CNHR]X (R = *t*Bu; X = I: **5a**, X = Br: **5b**) are formed. The complex **4a** (X = I, R = *t*Bu) converts to **5a** in the presence of water, suggesting successive protonation and intramolecular reductive isocyanide coupling mediated by the Nb^I centre. The V^I complexes [XV(CO)₂(CNR)₂dppe] (X = I, R = *t*Bu, *c*Hex; X = Br, R = *t*Bu) (**6**) and the V^{III} complex [I₂V(CN*t*Bu)₆]I (**7**) have been obtained from the system [V(CO)₆][−]/CNR/X₂ in dry THF, while the coupling product [I₂V(CN*t*Bu)₄*t*BuHNC≡CN*t*Bu]I (**8**) is recovered as water is added. In contrast to the Nb system, V^{II} complexes of composition [I₂V(CNR)₄] (**9**) and [I₂V(CN*t*Bu)₂(PR₃)₂] (**10**) can also be synthesised. The complex **10b** (PR₃ = PPhMe₂) has also been prepared from *cis*-[V(CO)₄(PPhMe₂)₂][−] (**11**). The system [Ta(CO)₆][−]/CNR/I₂ yielded the complexes [ITa(CO)₃(CN*t*Bu)₃] (**13a**), [ITa(CO)₃(CN*t*Bu)dpppe] (**13b**) and [I₂Ta(CN*t*Bu)₆]I (**14**). The chloro–isocyanide complexes [Cl₂V(CPh)(CN*t*Bu)₂] (**12**) and [Cl₂Ta(CN*c*Hex)₄] (**15**) have been generated from the metal chlorides as starting products. [INb(CO)₂(CN*t*Bu)₄]·2toluene (**4a**·2toluene), *trans*-[I₂V{CN(2,6-Me₂C₆H₃)₄}] (**9a**) and *cis*-[Et₄N][V(CO)₄(PPhMe₂)₂] ([Et₄N]-**11**) have been characterised by single-crystal X-ray diffraction. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Isocyanides; Niobium; Vanadium; Tantalum; Carbon–carbon coupling

1. Introduction

Reductive coupling of C₁ fragments is a generally occurring reaction in biosynthesis and in various in vitro reactions catalysed by metal centres. Understanding the mechanism that leads to the coupling products is an important goal in understanding and thus optimising catalytically conducted reactions with respect to both yield and selectivity. Coupling reactions involving isocyanides as C₁ fragments and the Group 6 metals as activating centres have been thoroughly investigated during the last two decades, starting with Lippard's discovery that the complexes [XMo(CNR)₆]X (X = halide) can be reduced to the aminoalkyne complexes [XMo(CNR)₄RHNC≡CNHR]X by zinc in the presence of water as the proton source [1]. This particular reaction has attained some importance also in the context

of the isocyanide-ligase activity of Mo- and V-nitrogenases from *Acetobacter*. While the main issue of these enzymes is the fixation of nitrogen, they also accept various other unsaturated substrates, one of which is methylisocyanide, which is reductively protonated to methane and methylamine and, in a side reaction, to ethylene and methylamine [2]. The mechanisms which have been proposed for the in vitro coupling of isocyanides (and the isoelectronic carbonyls) to acetylenes involve a η²-ketenyl intermediate [3], a carbene–carbyne intermediate [4], or a bis(carbyne) intermediate [5]. The present state of knowledge as revealed for the Mo systems favours the carbyne mechanism (where the first step is the reduction of Mo^{II} to Mo⁰) [6], which may also hold for the reductive homo- and hetero-coupling of CO and CNR by external reductants in the isoelectronic Nb^I system [3,7].

We have recently shown that the reaction between hexacarbonylniobate(−I), iodine and isocyanide in THF containing small amounts of water yields the Nb^{III} complex [I₂Nb(CNR)₄RHNC≡CNHR]I [8a]. Al-

* Corresponding author. Tel.: +49-40-428386087; fax: +49-40-428382893.

E-mail address: rehder@xray.chemie.uni-hamburg.de (D. Rehder)

though a hexakis(isocyanide) Nb^{III} complex, viz. [I₂Nb(CNR)₆]I, has also been isolated from dry THF [8a], this compound could not be converted to the coupling product by zinc or other reductants in the presence of water, and hence lacks analogy with the Mo^{II} case. This seems to exclude a reaction mechanism in which the two electrons necessary for the reductive coupling of two CNR stem from an external electron source. Instead, an intermediately formed Nb^I centre may deliver two electrons intramolecularly. Nb^I isocyanide complexes such as [INb(CO)₂dppe(CNR)₂] (dppe = Ph₂PCH₂CH₂PPh₂) [8a] have been synthesised. While this compound again resists conversion to an alkyne complex (as do the analogous vanadium and tantalum compounds; see below), its close analogue [INb(CO)₂(CNR)₄], as shown in this work, undergoes this conversion without additional reducing agents added.

2. Results and discussion

2.1. General reaction schemes

The precursor compound in all of the reactions leading to isocyanide–niobium complexes, and to most of the isocyanide–vanadium and –tantalum complexes, is [M(CO)₆][−], which, depending on the reaction conditions, yields seven-coordinate complexes of M^I, hexa-coordinate complexes of M^I and M^{III} (and M^{II} in the case of M = V) or octa-coordinate complexes of M^{III} (M = V, Nb). In contrast to the corresponding vanadium chemistry [8b], isocyanide complexes of Nb^{II} have not been observed. The oxidation of M^{−I} to M^{I–III} is carried out with iodine (or bromine, in some cases). In the absence of additional ligands, [M(CO)₄]₂(μ-I)₃[−] forms [8c]; in the presence of isocyanide, the reaction proceeds to the formation of (see Schemes 1 and 2 for the overall reactions for M = Nb and V/Ta)

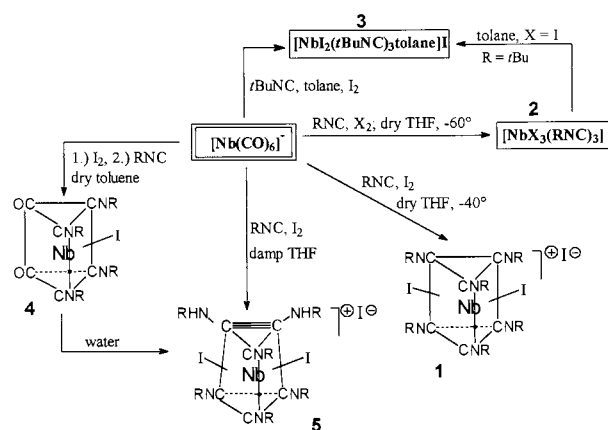
[I₂M(CNR)₆]⁺ (M = Nb: **1**, M = V: **7**, M = Ta: **14**; with a third iodide as the counter-ion), [I₃Nb(CNR)₃] (**2**), [I₂V(CNR)₂L₂] (**9** and **10**), or carbonyl–isocyanide complexes such as [INb(CO)₂(CNR)₄] (**4**), [IV(CO)₂(CNR)₂dppe] (**6**) and [ITa(CO)₃(CN*t*Bu)L₂] (**13**), if absolutely dry THF is used as a solvent. Which one of the complexes forms mainly depends on the metalate/isocyanide and metalate/iodine stoichiometries, reaction conditions and work-up of the reaction mixture. Compound **2**, which compares with the known complex [Cl₃Nb(CN*t*Bu)₃] [9], can be further converted to [I₂Nb(CN*t*Bu)₃tolane]I (**3**) by addition of toluene. Complexes with a mixed ligand sphere also form with phosphines; see **6**, **10** and **13b**. In the vanadium system, the anions [V(CO)₄(PR₃)₂][−] (**11**), generated photochemically from the hexacarbonylmetalate and phosphine, can also be used, although with less satisfactory yields, as precursor compounds in the preparation of the complexes **10**.

In the context of CC coupling, the formation of [INb(CO)₂(CNR)₄] (**4**) by consecutive addition of isocyanide and iodine to a solution of [Nb(CO)₆][−] in dry THF is of special interest. Compound **4** may also be obtained from [INb(CO)₄dppe] [10,11] with a four-fold molar excess of isocyanide. Exchanging THF for toluene slows down the reaction. Addition of water converts **4** to the alkyne complexes [I₂Nb(CNR)₄RHNC≡CNHR] (**5**). The direct conversion of [IM(CO)₂(CNR)₂dppe] (**6** for M = V), i.e. exchange of two of the isocyanide ligands in [IM(CO)₂(CNR)₄] by the bis(phosphine), inactivates the compound with respect to CC coupling. On the other hand, the coupling products **5** and **8** form by direct action of iodine upon a solution of [M(CO)₆][−] and CNR in THF plus a small amount of water added.

