Journal of Organometallic Chemistry, 426 (1992) 159–172
Elsevier Sequoia S.A., Lausanne
JOM 22348

Aspects of carbonyltantalum chemistry

Michael Fornalczyk, Frank Süssmilch, Wolfgang Priebsch and Dieter Rehder
Institut für Anorganische Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, W-2000 Hamburg 13 (Germany)

(Received June 17, 1991)

Abstract

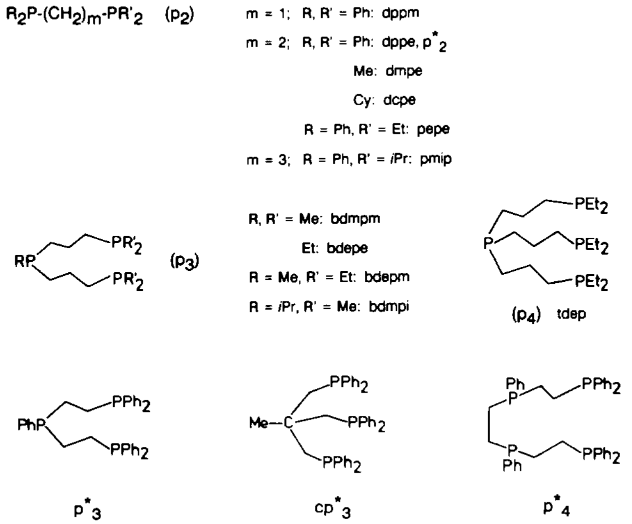
UV irradiation of $[Et_4N][Ta(CO)_6]$ in the presence of 2- to 4-dentate phosphines, p_n, yields $[Et_4N][Ta(CO)_4p_n]$. Ion exchange chromatography on silica gel affords the hydrido complexes $HTa(CO)_4p_2$ or $HTa(CO)_3p_n$ ($n = 3$, 4), which can be photochemically converted into $HTa(CO)_2p_n$. The structure in solution as judged from spectroscopic data is probably an octahedron capped by the hydride. In the solid state, an X-ray diffraction study of *trans*-$[HTa(CO)_2(dppe)_2]$ indicates the presence of a pentagonal bipyramid with H^-, Ta and the four P in the pentagonal plane. 2-methyl-2-butene is "hydrotantalated", mainly in the *anti*-Markovnikov manner, to yield the σ-alkyl complex $Me_2CH{-}H(Me)CTa(CO)_4p_2$ ($p_2 = Ph_2PCH_2CH_2PEt_2$). The complexes $HTa(CO)_{4/3}p_n$ react with pentafulvenes to form η^5-$(C_5H_4CHR_2)Ta(CO)_2p_n$ ($R_2 = Me_2$, Ph_2, $NMe_2 + H$; $p_n = PhP(CH_2CH_2PPh_2)_2$). The hepta-coordinated chloride complexes $ClTa(CO)_{6-n}p_n$ have been prepared photochemically from $[Et_4N]Cl$ and $HTa(CO)_4p_n$ ($n = 4$, $p_n = 2$ dppe), or by reductive carbonylation of $TaCl_4$ in the presence of p_n ($n = 3$, $p_n = MeP(CH_2CH_2CH_2PMe_2)_2$).

Introduction

Seven-coordinate hydrido complexes of the metals of the vanadium triad of the general formula $HM(CO)_{6-n}p_m$ (where m represents the number of coordinated phosphorus functions of a usually oligodentate phosphine, and n is 2–4) may be versatile reagents in H-transfer reactions, as has been shown, e.g., for M = V (see summary in ref. 1). This is especially so if the phosphine contains alkylated phosphorus functions and forms chelate-6 rings. Complexes formed with phenylated phosphines on the other hand, forming 5-ring structures with the metal centre, are often (but not always) remarkably stable towards potential substrates, even when activated chemically (e.g. by $H[BF_4]$) or photochemically [2]. It was the aim of the present study to evaluate the reactivity pattern of hydrido-carbonyltantalum complexes containing oligodentate phosphines as supporting ligands (Scheme 1), to assess their synthetic potential, and to provide structural information. Several features of hydridotantalum complexes containing phenylphosphines

---

Correspondence to: Professor D. Rehder, Department of Chemistry, University of Hamburg, Martin-Luther-King-Platz 6, W-2000 Hamburg 13, Germany.



Scheme 1.

(distinguished, in the following discussion, from alkylphosphines by a star, i.e. p_n^*,) were reported previously [3].

