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DICYCLOPENTADIENYLTANTALUM COMPLEXES

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Summary

The reduction of $(\eta^5\text{-}C_5H_5)_2TaCl_2$ with Na/Hg or NaNaph yields the dimer $(\eta^5\text{-}C_5H_5)_4Ta_2Cl_3$ (I) containing tantalum(III) and tantalum(IV), whereas the same reduction in a 1/1 molar ratio gives $(\eta^5\text{-}C_5H_5)_2TaCl$ (II). Use of $NaBH_4$ gives the boranate complex $(\eta^5\text{-}C_5H_5)_2TaBH_4$ (III). Complex II behaves as a Lewis acid with π-acid ligands and metal halides MXY_2 to give $(\eta^5\text{-}C_5H_5)_2TaClL$ (L = CO (IV), PMe_2Ph (V), PPh_3 (VI), PhC≡CPh (VII)) and $(\eta^5\text{-}C_5H_5)_2Ta(\mu\text{-}Cl)(\mu\text{-}X)MY_2$, (M = Fe, X = Y = Cl (VIII), M = Tl, X = Y = Cl (IX), M = Al, X = Y = Cl (X), M = Tl, X = Br, Y = C_6F_5 (XI)). Reactions of $(\eta^5\text{-}C_5H_5)_2TaCl_2$ with metal halides MXY_2 give $(\eta^5\text{-}C_5H_5)_2TaCl(\mu\text{-}Cl)MXY_2$ (M = Al, X = Y = Cl (XII), M = Fe, X = Y = Cl (XIII), M = Tl, X = Y = Cl (XIV), M = Tl, X = Br, Y = C_6F_5 (XV)) and $[(\eta^5\text{-}C_5H_5)_2Ta(\mu\text{-}Cl)_2MCl_2]^+ MCl_4^-$ (M = Fe (XVI), Al (XVII)). Reaction of I with $AgClO_4$ gives $[(\eta^5\text{-}C_5H_5)_4Ta_2Cl_2]^+ ClO_4^-$ (XVIII). Complex III behaves also as a Lewis acid and reacts with π-acid ligands to give $(\eta^5\text{-}C_5H_5)_2Ta(H)(L)$ (L = CO (XIX), PEt_3 (XX), PPh_3 (XXI)). The chemical and structural behaviour of these complexes are described.

Introduction

The preparation of the binuclear complex $(\eta^5\text{-}C_5H_5)_4Ta_2Cl_3$ by reduction of $TaCl_5$ with $LiPPh_2$ in the presence of NaC_5H_5 has been described [1] and a structure containing a triple chlorine bridge has been suggested. We reported the isolation of a similar niobium compound using Na/Hg as reducing agent [2]. We now present the results of a study of the reduction of $(\eta^5\text{-}C_5H_5)_2TaCl_2$ with various reducing agents as a method of preparing various tantalum(III) derivatives. The chemical behaviour of the new complexes has been studied and structural information obtained from IR and NMR spectroscopy.

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Results and discussion

Reduction of $(\eta^5\text{-}C_5H_5)_2TaCl_2$ in THF with sodium amalgam in a 1/0.5 molar ratio produces a purple solution from which complex I is obtained as red-purple crystals by evaporation (see eq. 1).

$$2(\eta^5\text{-}C_5H_5)_2TaCl_2 + Na/Hg \rightarrow (\eta^5\text{-}C_5H_5)_2TaCl_2 \cdot (\eta^5\text{-}C_5H_5)_2TaCl + NaCl \quad (1)$$

Analytical data are listed in Table 1 for this and other complexes.