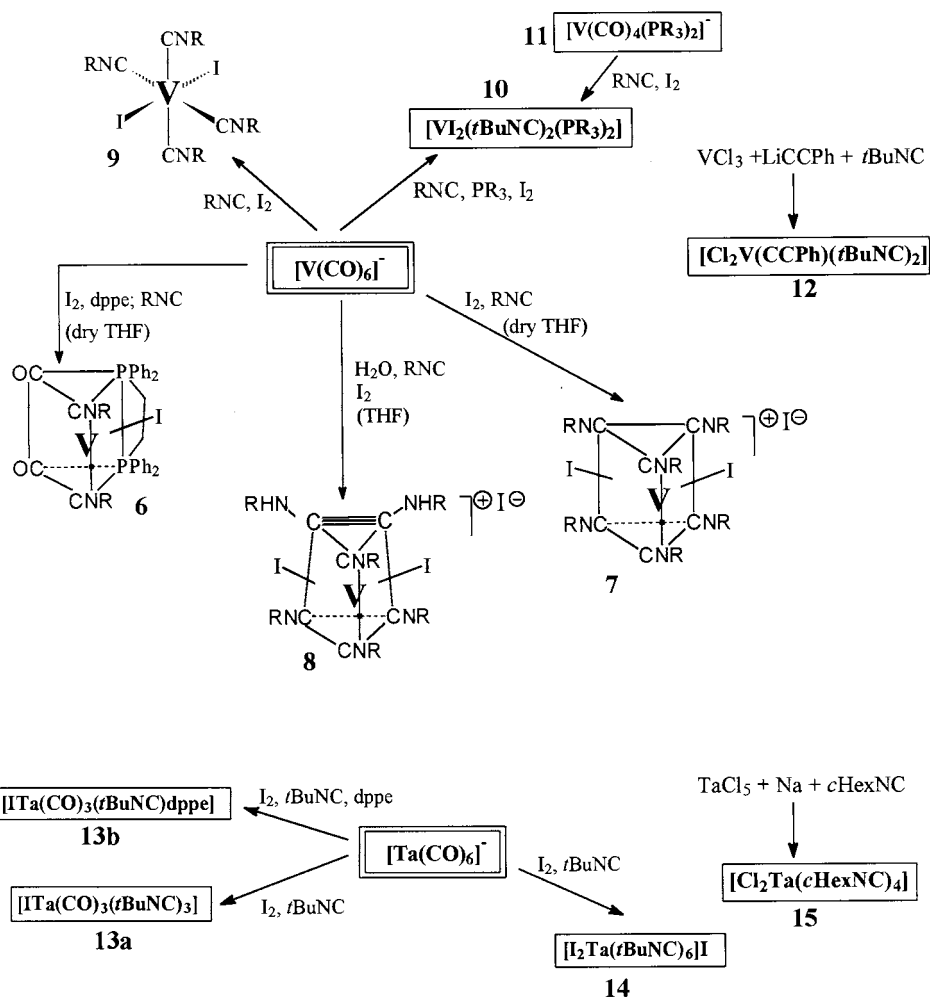
A similar reaction can, in principle, be carried out with bromine as the primary oxidising reagent—and has led to the characterisation of **5b**. In contrast, chlorine did not yield well defined isocyanide complexes or coupling products when employing [M(CO)₆][−] as precursor compounds. With the chlorides of vanadium and tantalum on the other hand, two chloro-isocyanide complexes (**12** and **15**) have been prepared.

2.2. Structures

The basic structures of the seven- (**4**, **6**, **12**) and eight-coordinate (**1**, **5**, **7**, **8**) complexes derive from a trigonal prism, with one or two of the tetragonal faces capped by the iodo ligands (see Schemes 1 and 2). The structures of **1a** (R = *t*Bu) and **5a** (R = *t*Bu) have been reported recently [8a]. [INb(CO)₂(CN*t*Bu)₄]·2toluene (**4a**·2toluene) crystallises in the orthorhombic space group P2₁2₁2₁. Crystal data and data on the structure refinement are collated in Table 1, selected bonding parameters in Table 2. Fig. 1 shows a plot and the



Scheme 1.



labelling scheme. In spite of the relatively high R value (9.4%), a consequence of the unfavourable cell dimensions (c is about four times as long as a and b) and high residual electron densities close to the heavy atoms, the molecular connectivities have been established unambiguously. The molecular point symmetry is C_{2v} . As in the case of similar Nb^I complexes with the co-ordination number 7, the arrangement for the Nb(CO)₂(CNR)₄ moiety is basically trigonal prismatic. Iodine is above the face occupied by the four isocyanide ligands, and opposite the edge formed by the two carbonyls—in accord with the complexes [XM(CO)_{6-np}]_n (p stands for a coordinated phosphorus function; M = V, Nb, Ta; X = Br, I) [12] and [INb(CO)₂(CNCy)₂dppc] [8a], and in accord with orbital calculations according to which the ligands with the higher π -acceptor capability (carbonyl) occupy the edge opposite the less powerful π -acceptors (isocyanide or phosphine) [13]. The bond lengths and bond angles are comparable to those of other isocyanide-niobium complexes such as **1**, **5** and [INb(CO)₂(CNCy)₂dppc] [8a], but differ from [XNb(CO)CNR(dmpe)₂] (dmpe =

Me₂PCH₂CH₂PMe₂) in that the Nb–C≡N–R groups are almost linear in the former, while they are strongly bent ($\angle C-N-R = 122-139^\circ$) [14] in the latter. Interatomic distances amount to ca. 2.7 Å [$d(C1\cdots C3)$ and $d(C2\cdots C4)$] and hence are short enough to enable C–C coupling. Hence, the trigonal prism is predesigned to allow for reductive coupling [13].

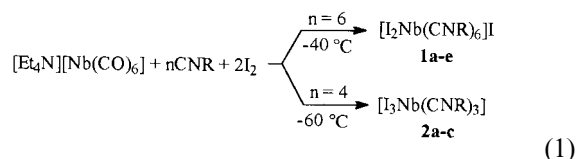
The six-coordinate V^{II} complexes **9** and **10** attain an octahedral geometry, as indicated by the X-ray structure of **9a** (Fig. 2, Tables 1 and 2) and thus resemble other isocyanide complexes belonging to this family [8b]. The two iodo ligands in **9a** are in *trans* positions. The local symmetry of the molecule is C_i ; the 2,6-dimethylphenyl rings are slightly bent towards each other. Again, the V-isocyanide moieties are essentially linear.

The octahedral anion of [Et₄N]-**11** (Fig. 3, Tables 1 and 2) shows the *cis*-configuration that has previously been documented for [V(CO)₄{(Ph₂P)₂C₆H₄}][−] [15a], where the *cis* configuration is imposed by the chelate structure. Bond lengths and angles are close to those for an ideal octahedral geometry, and bonding parame-

ters lie within the range observed for $[\text{V}(\text{CO})_4\{\text{(Ph}_2\text{P)}_2\text{-C}_6\text{H}_4\}]^-$ [15a] and $[\text{V}(\text{CO})_5\text{PPh}_3]^-$ [15b].

2.3. Preparation, characteristics and reactions

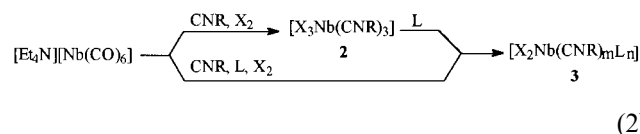
Complexes of types **1** and **2** have been prepared according to Eq. (1) under slightly different reaction conditions. The reaction proceeds through an intermediately formed complex **4** (IR evidence) which, however, cannot be isolated under the conditions provided for the direct generation of **1** or **2**. The characteristic $\nu(\text{C}\equiv\text{N})$ data are summarised in Table 3. Both **1a** and **2a**, when dissolved in THF, give rise to a single sharp $\nu(\text{C}\equiv\text{N})$ band at 2199 cm^{-1} , corresponding to an unidentified isocyanide species, a plausible formulation of which is $[\text{I}_2\text{Nb}(\text{CNR})_3(\text{THF})_3]\text{I}$.



Some insight into the solution structure has also been obtained from conductivity measurements of the complexes **1a**, **2a**, **1d** and $[\text{I}_2\text{Nb}(\text{CN}t\text{Bu})_3\text{tolane}]\text{I}$ (**3**) in

MeCN (Table 4 and Fig. 4), where the complexes retain their IR pattern pertinent from the solid state (Table 3): While the A_0 conductivities are similar for all four complexes, the κ coefficients (κ is the slope of the lines in Fig. 4 and is mainly a measure for the stoichiometry of the electrolyte) indicate that **1a** and **2a** are less dissociated than **1d** (and **3**).

The isocyanides in **1** and **2** cannot be replaced by ligands (L) such as alkynes and/or phosphines. The tolane complex **3**, however, can be generated as shown in Eq. (2). Compound **3** has been formulated as ionic complex based on the conductivity data (see above).



If the reactions represented by Eq. (1) are carried out in damp instead of absolutely dry THF, the coupling products **5** are obtained (idealised by Eq. (3)). The previously reported [8a] structure for $\text{R} = t\text{Bu}$ (**5a**) is related to that of **1a** (see Scheme 1); although the inter-atomic distance between the carbons of two adjacent isocyanides in **1a**, $2.6(1)\text{ \AA}$, allows for a coupling reaction, type **1** complexes are not likely to be precur-

Table 1
Data on the crystal structure and refinement of $[\text{INb}(\text{CO})_2(\text{CN}t\text{Bu})_4]\cdot 2\text{toluene}$ (**4a**·2toluene), $[\text{I}_2\text{V}\{\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}_4]$, (**9a**), and $[\text{Et}_4\text{N}][\text{V}(\text{CO})_4(\text{PPhMe}_2)_2]$ ($[\text{Et}_4\text{N}]\text{-11}$)

	4a ·2toluene	9a	$[\text{Et}_4\text{N}]\text{-11}$
Empirical formula	$\text{C}_{36}\text{H}_{52}\text{I}_4\text{NbO}_2$	$\text{C}_{40}\text{H}_{44}\text{I}_2\text{N}_4\text{OV}$	$\text{C}_{28}\text{H}_{42}\text{NO}_4\text{P}_2\text{V}$
Formula weight (g mol^{-1})	792.63	901.53	569.51
Temperature (K)	173(2)	153(2)	153(2)
Wavelength (\AA)	1.54178	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a (\AA)	9.577(2)	11.033(2)	9.975(3)
b (\AA)	10.724(3)	18.263(4)	11.900(5)
c (\AA)	38.907(14)	11.092(2)	25.65(2)
β ($^\circ$)		116.04(3)	90.05(4)
Z	4	2	4
V (\AA^3)	3966(2)	2008.1(7)	3044(2)
D_{calc} (g cm^{-3})	1.318	1.491	1.243
Absorption coefficient (mm^{-1})	8.77	1.82	0.426
$F(000)$	1624	898	1208
Crystal dimensions (mm)	$0.2 \times 0.1 \times 0.1$	$0.3 \times 0.3 \times 0.2$	$0.3 \times 0.2 \times 0.2$
θ Range ($^\circ$)	4.28–76.51	2.33–30.07	2.33–27.57
Index ranges	$-12 < h < 0$, $-12 < k < 0$, $-47 < l < 0$	$-1 < h < 14$, $-1 < k < 25$, $-15 < l < 14$	$-1 < h < 12$, $-15 < k < 15$, $-33 < l < 33$
Reflections collected	4295	6899	16 608
Independent reflections	4252	5850	7037
R_{int}	0.0264	0.0317	0.0591
Parameters	411	245	333
Goodness-of-fit	1.046	1.015	1.010
Final R indices [$I > 2\sigma(I_0)$]	$R_1 = 0.0942$, $wR_2 = 0.2153$	$R_1 = 0.0501$, $wR_2 = 0.1275$	$R_1 = 0.0567$, $wR_2 = 0.1196$
R indices (all data)	$R_1 = 0.1409$, $wR_2 = 0.2858$	$R_1 = 0.0647$, $wR_2 = 0.1369$	$R_1 = 0.0975$, $wR_2 = 0.1357$
Absolute structure parameter	$-0.01(3)$		
Largest difference peak and hole (e \AA^{-3})	3.02 and -2.30	1.439 and -1.282	0.707 and -0.733