The same compound can also be obtained by Reed's method [1]. A third method for preparing complex I consists in mixing THF solutions containing equimolar amounts of $(\eta^5\text{-}C_5H_5)_2TaCl_2$ and complex II, (see eq. 2).

$$(\eta^5\text{-}C_5H_5)_2TaCl_2 + (\eta^5\text{-}C_5H_5)_2TaCl \rightarrow (\eta^5\text{-}C_5H_5)_2TaCl_2 \cdot (\eta^5\text{-}C_5H_5)_2TaCl \quad (2)$$

The chlorotantalum(III) complex II was obtained by reducing a THF solution of $(\eta^5\text{-}C_5H_5)_2TaCl_2$ with a larger amount of sodium amalgam (molar ratio 1/1); after filtration the resulting brown-grey solution was concentrated by evaporation under vacuum to give brown-grey crystals which analysed as complex II (see Table 1, eq. 3).

$$(\eta^5\text{-}C_5H_5)_2TaCl_2 + Na/Hg \rightarrow (\eta^5\text{-}C_5H_5)_2TaCl \quad (3)$$

Similar results were obtained using NaNaph as reducing agent.

However, when the reduction is carried out using $NaBH_4$ in excess, rapid evolution of gas is observed and when the red solution is concentrated red crystals analysing as complex III are obtained, according to eq. 4:

$$2(\eta^5\text{-}C_5H_5)_2TaCl_2 + 4NaBH_4 \rightarrow 2(\eta^5\text{-}C_5H_5)_2TaBH_4 + 4NaCl + B_2H_6 + H_2 \quad (4)$$

Complex II behaves as a Lewis acid and reacts readily with π-acid ligands. The addition of different ligands to solutions of complex II gives the 18-electrons compounds $(\eta^5\text{-}C_5H_5)_2TaClL$, according to eq. 5:

$$(\eta^5\text{-}C_5H_5)_2TaCl + L \rightarrow (\eta^5\text{-}C_5H_5)_2TaClL \quad (5)$$

$(L = CO\ (IV),\ PMe_2Ph\ (V),\ PPh_3\ (VI),\ PhC{\equiv}CPh\ (VII))$

These complexes were isolated as crystalline products. Complex IV has been described previously [3].

The acidic character of II may account for the formation of I in the presence of an excess of $(\eta^5\text{-}C_5H_5)_2TaCl_2$ which donates a pair of electrons to form a chlorine bridge between both metal atoms.

On the other hand, the same donor capacity can be exhibited by other metal halides which form similar adducts of higher stability if the central metal atom can simultaneously act as an acceptor. Thus when THF solutions of I are treated with solutions of $FeCl_3$, $TlCl_3$, $AlCl_3$ and $(C_6F_5)_2TlBr$ in diethyl ether, $(\eta^5\text{-}C_5H_5)_2TaCl_2$ is displaced and the adducts $(\eta^5\text{-}C_5H_5)_2TaCl \cdot MXY_2$ (M = Fe, X = Y = Cl (VIII), M = Tl, X = Y = Cl (IX), M = Al, X = Y = Cl (X), X = Br, Y = C_6F_5 (XI)) are obtained, according to eq. 6 (see Table 1).

$$(\eta^5\text{-}C_5H_5)_4Ta_2Cl_3 + MXY_2 \rightarrow (\eta^5\text{-}C_5H_5)_2TaCl \cdot MXY_2 + (\eta^5\text{-}C_5H_5)_2TaCl_2 \quad (6)$$

The same compounds VIII–XI can also be obtained by addition of the metal halides to solutions of complex II.

When the reaction of I is carried out using an excess of the metal halide, a mixture of compounds is obtained which contains along with VIII–XI complexes other tantalum compounds presumably formed by reaction with the residual $(\eta^5\text{-}C_5H_5)_2TaCl_2$. The mixture is difficult to separate. To throw light on this result we carried out separate reactions between $(\eta^5\text{-}C_5H_5)_2TaCl_2$ and various metal halides, to give complexes XII–XV, according to eq. 7.

$$(\eta^5\text{-}C_5H_5)_2TaCl_2 + MXY_2 \rightarrow (\eta^5\text{-}C_5H_5)_2TaCl_2 \cdot MXY_2 \qquad (7)$$

$(M = Al, X = Y = Cl\ (XII);\ M = Fe, X = Y = Cl\ (XIII);$

$M = Tl, X = Y = Cl\ (XIV);\ M = Tl, X = Br, Y = C_6F_5\ (XV))$

These complexes are formed because of the acceptor character of the metal halide towards the tantalum(IV) complexes, the halide behaving as a base in the same way as it does with the tantalum(III) compound.

When the reaction of $(\eta^5\text{-}C_5H_5)_2TaCl_2$ with $FeCl_3$ and $AlCl_3$ is carried out in a 1/2 molar ratio or when one additional mol of metal halides is added to complexes XII and XIII, cationic complexes XVI and XVII are isolated, according to eq. 8 (see Table 1).

$$(\eta^5\text{-}C_5H_5)_2TaCl_2 + 2MXY_2 \rightarrow \left[(\eta^5\text{-}C_5H_5)_2Ta(\mu\text{-}Cl)_2MXY\right]^+ MX_2Y_2^- \qquad (8)$$

$(M = Fe, X = Y = Cl\ (XVI);\ M = Al, X = Y = Cl\ (XVII))$

On the other hand, complex I reacts with $AgClO_4$ with precipitation of AgCl from one of the chlorine atoms even when an excess of the silver salt is used, giving the cationic compound $[(\eta^5\text{-}C_5H_5)_4Ta_2Cl_2]^+\ ClO_4^-$ (XVIII), according to eq. 9 (see Table 1).

$$(\eta^5\text{-}C_5H_5)_4Ta_2Cl_3 + AgClO_4 \rightarrow \left[(\eta^5\text{-}C_5H_5)_4Ta_2Cl_2\right]^+ ClO_4^- + AgCl \qquad (9)$$

Complex XVIII does not react with ligands such as CO and PPh_3 at room temperature.

The boranate complex III behaves as a Lewis acid and reacts with ligands with displacement of BH_3, which is eliminated as the corresponding adduct. Only when this adduct is volatile can the reaction be carried out directly, since in other cases the $BH_3 \cdot L$ adduct is difficult to remove.

Bubbling of CO through the solution of III gives a red-purple solution, which on evaporation gives red-purple crystals analysing as the hydridocarbonyl complex XIX, (see eq. 10) (see Table 1)

$$(\eta^5\text{-}C_5H_5)_2TaBH_4 + CO \rightarrow (\eta^5\text{-}C_5H_5)_2TaH(CO) + CO \cdot BH_3 \qquad (10)$$

The reaction of III with PEt_3 gives complex XX and the $PEt_3 \cdot BH_3$ adduct is removed by sublimation. With PPh_3 a pure sample of the hydridophosphino complex cannot be obtained because its solubility is very similar to that of $PPh_3 \cdot BH_3$ and the adduct cannot be removed by sublimation. When the reactions of complex III with ligands are carried out in the presence of TMEDA(tetramethyl ethylen diamine) an insoluble adduct, $2BH_3 \cdot$ TMEDA, is formed and can easily be sep-

$$(\eta^5\text{-}C_5H_5)_2TaBH_4 + L + TMEDA \rightarrow (\eta^5\text{-}C_5H_5)_2TaHL + 2BH_3 \cdot TMEDA \qquad (11)$$