Table 2
Selected bond lengths (Å) and bond angles (°) for **4a**·2toluene, **9a** and [Et₄N]-**11**

[Nb(CO) ₂ (CN <i>t</i> Bu) ₄]·2toluene (4a ·2toluene)	[I ₂ V{CN(2,6-Me ₂ C ₆ H ₃) ₂ }] ₄ (9a)	[Et ₄ N][V(CO) ₄ (PPhMe ₂) ₂] ([Et ₄ N]- 11)			
<i>Bond lengths</i>					
Nb–I	2.945(3)	V–I	2.7699(5)	V–P1	2.439(2)
Nb–C1	2.22(2)	V–C1	2.128(3)	V–P2	2.451(1)
Nb–C2	2.23(2)	V–C2	2.158(4)	V–C1	1.910(3)
Nb–C3	2.17(3)	C1–N1	1.150(5)	V–C2	1.936(3)
Nb–C4	2.27(3)	C2–N2	1.139(5)	V–C3	1.896(3)
Nb–C5	2.10(3)	N1–C10	1.403(3)	V–C4	1.945(3)
Nb–C6	2.07(2)	N2–C20	1.401(5)	C1–O1	1.176(4)
C1–N1	1.19(3)			C2–O2	1.167(4)
C2–N2	1.12(2)			C3–O3	1.184(4)
C3–N3	1.20(3)			C4–O4	1.163(4)
C4–N4	1.14(3)				
C5–O1	1.17(2)				
C6–O2	1.19(2)				
C1···C3	2.69				
C1···C4	3.49				
<i>Bond angles</i>					
C1–Nb–I	87.4(5)	I–V–C1	88.34(9)	P1–V–P2	92.12(4)
C2–Nb–I	80.7(5)	I–V–C2	90.71(10)	P1–V–C1	170.84(9)
C3–Nb–I	85.7(6)	C1–V–C2	95.21(14)	P1–V–C2	88.41(9)
C4–Nb–I	83.2(6)	V–C1–N1	174.3(3)	P1–V–C3	89.26(10)
C5–Nb–I	145.3(9)	V–C2–N2	171.0(3)	P1–V–C4	91.40(10)
C6–Nb–I	145.5(8)	C1–N1–C10	178.8(4)	P2–V–C	195.43(10)
C1–Nb–C2	166.0(6)	C2–N2–C20	173.5(4)	P2–V–C2	92.77(9)
C1–Nb–C3	103.8(9)			P2–V–C3	176.34(10)
C1–Nb–C4	75.8(8)			P2–V–C4	91.05(11)
C1–Nb–C5	115.0(9)			C1–V–C2	86.09(13)
C1–Nb–C6	72.3(9)			C1–V–C3	83.51(13)
Nb–C–N, av.	176.1			C1–V–C4	93.62(13)
Nb–C5–O1	175(2)			C2–V–C3	90.66(13)
Nb–C6–O2	172(3)			C2–V–C4	176.18(14)
C–N–R, av.	175.5			V–C–O, av.	174.9

sors for type **5** complexes since, in contrast to the Mo analogues, **1** cannot be converted to the coupling product **5** with Zn/H₂O and other reductants such as Na/Hg, Na, Li, or Mg assisted by naphthalene or cyclo-octatetraene. We therefore suggest that an intermediately formed Nb^I complex, viz. **4**, is the precursor compound, and Nb^I itself delivers the electrons for the reductive coupling reaction in an intramolecular process. Evidence for an intermediate **4** formed in THF solution is provided as the reaction shown in Eq. (3) is monitored by IR, and by the isolation of the respective complexes in dry THF (or toluene). Compound **5** is formed in appreciable yields only if less than the six equivalents of CNR demanded by Eq. (3) are employed, hinting towards a stabilising role (with respect to minimised formation of Nb iodides) of the CO ligands present in **4**. Furthermore, only 1.5 (instead of the required two) equivalents of iodine have been used in order to prevent rapid oxidation to Nb^{IV/V}. If, instead of THF, dry toluene is the solvent, and if the hexacarbonylniobate(–I) is oxidised to [Nb(CO)₄]₂(μ-I)₃[–] prior to the addition of iso-

cyanide, **4a** can be isolated in crystalline form (Eq. (4)). As **4a** is redissolved in damp toluene, it converts to **5a** with a yield of 31%. The role of water suggests that it

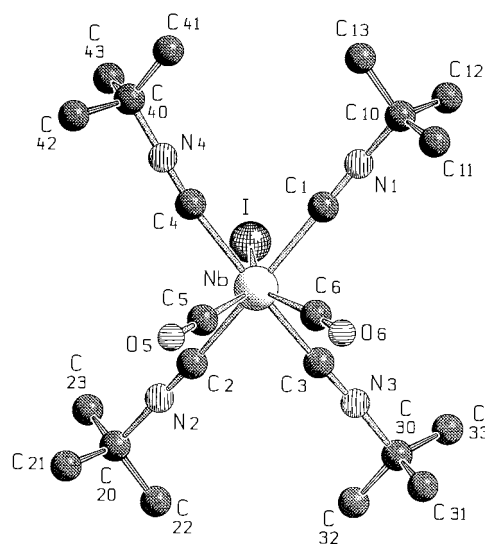
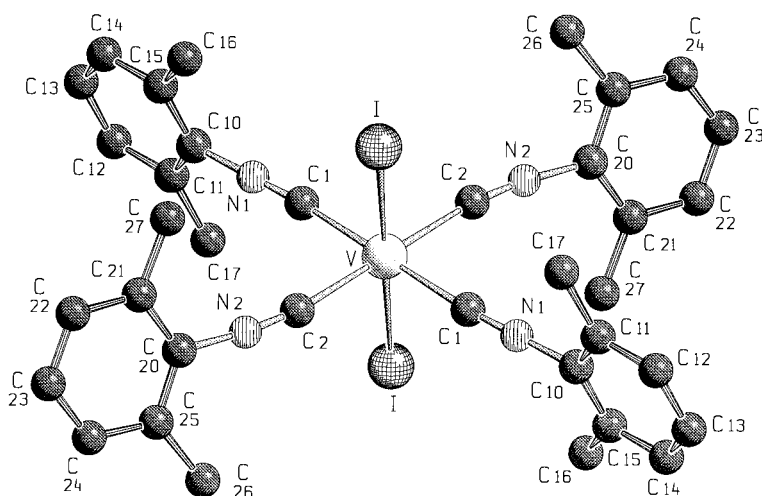
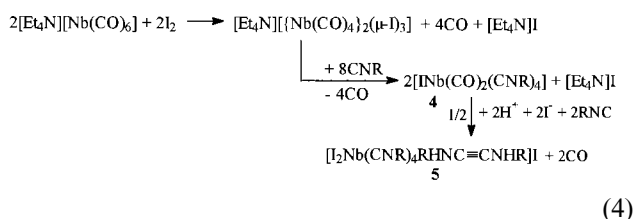
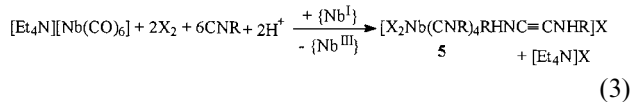


Fig. 1. SCHAKAL plot and numbering scheme for **4a**.

Fig. 2. SCHAKAL plot and numbering scheme for **9a**.

acts as a proton donor to the exposed nitrogen of an isocyanide ligand, thus initiating the coupling reaction. The first (irreversible) oxidation potential for **4a** amounts to 600 mV (vs. SCE).



From a general point of view, the reactions carried out in the V (and Ta) systems (Scheme 2) resemble those described for Nb. Selected IR data are collated in Table 5. The V^{III} and Ta^{III} complexes **7** and **14** are obtained in dry THF (**14** as the 1:1 adduct with $[\text{Et}_4\text{N}]\text{I}$), while the coupling product **8** forms as H_2O is added to the reaction mixture. Again, less than the stoichiometric amount of I_2 for a complete conversion of all of the $\text{V}^{-\text{I}}$ to V^{III} has to be used in order to keep yields at a reasonable level. A corresponding coupling product for Ta has also been obtained, evidenced by IR ($\nu(\text{C}=\text{N}) = 2211$, $\nu(\text{NH}) = 3210$, $\nu(\text{C}=\text{N}) = 1544 \text{ cm}^{-1}$) which, however, could not be isolated in pure form. Nor was it possible to convert the phosphine complex **6** to the coupling product **8**, in analogy to the respective inactivity observed for $[\text{INb}(\text{CO})_2(\text{CNR})_2\text{dppe}]$.

A special feature in the vanadium system, distinct from the niobium case, is the formation of isocyanide complexes with the metal in the +II oxidation state, viz. complexes **9** and **10**, if the molar ratio vanadate: I_2 is 1:1.5, i.e. in between the conditions pertinent for the formation of the V^{I} complexes **6** (1:1) and the V^{III} complexes **7** (1:2). As expected, the V^{II} complexes **9** are

paramagnetic, exhibiting a μ_{eff} of 3.89 (**9a**) and 4.07 (**9b**), hence close to the spin-only value of 3.87 BM. The structurally characterised compound **9a** (Fig. 2) indicates a *trans* configuration and thus local D_{4h} symmetry for the molecule. Accordingly, a single—though broad— $\nu(\text{CN})$ is observed. For **10a** and **10b** (one $\nu(\text{CN})$), we also assume the *all-trans* arrangement. In the case of **10c**, the chelating dppe prevents this configuration. Consequently, the IR shows two $\nu(\text{CN})$ bands.