$(L = CO\ (XIX),\ PEt_3\ (XX),\ PPh_3\ (XXI))$

TABLE 1

DATA FOR CYCLOPENTADIENYL TANTALUM COMPLEXES

Complex		Analysis (Found (calcd.) (%))		Colour	Yield (%)
		C	H		
$(\eta^5\text{-}C_5H_5)_2TaCl_2\cdot(\eta^5\text{-}C_5H_5)_2TaCl$	(I)	32.69 (32.94)	3.30 (2.75)	purple	75
$(\eta^5\text{-}C_5H_5)_2TaCl$	(II)	34.83 (34.63)	3.17 (2.89)	brown-grey	60
$(\eta^5\text{-}C_5H_5)_2TaBH_4$	(III)	36.46 (36.83)	5.15 (4.30)	red	60
$(\eta^5\text{-}C_5H_5)_2TaCl(CO)$	(IV)	35.44 (35.25)	2.80 (2.67)	grey-green	65
$(\eta^5\text{-}C_5H_5)_2TaCl(PMe_2Ph)$	(V)	44.90 (44.58)	4.87 (4.33)	brown-green	60
$(\eta^5\text{-}C_5H_5)_2TaCl(PPh_3)$	(VI)	55.55 (55.22)	4.50 (4.11)	yellow	60
$(\eta^5\text{-}C_5H_5)_2TaCl(PhC{\equiv}CPh)$	(VII)	54.97 (54.91)	3.94 (3.81)	pale-yellow	70
$(\eta^5\text{-}C_5H_5)_2Ta(\mu\text{-}Cl)_2FeCl_2$	(VIII)	23.65 (23.58)	2.58 (1.96)	orange	80
$(\eta^5\text{-}C_5H_5)_2Ta(\mu\text{-}Cl)_2TlCl_2$	(IX)	18.32 (18.25)	1.96 (1.52)	yellowish	75
$(\eta^5\text{-}C_5H_5)_2Ta(\mu\text{-}Cl)_2AlCl_2$	(X)	25.18 (25.00)	2.53 (2.08)	brown	80
$(\eta^5\text{-}C_5H_5)_2Ta(\mu\text{-}Cl)(\mu\text{-}Br)Tl(C_6F_5)_2$	(XI)	27.62 (27.36)	1.59 (1.04)	brown	80
$(\eta^5\text{-}C_5H_5)_2TaCl(\mu\text{-}Cl)AlCl_3$	(XII)	23.85 (23.28)	2.17 (1.94)	pale-brown	80
$(\eta^5\text{-}C_5H_5)_2TaCl(\mu\text{-}Cl)FeCl_3$	(XIII)	22.56 (22.05)	2.05 (1.84)	yellow-green	90
$(\eta^5\text{-}C_5H_5)_2TaCl(\mu\text{-}Cl)TlCl_3$	(XIV)	17.73 (17.33)	1.75 (1.44)	brown	90
$(\eta^5\text{-}C_5H_5)_2TaCl(\mu\text{-}Cl)TlBr(C_6F_5)_2$	(XV)	26.80 (26.40)	1.31 (1.00)	brown	90
$[(\eta^5\text{-}C_5H_5)_2Ta(\mu\text{-}Cl)_2FeCl_2]^+\ FeCl_4^-$	(XVI)	16.87 (16.99)	1.49 (1.42)	yellow	90
$[(\eta^5\text{-}C_5H_5)_2Ta(\mu\text{-}Cl)_2AlCl_2]^+\ AlCl_4^-$	(XVII)	18.32 (18.49)	1.97 (1.53)	brown-green	90
$[(\eta^5\text{-}C_5H_5)_4Ta_2Cl_2]^+\ ClO_4^-$	(XVIII)	30.10 (30.28)	3.20 (2.52)	yellow-green	70
$(\eta^5\text{-}C_5H_5)_2Ta(H)(CO)$	(XIX)	39.28 (38.82)	3.65 (3.24)	red-purple	80
$(\eta^5\text{-}C_5H_5)_2Ta(H)(PEt_3)$	(XX)	44.48 (44.65)	6.77 (6.05)	red	55
$(\eta^5\text{-}C_5H_5)_2Ta(H)(PPh_3)$	(XXI)	58.16 (58.45)	4.99 (4.53)	red-purple	70

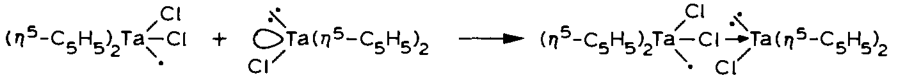
arated by filtration. The solutions after evaporation give crystalline complexes XIX, XX and XXI, according to eq. 11 (see Table 1). Complexes XIX and XX have been previously described [4,5].

All the complexes described are air sensitive but are stable as solids under nitrogen. Structural studies are limited by the relatively low stability. Thus, molecular weight determinations in solution are prevented by low solubility and low stability in suitable organic solvents, and crystals suitable for X-ray diffraction could not be obtained.

Complex I behaves as a paramagnetic binuclear compound with μ_{eff} 1.36 BM at 20°C which reveals the presence of one unpaired electron for each dimeric unit (cf. Ref. 1).

The IR spectrum shows absorptions due to the η^5-C_5H_5 ring [6] and the Ta–Cl region below 400 cm^{-1} is closely similar to that observed for $(\eta^5\text{-}C_5H_5)_2TaCl_2$ as indicated in Table 2.