The *trans* configuration is also realised in the Ta^{II} complex **15** (see Scheme 2), in analogy to the corresponding vanadium complexes **9**, and to $[\text{Cl}_2\text{Ta}(\text{PMe}_3)_4]$ [16]. In the dichloro- V^{III} complex **12**, which was isolated as a 1:1 adduct with LiCl, the two isocyanide ligands occupy *cis* positions, again based on IR evidence. The formation of **12** and **15** is depicted by Eq. (5) and Eq. (6). Eq. (6) is conducted so as to reduce

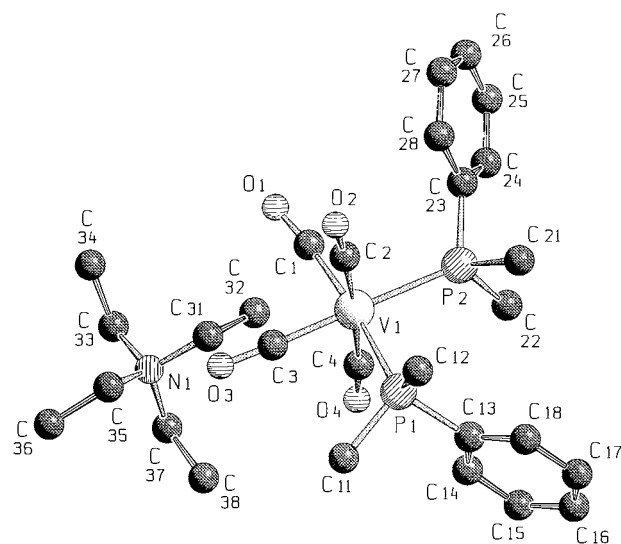
Fig. 3. SCHAKAL plot and numbering scheme for $[\text{Et}_4\text{N}]\text{-11}$.

Table 3
IR data ($\nu(\text{C}\equiv\text{N})$ and $\nu(\text{C}=\text{O})$ region) of isocyanide-niobium complexes

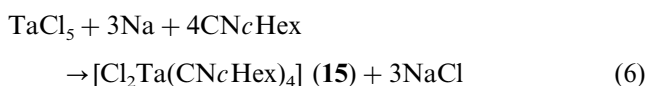
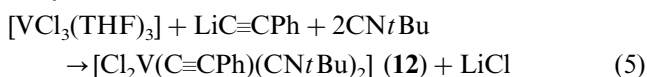
Compound ^a	$\nu(\text{C}\equiv\text{N})$ (cm^{-1}) ^b		Other
[I ₂ Nb(CNR) ₆]I (1)			
R = <i>t</i> Bu (1a)	2197sh	2154vs	2022sh
<i>i</i> Pr (1b)	2203sh	2160vs	2016sh
2-Pent (1c)	2204sh	2160vs	2020sh
CH ₂ Tos (1d)	2204sh	2156vs	2015sh
CH ₂ C(O)OMe (1e)		2178	
[I ₃ Nb(CNR) ₃] (2)			
R = <i>t</i> Bu (2a)		2203	
<i>c</i> Hex (2b)		2190	
[Br ₃ Nb(CN <i>c</i> Hex) ₄] (2c)	2205sh	2164vs	
[I ₂ Nb(CN <i>t</i> Bu) ₃ tolane]I ^c (3)		2202	
[XNb(CO) ₂ (CNR) ₄] (4)			
X = I, R = <i>t</i> Bu (4a)	2198s	2155vs	1874s, 1815m; $\nu(\text{CO})$
<i>c</i> Hex (4b)	2198s	2159vs	1868s, 1814m; $\nu(\text{CO})$
2,6-Me ₂ C ₆ H ₃ (4c)	2146vs	2107vs	1870s, 1809s; $\nu(\text{CO})$
X = Br, R = <i>t</i> Bu (4d)	2204s	2133vs	1871s, 1822m; $\nu(\text{CO})$
[X ₂ Nb(CNR) ₄ RHNC=CNHR]X (5)			
X = I, R = <i>t</i> Bu (5a)		2201	3196; $\nu(\text{NH})$ 1557; $\nu(\text{C}=\text{N})$
X = Br, R = <i>t</i> Bu (5b)	2194sh	2213vs	3189; $\nu(\text{NH})$ 1564; $\nu(\text{C}=\text{N})$

^a Abbreviations: *t*Bu, tertbutyl; *i*Pr, isopropyl; 2-Pent, 2-pentyl; Tos, tosyl; *c*Hex, cyclohexyl.

^b In KBr. Compare the $\nu(\text{C}\equiv\text{N})$ for the free isocyanide (in THF): CN*t*Bu (2134), CN*i*Pr (2144), CN(2-Pent) (2141), CN(2,6-Me₂C₆H₃) (2122, KBr), CNCH₂-Tos (2154, KBr), CNCH₂C(O)OMe (2149 cm^{-1}).

^c The ionic formulation has been chosen on the basis of conductivity measurements.

tantalum(V) to the +II state prior to coordination of isocyanide.



3. Conclusions

The isolation and structural characterisation of the carbonyl–isocyanide–niobium(I) complex **4a**, and its conversion to the aminoalkyneniobium(III) complex **5a** in the presence of small amounts of water but without an external reducing agent, has shown that type **4** complexes can be considered intermediates in reductive C–C coupling of isocyanides. In this reaction, Nb^I acts both as an activator (by coordination) of the substrate and an internal two-electron transfer agent for the substrate. This is different from the coupling reactions reported for {CINb^I(CNR)} and {IMo^{III}(CNR)} systems and probably reflects the greater basicity of the {INb^I(CNR)} centre. The reaction is reminiscent of the conversion of the Cr⁰ complex [Cr(CNR)₆] to the Cr^{II} complex [ICr(CNR)₄RNHC=CNHR]I [17]. A corresponding aminoalkyne–V^{III} complex, **8**, has also been obtained by direct interaction of [V(CO)₆][–] with isocyanide and iodine in the presence of water. The reac-

tions model the isocyanide reductase/ligase activity of nitrogenases as well as the role of low-valent Group 5 metals, generated in situ in the system MCl_{*n*}/Zn/H⁺, in the in vitro coupling reactions involving organic carbonyls [18,19], alkynes and nitriles [20], or alkynes [21]. Whether or not the first reaction step of the conversion of **4** to **5** is an electrophilic attack of protons to the nitrogen of the isocyanide, with the formation of a carbyne intermediate as proposed for coupling reactions with external electron donors [4,5], remains to be clarified and is presently under investigation in our laboratory.

4. Experimental

All operations were carried out under nitrogen, employing the common Schlenk techniques, and in absolute solvents, if not noted otherwise. THF was dried with lithium alanate and distilled in a N₂ stream. Mixtures of ethanol and liquid nitrogen were employed as cold baths. CO released during the reactions was allowed to evolve through a mercury valve (15 mm). All compounds were dried at room temperature (r.t.) under high vacuum prior to elemental analyses.

Starting materials were purchased (CN*c*Hex, CN*t*Bu, CNCH₂Tos, CNCH₂C(O)OMe, CN(2,6-Me₂C₆H₃), toluene, dppe, PPhMe₂, NbCl₅, VCl₃, TaCl₅) or prepared according to literature procedures (CN*i*Pr, CN2–Pent

Table 4
Selected conductivity data for some isocyanide–niobium complexes in MeCN^a

Complex	<i>c</i> (mmol l ⁻¹)	<i>A_M</i> (S cm ² mol ⁻¹)	<i>A₀</i> (S cm ² mol ⁻¹)	<i>κ</i> (S cm ² l ^{-1/2} mol ^{-3/2})
1a	0.724	218	245	32.3
	0.329	228		
2a	0.692	217	235	21.7
	0.314	223		
1d	0.835	226	274	57.3
	0.379	242		
3a ·THF	0.761	195	244	57.1
	0.346	211		

^a The quantities in this table are connected by the relation $A_M = A_0 - \kappa \times c^{1/2}$.

[22], [Et₄N][Nb(CO)₆] [10c,23], [INb(CO)₄dppe] [10c,11], [Et₄N][{Nb(CO)₄}₂(μ-I)₃] [8c,24], [Et₄N][V(CO)₆] [8b,23], [Et₄N][Ta(CO)₆] [25]).

IR spectra were obtained in KBr, nujol or THF (0.1 mm CaF₂ cuvette) on a Perkin–Elmer spectrometer 1720 FT. Characteristic data are summarised in Table 3 (Nb complexes) and Table 5 (V and Ta complexes). For the cyclovoltammetric measurement of **4a**, an EG&G Princeton Applied Research potentiostat 273A was employed. The working electrode was a platinum foil and the counter electrode a platinum wire. The potential was internally standardised against Fc/Fc⁺, and referenced against the saturated calomel electrode (SCE). The measurements were carried out in MeCN at concentrations of approximately 1 mM and with 0.2 M TBAP as conducting salt. Conductivity measurements were carried out with a WTW type LF 315/Set 300230 electrode in MeCN at 25°C (constant) under N₂. Magnetic measurements were carried out with a Johnson Matthey Chemicals Ltd. susceptibility balance in 4 mm diameter vials. The calculated magnetic moments were corrected for diamagnetic contributions.

NMR spectra were scanned on a Bruker AM 360 spectrometer with the usual instrument settings. Due to the quadrupolar nature of the nuclei ⁹³Nb (nuclear spin *I* = 9/2, quadrupole moment *Q* = -0.28 × 10⁻²⁸ m²), ⁵¹V (*I* = 7/2, *Q* = -0.052 × 10⁻²⁸ m²) and ¹⁸¹Ta (*I* = 7/2, *Q* = 3.4 × 10⁻²⁸ m²), and the non-cubic symmetry of the complexes, NMR spectroscopy for the nuclei directly bonded to these nuclei (¹³C, ³¹P) usually show, if any, complex and broad signals which are of limited analytical significance for the complexes [26]. Typically, ³¹P resonances are ca. 35–50 (dppe) or centred at ca. 25 ppm (alkyl phosphines). The ¹H-NMR data of the coordinated ligands are of restricted diagnostic value since they do not differ significantly from those of the free ligands (e.g. δ(¹H) = 1.29–1.77 for CH₂ in *c*Hex, 2-Pent, dppe; 3.50–3.92 for CH in *c*Hex and 2-Pent; 1.3–1.5 for CH₃ in *t*Bu; 7.1–7.4 for the phenyls of tolane and phosphines (type **3**, **6** and **13b** complexes)); they are

not presented in detail for this reason. δ(¹³C) values for methyl groups of coordinated *t*BuNC cover the range 30–32 ppm, the shift ranges for the phenyl rings of tolane and the phosphines amount to δ(¹³C) = 126–135. δ(¹³C) resonances for selected compounds are provided in the respective experimental sections. The ⁵¹V-NMR spectra, obtained at 94.73 MHz, are referenced against VOCl₃.