The data suggest that the most reasonable structure includes a single chlorine bridge, since this places 18 or 17 electrons on the tantalum(III) and tantalum(IV) atoms, respectively, although other structures with two or three chlorine bridges cannot be excluded. The formation of complex I is thus the consequence of the acidic character of complex II, which achieves 18 electrons by accepting one pair from one of the chlorine atoms of $(\eta^5\text{-}C_5H_5)_2TaCl_2$, as depicted in eq. 12.



(12)

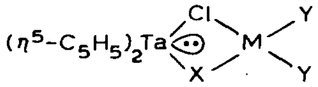
The IR spectrum of complex II shows bands due to the $(\eta^5\text{-}C_5H_5)$ ring [6] and the ν(Ta–Cl) band at 310 cm^{-1}. Complex II is diamagnetic and gives a ^1H NMR spectrum with a single resonance due to both $(\eta^5\text{-}C_5H_5)$ rings and its chemical shift is similar to that reported for $(\eta^5\text{-}C_5H_5)_2NbCl$ [7].

A structure containing the bridge boranate system in complex III is confirmed by the ^1H NMR spectrum, which shows two singlet resonances assignable to terminal B–H and bridge Ta–H–B protons, and a single resonance due to both $(\eta^5\text{-}C_5H_5)$ rings, showing that the two rings are equivalent. The IR spectrum of III shows absorptions due to the $(\eta^5\text{-}C_5H_5)$ rings [6], and the ν(B–H) and the ν(B–H–Ta) (See Table 2).

The chloro complexes IV–VII must have structures analogous to those of the corresponding niobium derivatives [8,9].

All the complexes are diamagnetic and show a single peak in the ^1H NMR spectrum, showing that the two $(\eta^5\text{-}C_5H_5)$ rings are equivalent, and the chemical shifts are in agreement with those previously observed for analogous niobium derivatives [8,9]. (See Table 3). The IR spectra show the absorptions of the $(\eta^5\text{-}C_5H_5)$ ring [6] and the ν(Ta–Cl) band, as in Table 2.

A double bridge binuclear structure is proposed for tantalum(III) adducts VIII–XI, with an 18 electron configuration for the tantalum atom



Complexes IX, X and XI are diamagnetic, but VIII is paramagnetic with a μ_{eff} 4.92 BM at 20°C due to the tetrahedral Fe^{III} d^5 center, so that the tantalum(III) unit is diamagnetic in all the complexes.

The ^1H NMR spectra of IX, X and XI complexes exhibit two peaks showing that

TABLE 2

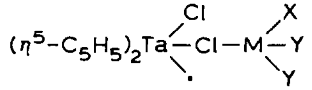
IR ABSORPTIONS OF TANTALUM COMPLEXES (ν in cm^{-1})

Complex	
I [1]	320s, 285s, 270s
II	310s, ν(Ta–Cl)
III	1820–1860s, ν(Ta–H) 2410–2250s, ν(B–H)
IV [3]	312s, ν(Ta–Cl) 1875vs, ν(C≡O)
V	312s, ν(Ta–Cl)
VI	312s, ν(Ta–Cl)
VII	303s, ν(Ta–Cl) 1720m, ν(C≡C)
VIII	380vs, ν(Fe–Cl)
IX	265s, ν(Tl–Cl)
X	500vs, ν(Al–Cl)
XII	500s, ν(Al–Cl)
XIII	380s, ν(Fe–Cl)
XIV	265s, ν(Tl–Cl)
XVI	380s, ν(Fe–Cl)
XVII	500s, ν(Al–Cl)
XIX [17]	1875vs, ν(C≡O) 1725–1680s, ν(Ta–H)
XX [18]	1735vs, ν(Ta–H)
XXI	1695s, ν(Ta–H)

the (η^5-C_5H_5) rings are not equivalent, and thus that the tetrahedral environment of both Al and Tl atoms is asymmetric with respect to the reflection plane of the rings (See Table 3).