Data for the X-ray structure analyses were collected in the θ/2θ scan mode on a Hilger & Watts diffractometer with monochromatic (graphite monochromator) Mo–K_α irradiation. The structure of **4a** was determined with Mo–K_α and also, on a CAD-4 diffractometer, with monochromatic (graphite monochromator) Cu–K_α irradiation. The quality of the structure determination did not significantly differ in these two measurements. The program packages SHELXS-86 and SHELXL-93 were used throughout. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were put into calculated positions and included with isotropic displacement factors in the last cycles of the structure refinement. Absorption corrections were carried out for **4a** and **9a** (see Table 1 for details on the structure solution and refinement).

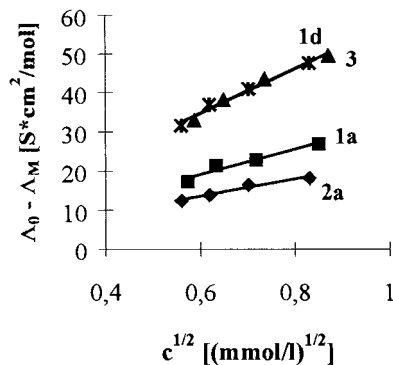


Fig. 4. Graphical presentation of conductivity data for the complexes **1a**, **2a**, **1d** and **3a** (see Table 4).

Table 5
IR data [$\nu(\text{C}\equiv\text{N})$ and $\nu(\text{C}=\text{O})$ region] of isocyanide–vanadium and –tantalum complexes ^{a,b}

Compound ^a	$\nu(\text{C}\equiv\text{N})$ (cm^{-1})		Other
[XV(CO) ₂ (CN <i>t</i> Bu) ₂ dppe] (6)			
X = I (6a)	2168vs	2098vs	1889vs, 1842vs; $\nu(\text{CO})$
Br (6b)	2159vs	2105vs	1887vs, 1841vs; $\nu(\text{CO})$
[ITa(CO) ₃ (CN <i>t</i> Bu)L ₂] (13)			
L = CN <i>t</i> Bu (13a)	2145vs	2125vs	1887s, 1863s, 1824s; $\nu(\text{CO})$
2L = dppe (13b)	2135vs		1955vs, 1868vs, 1840vs; $\nu(\text{CO})$
[I ₂ V(CN <i>t</i> Bu) ₆]I (7)	2173br		
[I ₂ Ta(CN <i>t</i> Bu) ₆]I (14) ^c	2148br		
[I ₂ V(CN <i>t</i> Bu) ₄ (<i>t</i> BuHNC=CNH <i>t</i> Bu)]I (8)	2208		3204; $\nu(\text{NH})$, 1561; $\nu(\text{C}=\text{N})$
[I ₂ V(CNR) ₄] (9)			
R = 2,6-Me ₂ C ₆ H ₃ (9a)	2137br		
CH ₂ Tos (9b)	2136br		
[X ₂ V(CN <i>t</i> Bu) ₂ (PR ₃) ₂] (10)			
X = I, PR ₃ = PPh ₃ (10a)	2171		
PPhMe ₂ (10b)	2156 ^d		
X = Br, 2PR ₃ = dppe (10c)	2155vs	2145sh	
[V(CO) ₄ (PPhMe ₂) ₂] ⁻ (11)			1891s, 1774vs, 1760sh, 1724m; $\nu(\text{CO})$ ^e
[Cl ₂ V(C≡CPh)(CN <i>t</i> Bu) ₂] (12) ^f	2207vs	2174vs	
[Cl ₂ Ta(CN <i>c</i> Hex) ₄] (15)	2151br		

^a For abbreviations, see legend to Table 3.

^b In KBr or nujol, if not noted otherwise.

^c Isolated as the 1:1 adduct with [Et₄N]I.

^d In THF.

^e $\nu(\text{CO})$ in THF: 1896s, 1786vs, 1762sh, 1731m.

^f Isolated as the 1:1 adduct with LiCl.

4.1. [I₂Nb(CNR)₆]I (**1**)

The type **1** complexes were prepared as described previously for **1a** (R = *t*Bu) [8a]. Colour, IR data, yields and elemental analyses are summarised in Table 6.

4.2. [NbI₃(CN*t*Bu)₃] (**2a**)

[Et₄N][Nb(CO)₆] (604 mg, 1.54 mmol), dissolved in dry THF (30 ml), was treated with CN*t*Bu (1.05 ml, 6.04 mmol) and after cooling to -60°C , with iodine (784 mg, 3.09 mmol) in eight successive portions, keeping the temperature constantly at -60°C . The solution, while stirred continuously, was slowly warmed to r.t. within 30 h. [Et₄N]I was filtered off, the filtrate was evaporated to dryness (r.t., vacuum), washed with two 5 ml portions of pentane and dried under high vacuum to yield a red–brown powder. Yield 1.030 g (93% based on [Et₄N][Nb(CO)₆]). IR (KBr) $\nu(\text{CH})$ 2981 and 2933, $\nu(\text{CN})$ 2203, $\delta(\text{CH})$ 1450 cm^{-1} . Anal. Calc. for C₁₅H₂₇I₃N₃Nb ($M = 723.02 \text{ g mol}^{-1}$): C, 24.92; H, 3.76; N, 5.81. Found: C, 25.76; H, 3.92; N, 6.17%.

Ochre [I₃Nb(CN*c*Hex)₃]·THF (**2b**·THF) was prepared accordingly from [Et₄N][Nb(CO)₆] (240 mg, 0.61 mmol), CN*c*Hex (226 μl , 1.83 mmol) and iodine (311 mg, 1.23 mmol) in 82% yield. IR (KBr) $\nu(\text{CH})$ 2931 and 2854, $\nu(\text{CN})$ 2190, $\delta(\text{CH})$ 1448 cm^{-1} . Anal. Calc. for C₂₅H₂₁I₃N₃NbO ($M = 873.24 \text{ g mol}^{-1}$): C, 34.39; H, 4.73; N, 4.81. Found: C, 34.63; H, 4.90; N, 5.15%.

The same procedure was also applied for the preparation of [Br₃Nb(CN*c*Hex)₄] (**2c**), from [Et₄N][Nb(CO)₆] (230 mg, 0.59 mmol), CN*c*Hex (290 μl , 2.36 mmol) and bromine (61 μl , 1.19 mmol). Reaction temperature in this case was -80°C (toluene–N₂ cold bath), and reaction time 24 h. Yield of red–brown **2c**, 354 mg (82%). IR (KBr) $\nu(\text{CH})$ 2931 and 2854, $\nu(\text{CN})$ 2205vs and 2164s, $\delta(\text{CH})$ 1448 cm^{-1} . Anal. Calc. for C₂₈H₄₄Br₃N₄Nb ($M = 769.30 \text{ g mol}^{-1}$): C, 43.72; H, 5.76; N, 7.28; Br, 31.16; Nb, 12.08. Found: C, 43.22; H, 5.62; N, 6.85; Br, 30.3; Nb, 12.4%.

4.3. [I₂Nb(CN*t*Bu)₃tolane]I·THF (**3**·THF)

[Et₄N][Nb(CO)₆] (210 mg, 0.54 mmol) was dissolved in THF (25 ml). To this solution, CN*t*Bu (182 μl , 1.61 mmol) and toluene (96 mg, 0.54 mmol) were added. The solution was cooled to -60°C and treated with iodine (273 mg, 1.07 mmol). This reaction mixture was stirred for 12 h while warmed to r.t., and stirred at r.t. for an additional two days. [Et₄N]I was filtered off, the filtrate evaporated to dryness, washed with three 5 ml portions of pentane and dried to yield an orange–red powder. Yield 489 mg (93% based on [Et₄N][Nb(CO)₆]). IR (KBr): $\nu(\text{CH})_{\text{arom}}$ 3051, $\nu(\text{CH})$ 2981, 2933 and 2868, $\nu(\text{CN})$ 2202 cm^{-1} . ¹³C-NMR (THF-*d*₈) δ 30.7 [C(CH₃)₃], 58.5 [C(CH₃)₃], 128.3 to 129.5 (Ph), 207.7 (C≡C), 253.0 (CN*t*Bu). Anal. Calc. for C₃₃H₄₅I₃N₃NbO ($M = 973.36 \text{ g mol}^{-1}$): C, 40.72; H, 4.66; N, 4.32; I,

39.11; Nb, 9.54. Found: C, 40.49; H, 4.44; N, 5.15; I, 39.1; Nb, 9.7%.

Alternatively, **3** can be prepared by adding, at r.t., toluene to a THF solution of **2**, reaction time of two days and work-up as described above.

4.4. $[\text{INb}(\text{CO})_2(\text{CN}t\text{Bu})_4]$ (**4a**)

4.4.1. Method A

$[\text{INb}(\text{CO})_4\text{dppe}]$ (630 mg, 0.86 mmol), dissolved in THF (25 ml) was cooled to -40°C and treated, while stirred vigorously, with $\text{CN}t\text{Bu}$ (390 μl , 3.45 mmol). The solution was warmed to r.t. within 24 h. During this time, the colour gradually changed from brown to light red. The solution was concentrated to about one fifth of its original volume and allowed to stand at -20°C . Compound **4a** precipitated as a dark yellow powder, which was filtered off and dried. Yield 274 mg (52% based on $[\text{INb}(\text{CO})_4\text{dppe}]$). IR (KBr) $\nu(\text{CH})$ 2981 and 2934, $\nu(\text{CN})$ 2198m and 2155vs, $\nu(\text{CO})$ 1874m and 1815m cm^{-1} . Anal. Calc. for $\text{C}_{22}\text{H}_{36}\text{IN}_4\text{NbO}_2$ ($M = 608.36 \text{ g mol}^{-1}$): C, 43.43; H, 5.96; N, 9.21. Found: C, 43.40; H, 6.01; N, 9.23%.