The IR spectra of complexes VIII–XI show the expected bands due to the (η^5-C_5H_5) ring [6], the C_6F_5 group [10] for XI, ν(Fe–Cl) [11] for VIII, ν(Tl–Cl) [12] for IX, and ν(Al–Cl) [13] for X.

A structure containing a single chlorine bridge is suggested for the tantalum(IV) adducts XII–XV in the light of the high energy of the tantalum orbital to which the electrons must be excited to form a double bridge [14].



$(\eta^5\text{-}C_5H_5)_2Ta(Cl)\text{–}Cl\text{–}M(X)(Y)_2$

The tantalum(IV) unit in complexes XII–XV is paramagnetic due to the presence of one unpaired electron, so that the complexes are paramagnetic.

The μ_{eff} at 20°C for complexes XII, XIV and XV have values between 1.35 and 1.49 BM which correspond to the presence of one unpaired electron. Complex XIII has μ_{eff} 6.22 BM, as expected for a system with six unpaired electrons, one for the tantalum(IV) atom and five for the tetrahedral Fe^{III} d^5 center. The IR spectra show characteristic absorptions due to (η^5-C_5H_5) ring [6] and the (C_6F_5) group [10] for XV. Absorptions quite close to those observed for $(\eta^5\text{-}C_5H_5)_2TaCl_2$ are present below 400 cm^{-1}; along with other absorptions due to ν(Al–Cl) [13] for XII, ν(Fe–Cl) [11] for XIII and ν(Tl–Cl) [12] for XIV and XV.

Complexes XVI and XVII behave as conductors in acetone (Λ 177.6 and 117.9 ohm^{-1} cm^2 mol^{-1} respectively), and in the light of the conductances we propose the

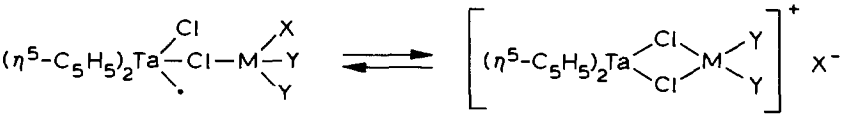
TABLE 3

^{1}H NMR DATA FOR TANTALUM COMPLEXES

	$(\eta^5\text{-}C_5H_5)$	Ta–H	Ta–H–B	Ph	Me	Et
II [a]	5.75(s)					
III [a]	5.21(s)	14.00(m)	13.06(m)			
IV [a] [3]	5.36(s)					
V [b]	4.33(d, *J*(P–H) 1.6 Hz)			2.46(m)	9.12–8.70(m)	
VI [b]	4.41(d, *J*(P–H) 1.6 Hz)			2.42(s)		
VII [b]	4.10(s)			2.48–2.56–2.75(m)		
IX [b]	2.87–2.95(s)					
X [b]	2.86–3.05(s)					
XI [b]	2.87–2.98(s)					
XIX [a] [17]	5.32(s)	16.80(s)				
XX [a] [18]	5.94(d, *J*(P–H) 1.5 Hz)	19.80(d, *J*(P–H) 27.7 Hz)				8.80–8.88–8.97– 9.16–9.24–9.31 (m)
XXI [b]	5.73(d, *J*(P–H) 1.6 Hz)	18.97(d, *J*(P–H) 30 Hz)		2.58(s)		

[a] Benzene-d_6. [b] Acetone-d_6. s = singlet, d = doublet, m = multiplet. The chemical shifts (τ) are given in ppm.

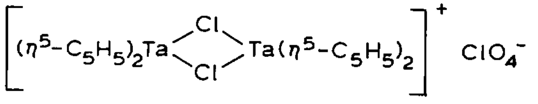
existence of the following equilibrium in solution:



The formation of XVI and XVII is a consequence of the displacement of this equilibrium towards the right. A double bridge binuclear structure is proposed for XVI and XVII. They are paramagnetic species, and the μ_{eff} values at 20°C are 11.73 and 1.33 BM, respectively.

The IR spectra show characteristic absorptions of the (η^5-C_5H_5) ring [6] and of ν(Fe–Cl) [11] for XVI and ν(Al–Cl) [13] for XVII.