4.4.2. Method B

$[\text{Et}_4\text{N}][\text{Nb}(\text{CO})_6]$ (510 mg, 1.30 mmol) dissolved in 30 ml of THF was treated with $t\text{BuNC}$ (440 μl , 3.9 mmol) and cooled to -70°C . Upon addition of I_2 (330 mg, 1.3 mmol), vigorous CO formation was observed. The solution was warmed to r.t. within 15 h, filtered, treated with 3 ml of pentane and stored at -20°C . After 4 h, orange, crystalline **4a** was obtained which was filtered off and dried under vacuum for 4 h. Yield: 500 mg (63% based on $[\text{Et}_4\text{N}][\text{Nb}(\text{CO})_6]$). IR (nujol) $\nu(\text{CN})$ 2190vs and 2150vs, $\nu(\text{CO})$ 1875s and 1817s. Anal. Calc. for $\text{C}_{22}\text{H}_{36}\text{IN}_4\text{O}_2\text{Nb}$ ($M = 608.4 \text{ g mol}^{-1}$): C, 43.43; H, 5.96; N, 9.21. Found: C, 43.63; H, 6.08; N, 9.11%.

4.4.3. Method C

A 25 ml sample of a toluene solution containing $[\text{Et}_4\text{N}][\{\text{Nb}(\text{CO})_4\}_2(\mu\text{-I})_3]$ (589 mg, 0.64 mmol) was cooled to -40°C and treated with $\text{CN}t\text{Bu}$ (578 μl , 5.12 mmol). The solution was stirred for 16 h while warmed back to r.t. and filtered. The filtrate was kept at 4°C to yield orange-red crystals of **4a**·2toluene, suitable for X-ray analysis. Yield 584 mg (68% based on $[\text{Et}_4\text{N}][\{\text{Nb}(\text{CO})_4\}_2(\mu\text{-I})_3]$).

$[\text{INb}(\text{CO})_2(\text{CN}c\text{Hex})_4]$ (**4b**), $[\text{INb}(\text{CO})_2\{\text{CN}(\text{2,6-Me}_2\text{C}_6\text{H}_3)_4\}]$ (**4c**) and $[\text{BrNb}(\text{CO})_2(\text{CN}t\text{Bu})_4]$ (**4d**), were prepared accordingly. **4b**: IR (KBr) $\nu(\text{CH})$ 2933 and 2854, $\nu(\text{CN})$ 2198s, 2159s and 2125sh, $\nu(\text{CO})$ 1868m and 1814m cm^{-1} . Anal. Calc. for $\text{C}_{30}\text{H}_{44}\text{IN}_4\text{NbO}_2$ ($M = 712.52 \text{ g mol}^{-1}$): C, 50.57; H, 6.22; N, 7.86. Found: C, 51.10; H, 6.35; N, 8.06%. **4c**: IR (KBr) $\nu(\text{CN})$ 2146vs and 2107vs, $\nu(\text{CO})$ 1870s and 1809s cm^{-1} . Anal. Calc. for $\text{C}_{38}\text{H}_{36}\text{IN}_4\text{NbO}_2$ ($M = 800.6 \text{ g mol}^{-1}$): C, 57.01; H, 4.53; N, 7.00. Found: C, 58.35; H, 5.03; N, 7.48%. **4d**: IR (KBr): $\nu(\text{CH})$ 2978, 2933 and 2871, $\nu(\text{CN})$ 2204m, 2133m and 2111s, $\nu(\text{CO})$ 1871s and 1822 cm^{-1} . Anal. Calc. for $\text{C}_{22}\text{H}_{36}\text{BrN}_4\text{NbO}_2$ ($M = 561.36 \text{ g mol}^{-1}$): C, 47.07; H, 6.46; N, 9.98. Found: C, 47.56; H, 6.71; N, 9.93%.

4.5. $[\text{I}_2\text{Nb}(\text{CN}t\text{Bu})_4t\text{BuHNC}\equiv\text{CNH}t\text{Bu}]\text{I}$ (**5a**)

4.5.1. Method A (see also Ref. [8a])

$[\text{Et}_4\text{N}][\text{Nb}(\text{CO})_6]$ (426 mg, 1.09 mmol) was dissolved in 25 ml of THF (Merck, proanalysis, water content 4.2 mmol in 25 ml) and treated with $\text{CN}t\text{Bu}$ (491 μl , 4.4 mmol). The solution was stirred, cooled to -40°C and treated with iodine (369 mg, 1.45 mmol). The reaction mixture was warmed to r.t. within 28 h, accompanied with a colour change from yellow to red-brown. A solid residue consisting of $[\text{Et}_4\text{-N}]\text{I}$ and NbI_x (x , according to elemental analyses of the vacuum-dried residue, varies between 2.1 and 2.3) was filtered off. In order to obtain crystalline material, pentane (5 ml) was added to

Table 6
Experimental details for the compounds $[\text{I}_2\text{Nb}(\text{CNR})_6]\text{I}$ (**1**)

R	Complex	$\nu(\text{CH})$ (cm^{-1})	Colour	Yield (%)	M (g mol^{-1})	Formula	Anal. (Calc./Found) (%)		
							C	H	N
$t\text{Bu}$	1a	2978, 2933	red	87	972.42	$\text{C}_{30}\text{H}_{54}\text{I}_3\text{N}_6\text{Nb}$	37.06/36.57	5.60/5.55	8.64/8.43
$i\text{Pr}$	1b	2936, 2880	red	81	888.26	$\text{C}_{24}\text{H}_{42}\text{I}_3\text{N}_6\text{Nb}$	32.45/32.70	4.77/5.01	9.46/9.84
2-Pent	1c	2939, 2877	red	82	1056.58	$\text{C}_{36}\text{H}_{66}\text{I}_3\text{N}_6\text{Nb}$	40.92/41.16	6.30/6.58	7.95/8.09
CH_2Tos	1d	3011, 2922	dark brown	92	1645.07	$\text{C}_{54}\text{H}_{54}\text{I}_3\text{N}_6\text{NbO}_{12}\text{S}_6$	39.43/39.72	3.31/3.50	5.11/5.28
$\text{CH}_2\text{C}(\text{O})\text{OMe}$	1e	2953	black	88	1068.16	$\text{C}_{24}\text{H}_{30}\text{N}_6\text{NbO}_{12}$	26.99/27.34	2.83/3.01	7.87/8.11

the filtrate. This solution was refluxed for 30 min and cooled back to r.t. Orange–red crystalline **5a** separated during 3 days. Yield 478 mg (45% based on $[\text{Et}_4\text{N}][\text{Nb}(\text{CO})_6]$). IR (KBr) $\nu(\text{NH})$ 3196, $\nu(\text{CH})$ 2978, 2933 and 2871, $\nu(\text{C}\equiv\text{N})$ 2201, $\nu(\text{C}=\text{N})$ 1557 cm^{-1} . ^{13}C -NMR (THF- d_8) δ 31.2 [$-\text{NH}-\text{C}(\text{CH}_3)_3$], 30.1 [$\text{CNC}(\text{CH}_3)_3$], 58.8 [$-\text{NH}-\text{C}(\text{CH}_3)_3$], 49.9 [$\text{CNC}(\text{CH}_3)_3$]. Anal. Calc. for $\text{C}_{30}\text{H}_{56}\text{I}_3\text{N}_6\text{Nb}$ ($M = 974.44 \text{ g mol}^{-1}$): C, 36.50; H, 5.77; N, 8.73. Found: C, 36.27; H, 5.77; N, 8.61%.

4.5.2. Method B

Compound **4a** (121 mg, 0.20 mmol; prepared by method A) was dissolved in toluene- d_8 (20 ml; source: Deutero GmbH; not specifically dried) and allowed to stand at r.t. for five days. Crystalline **5a** formed, which was filtered off the yellow solution and dried under high vacuum. Yield: 59 mg (31% based on **4a**). Spectral parameters and analytical data corresponded to those of **5a** prepared according to method A.

4.6. $[\text{Br}_2\text{Nb}(\text{CN}t\text{Bu})_4t\text{BuHNC}\equiv\text{CNH}t\text{Bu}]\text{Br}\cdot\text{THF}$ (**5b**·THF)

The compound was prepared as described for **5a** (method A), and isolated as a brown, microcrystalline powder in 42% yield. IR (KBr) $\nu(\text{NH})$ 3189, $\nu(\text{CH})$ 2976, 2933 and 2871, $\nu(\text{C}\equiv\text{N})$ 2213 and 2194, $\nu(\text{C}=\text{N})$ 1564 cm^{-1} . Anal. Calc. for $\text{C}_{34}\text{H}_{64}\text{Br}_3\text{N}_6\text{NbO}$ ($M = 905.54 \text{ g mol}^{-1}$): C, 45.10; H, 7.12; N, 9.28. Found: C, 44.95; H, 7.04; N, 8.91%.

4.7. $[\text{IV}(\text{CO})_2(\text{CN}t\text{Bu})_2\text{dppe}]$ (**6a**)

$[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$ (708 mg, 2.03 mmol), dppe (808 mg, 2.03 mmol) and $t\text{BuNC}$ (459 μl , 4.06 mmol) were dissolved in 30 ml of THF and cooled to -60°C . Addition of iodine (515 mg, 2.03 mmol) immediately produced a red colour ($[\text{V}_2(\text{CO})_8(\mu\text{-I})_3]^-$). The solution was warmed to 8°C , stirred for 12 h, and further at r.t., until the IR spectrum indicated complete conversion to the isocyanide complex (ca. 6 h). The black solution was then filtered, the filtrate evaporated to dryness and washed with pentane to yield, after drying, 910 mg (1.14 mmol, 56%) of brown, powdery **6a**. ^{13}C -NMR (THF- d_8) δ 22.8 (CH_2), 30.1 [$\text{C}(\text{CH}_3)_3$], 49.8 [$\text{C}(\text{CH}_3)_3$], 127.8 to 133.2 (Ph). Anal. Calc. for $\text{C}_{38}\text{H}_{42}\text{IN}_2\text{O}_2\text{P}_2\text{V}$ ($M = 798.56 \text{ g mol}^{-1}$): C, 57.16; H, 5.30; N, 3.51. Found: C, 56.82; H, 5.51; N, 3.74%. $\delta(^{51}\text{V})$ (THF- d_8) = -849 , $W_{1/2} = 470 \text{ Hz}$.