We suggest a double bridge structure for cationic complex XVIII, in agreement with the observed absence in the IR spectrum of the absorptions below 300 cm^{-1} which are present in complex I and assigned to terminal Ta–Cl stretching vibrations



On the other hand, the cationic complex XVIII probably contains a double bridge in order to retain 17 and 18 electrons, respectively, on the two Ta atoms.

Complex XVIII is paramagnetic with μ_{eff} 1.40 BM at 20°C. Complex XVIII behaves as a conductor in acetone (Λ 116.33 ohm^{-1} cm^2 mol^{-1}), and its IR spectrum shows absorptions due to the (η^5-C_5H_5) ring [6] and the ClO_4^- ion [15].

The hydrido complexes XIX, XX, XXI are diamagnetic, and the ^{1}H NMR spectra show a single resonance from the (η^5-C_5H_5) rings (See Table 3).

The IR spectra show the absorptions of the (η^5-C_5H_5) ring [6], and ν(Ta–H) appears as a broad band (See Table 2).

All the complexes described are air sensitive, and rigorous precautions must be taken during their handling to avoid decomposition.

Experimental

All operations were carried out under vacuum or in an inert atmosphere using Schlenk-type glassware. IR spectra were recorded on a Perkin–Elmer spectrophotometer (over the range 4000–200 cm^{-1}) using Nujol between CsI plates. Magnetic measurements were carried out by the Faraday method with a Bruker magnet system. ^{1}H NMR spectra were determined on a Varian FT 80 A spectrometer. C,H analyses were carried out with a Perkin–Elmer 204 B microanalyzer. Solvents were dried and distilled before use. (η^5-C_5H_5)$_2$$TaCl_2$ was prepared as in ref. [16].

(η^5-C_5H_5)$_2$$TaCl_2$ · (η^5-C_5H_5)$_2$TaCl (I)

Method A. (η^5-C_5H_5)$_2$$TaCl_2$ (1.000 g, 2.62 mmol) was added to sodium amalgam (1.31 mmol of sodium) in THF (50 ml). After 4 h stirring at room temperature a purple solution and a grey precipitate were obtained. The solution was filtered and then concentrated under reduced pressure to give purple crystals of I, which were dried under vacuum. Yield 70%.

Method B. $(\eta^5\text{-}C_5H_5)_2TaCl_2$ (0.550 g, 1.44 mmol) was added to a solution of II (0.500 g, 1.44 mmol) in THF (50 ml). After 2 h stirring at room temperature a precipitate was formed and the solution became purple. The solution was filtered and the filtrate concentrated under reduced pressure to give purple crystals of I, which were dried under vacuum. Yield 80%.

$(\eta^5\text{-}C_5H_5)_2TaCl$ (II)

Method A. THF (50 ml)was added to a mixture of $(\eta^5\text{-}C_5H_5)_2TaCl_2$ (1.000 g, 2.62 mmol) and sodium amalgam (2.62 mmol of Na). After 3 h of stirring at room temperature a brown-grey solution and a large precipitate were obtained. The solution was filtered and then concentrated under reduced pressure to give brown-grey crystals of II, which were dried under vacuum. Yield 60%.

Method B. When a solution of NaNaph (0.053 *M* in Na) in THF (50 ml) was added to $(\eta^5\text{-}C_5H_5)_2TaCl_2$ (1.000 g, 2.62 mmol) the original green solution became brown after 3 h of stirring at room temperature. The solution was filtered and then concentrated under reduced pressure, to give brown-grey crystals of II, which were washed with pentane and dried under vacuum. Yield 60%.

$(\eta^5\text{-}C_5H_5)_2TaBH_4$ (III)

$NaBH_4$ (0.300 g, 7.86 mmol) was added to a suspension of $(\eta^5\text{-}C_5H_5)_2TaCl_2$ (1.000 g, 2.62 mmol) in 1,2-dimethoxyethane (50 ml). A rapid evolution of gas was observed, and after 12 h of stirring at room temperature a red solution and a precipitate were obtained. The solution was filtered, and concentrated under reduced pressure to give red crystals of III, which were dried under vacuum. Yield 60%.