4.8. $[\text{BrV}(\text{CO})_2(\text{CN}t\text{Bu})_2\text{dppe}]$ (**6b**)

$[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$ (524 mg, 1.50 mmol), dppe (597 mg, 1.50 mmol) and $t\text{BuNC}$ (339 μl , 3.00 mmol), dissolved in 30 ml of THF and cooled to -70°C , were treated

with bromine (77 μl , 1.50 mmol) and stirred overnight. $[\text{Et}_4\text{N}]\text{Br}$ was filtered off, the filtrate evaporated to dryness, and the residue washed with pentane. The yellow–brown powder thus obtained contained $[\text{Br}_2\text{V}(\text{CN}t\text{Bu})_4]$, which was extracted with a pentane/THF mixture. From the extract, yellow crystals with the cell parameters reported for $[\text{Br}_2\text{V}(\text{CN}t\text{Bu})_4]$ [**8b**] were isolated. The remaining powder (**6b**) was dried. Yield 517 mg (46%). Anal. Calc. for $\text{C}_{33}\text{H}_{42}\text{BrN}_2\text{O}_2\text{P}_2\text{V}$ ($M = 751.56 \text{ g mol}^{-1}$): C, 60.73; H, 5.63; N, 3.73. Found: C, 60.52; H, 5.89; N, 3.70%. A ^{51}V -NMR signal was not detected, probably due to residual admixtures of paramagnetic $[\text{Br}_2\text{V}(\text{CN}t\text{Bu})_4]$.

4.9. $[\text{I}_2\text{V}(\text{CN}t\text{Bu})_6]\text{I}$ (**7**)

A solution of $[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$ (349 mg, 1 mmol) and $\text{CN}t\text{Bu}$ (678 μl , 6 mmol) in 20 ml of THF was cooled to -70°C and treated with iodine (508 mg, 2 mmol). The mixture immediately turned red and CO developed vigorously. The finally green–black solution was warmed to r.t. within 20 h. After filtration, the filtrate was treated with 10 ml of pentane and allowed to stand at -20°C for two days. The green powder that precipitated during this time was recovered and dried. Yield 631 mg (68%). Anal. Calc. for $\text{C}_{30}\text{H}_{54}\text{I}_3\text{N}_6\text{V}$ ($M = 930.45 \text{ g mol}^{-1}$): C, 38.71; H, 5.85; N, 9.03. Found: C, 36.34; H, 5.61; N, 8.62%.

4.10. $[\text{I}_2\text{V}(\text{CN}t\text{Bu})_4(t\text{BuHNC}\equiv\text{CNH}t\text{Bu})]\text{I}$ (**8**)

$[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$ (508 mg, 1.45 mmol) was dissolved in 30 ml of THF and treated with water (150 μl , 8.3 mmol) and $\text{CN}t\text{Bu}$ (657 μl , 5.82 mmol). The solution was cooled to -50°C , and iodine (508 mg, 2.0 mmol) was added. The mixture was stirred at -50°C for 12 h to yield a black brown solution which was warmed to r.t. and refluxed for 1 h. The still-hot solution was filtered. The red–brown residue consisted of $[\text{Et}_4\text{N}]\text{I}$ and an unidentified isocyanide complex with a characteristic IR absorption at 2161 cm^{-1} . The brown–red filtrate (ca. 28 ml) was treated with 7 ml of pentane and allowed to stand at -20°C for three days. Bordeaux-red, microcrystalline **8** was then recovered by filtration. Yield 410 mg (30%). ^{13}C -NMR (THF- d_8) δ 31.4 [$-\text{NH}-\text{C}(\text{CH}_3)_3$], 30.4 [$\text{CNC}(\text{CH}_3)_3$], 58.6 [$-\text{NH}-\text{C}(\text{CH}_3)_3$], 49.5 [$\text{CNC}(\text{CH}_3)_3$]. Anal. Calc. for $\text{C}_{30}\text{H}_{56}\text{I}_3\text{N}_6\text{V}$ ($M = 932.47 \text{ g mol}^{-1}$): C, 38.64; H, 6.05; N, 9.01. Found: C, 38.34; H, 6.39; N, 8.88%.

4.11. $[\text{I}_2\text{V}(\text{CNR})_4]$, $R = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ (**9a**) and CH_2Tos (**9b**)

Preparation of **9a**: $[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$ (349 mg, 1.00 mmol) and 2,6-dimethylphenylisocyanide (523 mg, 4.00

mmol) were dissolved in 20 ml of THF and cooled to -50°C . After addition of I_2 (381 mg, 1.50 mmol), the solution was warmed to r.t. within 12 h, during which time the colour gradually changed from red to black and finally green. A yellowish to light green precipitate (mainly $[\text{Et}_4\text{N}]\text{I}$) was filtered off, the filtrate treated with 2 ml of pentane and cooled to -20°C . Green–black crystals, suitable for X-ray analysis, separated within three days and were collected, washed with pentane and dried. Yield 280 mg (34%). Anal. Calc. for $\text{C}_{36}\text{H}_{36}\text{I}_2\text{N}_4\text{V}$ ($M = 829.50 \text{ g mol}^{-1}$): C, 52.13; H, 4.38; N, 6.76. Found: C, 52.36; H, 4.91; N, 6.31%.

Compound **9b** was prepared accordingly. In contrast to **9a**, **9b** is only sparingly soluble in THF. Compound **9b** was separated from $[\text{Et}_4\text{N}]\text{I}$ by extraction with hot methanol. Evaporation and drying yielded 387 mg (27%) of brown, powdery **9b**. Anal. Calc. for $\text{C}_{36}\text{H}_{36}\text{I}_2\text{N}_4\text{O}_8\text{S}_4\text{V}$ ($M = 1085.72 \text{ g mol}^{-1}$): C, 39.82; H, 3.34; N, 5.16. Found: C, 39.55; H, 3.51; N, 5.37%.

4.12. $[\text{I}_2\text{V}(\text{CNtBu})_2(\text{PPh}_3)_2]$ (**10a**) and $[\text{Br}_2\text{V}(\text{CNtBu})_2\text{-dppe}]$ (**10c**)

Preparation of **10a**: $[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$ (349 mg, 1 mmol), PPh_3 (525 mg, 2 mmol) and CNtBu (226 μl , 2.2 mmol) were dissolved in 25 ml of THF, cooled to -45°C and treated with I_2 (381 mg, 1.5 mmol). The solution was warmed to r.t. within 12 h and stirred for 30 min on a water bath at 50°C . $[\text{Et}_4\text{N}]\text{I}$ was filtered off, the filtrate evaporated to dryness and the residue washed with hot pentane. The green powder thus obtained was dried to yield 760 mg (77%) of **10a**. Anal. Calc. for $\text{C}_{46}\text{H}_{48}\text{I}_2\text{N}_2\text{P}_2\text{V}$ ($M = 995.60 \text{ g mol}^{-1}$): C, 55.50; H, 4.86; N, 2.81. Found: C, 55.61; H, 5.25; N, 2.89%.

Compound **10c** was prepared accordingly. Br_2 was added at -70°C , and the green–black product isolated at r.t. Anal. Calc. for $\text{C}_{36}\text{H}_{42}\text{Br}_2\text{N}_2\text{P}_2\text{V}$ ($M = 775.44 \text{ g mol}^{-1}$): C, 55.76; H, 5.46; N, 3.61. Found: C, 55.41; H, 5.41; N, 3.63%.

4.13. $[\text{Et}_4\text{N}][\text{V}(\text{CO})_4(\text{PPhMe}_2)_2]$ ($[\text{Et}_4\text{N}]\text{-11}$) and its conversion to $[\text{I}_2\text{V}(\text{CNtBu})_2(\text{PPhMe}_2)_2]$ (**10b**)

$[\text{Et}_4\text{N}]\text{-11}$ was prepared in analogy to other phosphine substituted carbonylvanadates (Ref. [27] and literature cited therein): $[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$ (328 mg, 0.94 mmol) was dissolved in 20 ml of THF, treated with PPhMe_2 (268 μl , 1.88 mmol), and irradiated with an externally installed UV source (high pressure mercury lamp Philips HPK 125). Care was taken to maintain the reaction temperature below 40°C . After 12 h of irradiation time, the mixture was stirred at r.t. for one day, filtered, the filtrate concentrated to 10 ml and treated with an equal volume of pentane. The red precipitate was filtered off, washed twice with 10 ml of pentane

and dried. Yield 345 mg (66%). $\delta(^{51}\text{V})$ (THF- d_8) = -1710 (t), $J(^{51}\text{V}-^{51}\text{P}) = 216$ Hz, $W_{1/2} = 59$ Hz. Anal. Calc. for $\text{C}_{28}\text{H}_{42}\text{NO}_4\text{P}_2\text{V}$ ($M = 569.54 \text{ g mol}^{-1}$): C, 59.05; H, 7.43; N, 2.50. Found: C, 58.74; H, 7.29; N, 2.64%. Crystals suitable for X-ray analysis formed in a concentrated solution of $[\text{Et}_4\text{N}]\text{-11}$ in THF after standing at 2°C for several weeks.

For a conversion of **11** to **10b**, 310 mg (0.54 mmol) of $[\text{Et}_4\text{N}]\text{-11}$ and 123 μl (1.1 mmol) of CNtBu were dissolved in 15 ml of THF, cooled to -60°C and treated with I_2 (406 mg, 1.6 mmol). The solution was stirred for 10 h, while gradually warmed to r.t., and further 12 h at r.t. After filtration, 15 ml of pentane was added to the filtrate and this mixture was allowed to stand at 2°C for two days. The dark green precipitate of **10b** thus formed was filtered off and dried. Yield 306 mg (75.4%). Anal. Calc. for $\text{C}_{26}\text{H}_{40}\text{I}_2\text{N}_2\text{P}_2\text{V}$ ($M = 747.32 \text{ g mol}^{-1}$): C, 41.79; H, 5.40; N, 3.75; P, 8.29. Found: C, 41.90; H, 4.32; N, 3.85; P, 8.11%.

4.14. $[\text{Cl}_2\text{V}(\text{C}\equiv\text{CPh})(\text{CNtBu})_2]\cdot\text{LiCl}$ (**12·LiCl**)

$[\text{VCl}_3(\text{THF})_3]$ [28] (950 mg, 2.54 mmol), dissolved in 25 ml of THF and cooled to -60°C , was treated dropwise within 1 h with 2.54 ml of a 1 M THF solution of LiCCPh , followed by CNtBu (0.86 ml, 7.62 mmol). The black solution was warmed to r.t. within 15 h. A 6.5 ml sample of pentane was added, and the mixture stored for 2 days at -20°C to yield brown **12·LiCl**, which was filtered off and dried. Yield 515 mg (47%). Anal. Calc. for $\text{C}_{18}\text{H}_{23}\text{Cl}_2\text{N}_2\text{V}\cdot\text{LiCl}$ ($M = 431.64 \text{ g mol}^{-1}$): C, 50.09; H, 5.37; N, 6.49. Found: C, 49.68; H, 5.65; N, 6.51%.

4.15. $[\text{ITa}(\text{CO})_3(\text{CNtBu})_3]$ (**13a**) and $[\text{ITa}(\text{CO})_3\text{-}(\text{CNtBu})\text{dppe}]$ (**13b**)

Preparation of **13a**: $[\text{Et}_4\text{N}][\text{Ta}(\text{CO})_6]$ (148 mg, 0.31 mmol) and CNtBu (105 μl , 0.93 mmol) were dissolved in 25 ml of THF and cooled to -45°C . Addition of iodine (79 mg, 0.31 mmol) caused a slow colour conversion from yellow to red–orange. The mixture was warmed to r.t. within 15 h, filtered and the filtrate evaporated to dryness and washed with pentane. Yield 130 mg (68%). Anal. Calc. for $\text{C}_{18}\text{H}_{27}\text{IN}_3\text{O}_3\text{Ta}$ ($M = 641.28 \text{ g mol}^{-1}$): C, 33.71; H, 4.24; N, 6.55. Found: C, 33.61; H, 4.51; N, 6.86%.

Compound **13b** was obtained analogously by employing one equivalent each of isocyanide and dppe. Yield 210 mg (58%). ^{13}C -NMR (THF- d_8) δ 23.2 (CH_2), 31.6 [$\text{C}(\text{CH}_3)_3$], 58.9 [$\text{C}(\text{CH}_3)_3$], 128.5 to 136.8 (Ph). Anal. Calc. for $\text{C}_{34}\text{H}_{33}\text{INO}_3\text{P}_2\text{Ta}$ ($M = 873.44 \text{ g mol}^{-1}$): C, 46.76; H, 3.81; N, 1.60. Found: C, 47.56; H, 4.02; N, 1.84%.

4.16. $[I_2Ta(CNtBu)_6]I \cdot [Et_4N]I$ (**14**· $[Et_4N]I$)

$[Et_4N][Ta(CO)_6]$ (327 mg, 0.76 mmol), dissolved in 30 ml of THF and cooled to -78°C was treated with I_2 (386 mg, 1.52 mmol) to yield a red–brown solution containing the $[Ta(CO)_4\{\mu-I\}_3]^-$ anion. Thirty minutes after addition of the iodine, $CNtBu$ (680 μl , 6.1 mmol) was added. The reaction mixture was warmed to r.t. within 16 h and filtered. The beige residue on the filter plate was washed with THF and pentane and dried. According to the elemental analysis, its composition corresponded to **14**· $[Et_4N]I$. Yield 450 mg (55%). Anal. Calc. for $C_{30}H_{54}I_3N_6Ta \cdot C_8H_{20}IN$ ($M = 1317.62 \text{ g mol}^{-1}$): C, 34.64; H, 5.66; N, 7.44. Found: C, 34.44; H, 5.62; N, 7.59%.

4.17. $[Cl_2Ta(CNcHex)_4]$ (**15**)

$TaCl_5$ (500 mg, 1.4 mmol) was added cautiously, and in several portions to 30 ml of THF, previously cooled down to -80°C . This solution was treated with 1 ml of 10% sodium amalgam (4.35 mmol of Na) and warmed to 0°C within 3 h. After addition of $CNcHex$ (690 μl , 5.6 mmol) the formerly beige solution took on a dark brown colour. After 10 min of reaction time, the solution was poured off the deposit. Addition of 10 ml of pentane precipitated dark brown solid, which was dried to yield 450 mg (47%) of **15**. Anal. Calc. for $C_{28}H_{44}Cl_2N_4Ta$ ($M = 688.54 \text{ g mol}^{-1}$): C, 44.84; H, 6.44; N, 8.14. Found: C, 45.06; H, 6.32; N, 7.99%.

If the isocyanide is added to the THF solution of $TaCl_5$ prior to Na/Hg, the insertion product $[Cl_4TaC(Cl)NcHex]$ is formed (identified by elemental analysis and its essential characteristics, identical to those of $[Cl_4TaC(Cl)NtBu]$ [29]), which is resistant to reduction by Na/Hg.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. CSD-8/07562J, CSD-115347 and CSD-115348 for compounds **4a**, **9a**, and $[Et_4N]$ -**11**, respectively.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

References

- [1] C.T. Lam, P.W.R. Corfield, S.J. Lippard, *J. Am. Chem. Soc.* 99 (1977) 617.
- [2] R.W. Miller, in: M.J. Dilworth, A.R. Glenn (Eds.), *Biology and Biochemistry of Nitrogen Fixation*, Elsevier, Amsterdam, 1991, pp. 20–23.
- [3] R.N. Vrtis, S. Liu, C.P. Rao, S.G. Bott, S.J. Lippard, *Organometallics* 10 (1991) 275.
- [4] (a) R.N. Vrtis, C.P. Rao, S. Warner, S.J. Lippard, *J. Am. Chem. Soc.* 110 (1988) 2669. (b) S. Warner, S.J. Lippard, *Organometallics* 8 (1989) 228. (c) E.M. Carnahan, Lippard, *J. Chem. Soc. Dalton Trans.* (1991) 699. (d) B.S. Bronk, J.D. Protasiewicz, L.E. Pence, S.J. Lippard, *Organometallics* 14 (1995) 2177.
- [5] (a) A.C. Filippou, W. Grünleitner, C. Völkl, P. Kiprof, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 1167. (b) A.C. Filippou, C. Völkl, W. Grünleitner, P. Kiprof, *J. Organomet. Chem.* 434 (1992) 201.
- [6] (a) For a review, see: A. Mayr, C.M. Bastos, *Progr. Inorg. Chem.* 40 (1992) 1. (b) Y. Wang, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, M.A. Pellinghelli, A. Tiripicchio, R.A. Henderson, R.L. Richards, *J. Chem. Soc. Dalton Trans.* (1995) 1183.
- [7] (a) E.M. Carnahan, S.J. Lippard, *J. Am. Chem. Soc.* 112 (1990) 3230. (b) E.M. Carnahan, S.J. Lippard, *J. Am. Chem. Soc.* 114 (1992) 4166.
- [8] (a) C. Collazo, D. Rodewald, H. Schmidt, D. Rehder, *Organometallics* 15 (1996) 4884. (b) C. Bötcher, D. Rodewald, D. Rehder, *J. Organomet. Chem.* 496 (1995) 43. (c) F. Calderazzo, M. Castellani, G. Pampaloni, P.F. Zanazzi, *J. Chem. Soc. Dalton Trans.* (1985) 1989.
- [9] F.A. Cotton, W.J. Roth, *J. Am. Chem. Soc.* 105 (1983) 3734.
- [10] (a) C. Felten, D. Rodewald, W. Priebsch, F. Olbrich, D. Rehder, *J. Organomet. Chem.* 480 (1994) 51. (b) D. Rodewald, C. Schulzke, D. Rehder, *J. Organomet. Chem.* 498 (1995) 29. (c) F. Calderazzo, C. Felten, G. Pampaloni, D. Rehder, *J. Chem. Soc. Dalton Trans.* (1992) 2003.
- [11] F. Calderazzo, G. Pampaloni, G. Pelizzi, F. Vitali, *Organometallics* 7 (1988) 1083.
- [12] C. Felten, J. Richter, W. Priebsch, D. Rehder, *Chem. Ber.* 122 (1989) 1617.
- [13] R. Hoffmann, B.F. Bayer, E.L. Muetterties, A.R. Rossi, *Inorg. Chem.* 16 (1977) 511.
- [14] E.M. Carnahan, R.L. Rardin, S.G. Bott, S.J. Lippard, *Inorg. Chem.* 31 (1992) 5193.
- [15] (a) R. Talay, D. Rehder, *Z. Naturforsch.* 36b (1981) 451. (b) D. Rodewald, F. Süßmilch, D. Rehder, *Anal. Quim.* 92 (1996) 269.
- [16] M.L. Luetgens Jr., J.C. Huffman, A.P. Sattelberger, *J. Am. Chem. Soc.* 105 (1983) 4474.
- [17] J. Acho, S.J. Lippard, *Organometallics* 13 (1994) 1294.
- [18] J. Park, S.F. Pedersen, *Tetrahedron* 48 (1992) 2069.
- [19] T. Hirao, T. Hasegawa, Y. Maguruma, I. Ikeda, *Org. Chem.* 61 (1996) 366.
- [20] P. Lorente, C. Carfagna, M. Etienne, B. Donnadiu, *Organometallics* 15 (1996) 1090.
- [21] F.A. Cotton, L.R. Falvello, R.C. Najjar, *Organometallics* 1 (1982) 1640.
- [22] W.P. Weber, G.W. Gokel, *Phase Transfer Catalysis in Organic Synthesis*, Springer, Heidelberg, 1977, p. 18.
- [23] F. Calderazzo, U. Englert, G. Pampaloni, G. Pelizzi, R. Zamboni, *Inorg. Chem.* 22 (1983) 1865.
- [24] F. Calderazzo, G. Pampaloni, *J. Chem. Soc. Chem. Commun.* (1984) 1249.

- [25] J.E. Ellis, G.F. Warnock, M.V. Barybin, M.K. Pomije, *Chem. Eur. J.* 1 (1995) 521.
- [26] D. Rodewald, D. Rehder, in: M. Gielen, R. Willem, B. Wrackmeyer (Eds.), *Advanced Applications of NMR to Organometallic Chemistry*, Wiley, Chichester, 1996, Ch. 10.
- [27] F. Süßmilch, W. Glöckner, D. Rehder, *J. Organomet. Chem.* 388 (1990) 95.
- [28] L.E. Manzer, *Inorg. Synth.* 21 (1982) 135.
- [29] M. Behnam-Dahkordy, B. Crociani, R.L. Richards, *J. Chem. Soc. Dalton Trans.* (1977) 2015.