$(\eta^5\text{-}C_5H_5)_2TaClL$ ($L = CO$ (IV), PMe_2Ph (V), PPh_3 (VI), $PhC{\equiv}CPh$ (VII))

A solution of II (0.500 g, 1.44 mmol) was treated with $PhC{\equiv}CPh$ (0.260 g, 1.44 mmol). After 2 h of stirring at room temperature a grey solution was obtained. The solvent was removed under reduced pressure and the resulting solid was extracted with hot pentane to yield a yellow solution. This solution gave complex VII as pale-yellow needles after concentration and cooling at −30°C. Yield 70%.

Compounds IV, V and VI were prepared similarly.

$(\eta^5\text{-}C_5H_5)_2TaCl(\mu\text{-}X)MY_2$ ($M = Fe$, $X = Y = Cl$ (VIII); $M = Tl$, $X = Y = Cl$ (IX); $M = Al$, $X = Y = Cl$ (X); $M = Tl$, $X = Br$, $Y = C_6F_5$ (XI))

When a solution of $FeCl_3$ (0.8 ml of a solution 1.75 *M*) in diethyl ether was added to a solution of II (0.500 g, 1.44 mmol) in THF (50 ml) an orange solid separated immediately. The solid was filtered and repeatedly washed with diethyl ether, then dried under vacuum and identified as complex VIII. Yield 80%.

Complexes IX, X and XI were prepared similarly.

$(\eta^5\text{-}C_5H_5)_2TaCl(\mu\text{-}Cl)MXY_2$ ($M = Al$, $X = Y = Cl$ (XII); $M = Fe$, $X = Y = Cl$ (XIII); $M = Tl$, $X = Y = Cl$ (XIV); $M = Tl$, $X = Br$, $Y = C_6F_5$(XV))

$TlCl_3$ (0.290 g, 1.31 mmol) was added to a suspension of $(\eta^5\text{-}C_5H_5)_2TaCl_2$ (0.500 g, 1.31 mmol). After 0.5 h of stirring at room temperature the initially brown solid became pale-brown. The solid was filtered off and repeatedly washed with diethyl ether, and after being dried under vacuum was identified as complex XIV. Yield 90%.

Compounds XII, XIII and XV were prepared similarly.

$[(\eta^5\text{-}C_5H_5)_2Ta(\mu\text{-}Cl)_2MCl_2]^+MCl_4^-$ *(M = Fe (XVI), Al(XVII))*

$AlCl_3$ (0.350 g, 2.62 mmol) was added to a suspension of $(\eta^5\text{-}C_5H_5)_2TaCl_2$ (0.500 g, 1.31 mmol) in diethyl ether (50 ml). After 1 h of stirring at room temperature the original brown solid became brown-green. The solid was filtered off and repeatedly washed with diethyl ether, then dried under vacuum and identified as complex XVII. Yield 90%.

Compound XVI was prepared similarly.

$[(\eta^5\text{-}C_5H_5)_4Ta_2Cl_2]^+\ ClO_4^-$ *(XVIII)*

$AgClO_4$ (0.220 g, 0.96 mmol) was added to a solution of I (0.700 g, 0.96 mmol) in THF (50 ml). After 1 h of stirring at room temperature a large amount of brown solid was formed. The solid was filtered off and dried under vacuum. The resulting brown solid was extracted with acetone (2 × 25 ml) to yield a yellow solution. This solution yielded complex XVIII as yellow-green crystals after concentration and cooling at −78°C. The crystals were washed with pentane and dried under vacuum. Yield 70%.

$(\eta^5\text{-}C_5H_5)_2Ta(H)L$ *(L = CO (XIX), PEt_3 (XX), PPh_3 (XXI))*

TMEDA (0.900 g, 0.12 ml) was added to a solution of III (0.500 g, 1.52 mmol) in THF (50 ml). A white precipitate was formed and the solution became deep red. The solution was filtered and PPh_3 (0.400 g, 1.52 mmol) was added; after 1 h of stirring at room temperature the deep red solution was concentrated under reduced pressure. Addition of pentane (10 ml) and cooling gave red-purple needles of XXI. Yield 70%.

Complexes XIX, XX were prepared similarly.

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