Results and discussion

Carbonyltantalates(−I)

Substitution of CO ligands by phosphines p_n in hexacarbonyltantalate is carried out photochemically. The reaction occurs in two steps; the final product is *cis*-$[Ta(CO)_4p_n]^-$. Substitution of a third CO, as observed in the corresponding vanadium system [4], does not take place. Mono- and di-substitution products can easily be distinguished by their characteristic IR patterns in the CO stretching region (Table 1). Further support for the composition of the anionic compounds comes from the ^{31}P NMR spectra, selected data for which are summarized in Table 1. There is the usual down-field coordination shift as phosphorus becomes coordinated. In contrast to the results with vanadium (and, in part, also the niobium) complexes [2,4,5], the ^{31}P resonances are sharp. The reason for this is the very large nuclear quadrupole moment of ^{181}Ta ($3.4\ 10^{-28}$ m^2), which causes complete relaxation decoupling of ^{31}P and ^{181}Ta. It is evident from the ^{31}P NMR spectra that the tridentate ligands bdepm and bdmpm (see Scheme 1) can coordinate through the two terminal, or through one terminal plus the central phosphorus functions (**1** and **2** in Scheme 2), leaving one P dangling. We have also confirmed this statistically unfavourable "head/tail" coordination in the corresponding vanadium systems by ^{51}V NMR [1]. ^{31}P–^{31}P coupling is observed if two inequivalent P-functions are separated by two CH_2 groups (25–35 Hz; ^3J) or, when separated by three CH_2 groups, if coordinated to Ta (12–14 Hz). The latter apparently is a two-bond through-metal coupling.

Carbonylhydridotantalum(I)

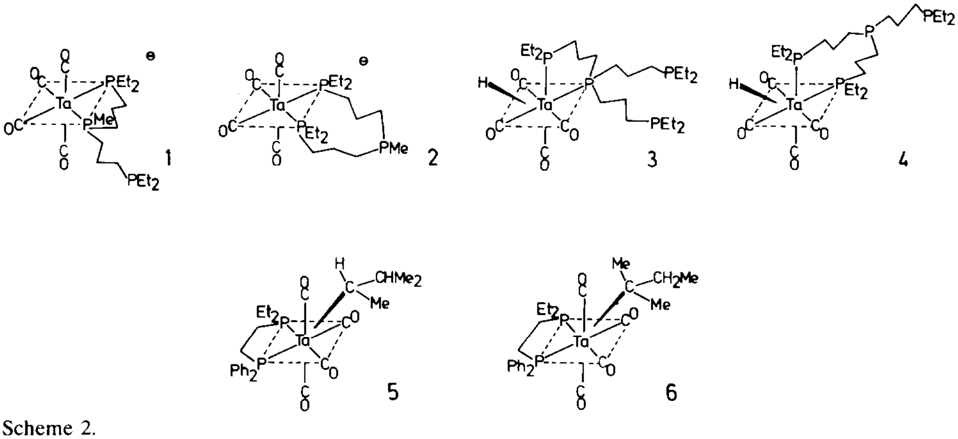
On silica gel, the tetracarbonyltantalates are converted into the hydrido complexes, while pentacarbonyltantalate remains unchanged on the gel. For $n = 2$, the

Table 1

Spectroscopic data for carbonyltantalates(−I) in THF solution

Complex [a]	ν(CO) (cm^{-1})				^{31}P NMR data [b]				
					Spin system [c]	δ_A	$\delta_{A'/B}$	$\delta_{X/Y}$	J_{AB}; $J_{A/BX}$
$[Ta(CO)_5p_n]^-$									
p_n = pepe [d]	1960m	1850vs	1810vs		AX	15.6(d)		(−10.5(d))	31.6
dcpe	1960m	1850s	1810s		AX	37.1(d)		(2.9(d))	30
cis-$[Ta(CO)_4p_n]^-$									
p_n = pepe	1895s	1785vs	1770sh	1745vs	AA′	50.2(d)	42.2(d)		19.3
dcype	1885s	1765vs	1750vs	1735vs	A_2	61.8			
pmip	1890s		1750vs		AA′	29.4(d)	−26.6(d)		14.3
dppm	1900s	1800vs	1750sh		A_2	21.4			
p_3^*	1900s	1790vs	1770sh	1750sh	ABX	49.3(d)	48.7(dd)	(−11.4(d))	22; 35
cp_3^*	1900s	1800vs	1760sh	1750sh	A_2	10.1			
bdmpm	1885s	1800vs	1750vs		ABX	−28.7(d)	−16.0(d)	(−52.6)	13.3
					A_2Y	−28.9		(−42.8)	
bdepm	1890s	1790vs	1760sh	1730vs	ABX	0.3(d)	−16.3(d)	(−22.4)	12.5
					AA′Y	0.2		(−42.6)	
bdepe	1890s	1770vs	1750sh	1730sh	ABX	0.2(d)	5.0(d)		11.8
bdmpi	1890s	1750vs			ABX	−28.4(d)	11.9(d)	(−52.6)	13.2
tdep	1890s	1770vs	1750sh	1730sh	ABX_2	0.0(d)	−5.0(d)	(−22.6)	13.4

[a] For abbreviations of the phosphines see Scheme 1. [b] Chemical shifts in ppm (values in brackets are for dangling Ps); coupling constants in Hz. [c] Coordinated terminal Ps are labelled A (or A′ if carrying different substituents), coordinated central (bridge-head) Ps are labelled B, and dangling Ps are labelled X (terminal) and Y (central). [d] Coordinates through PEt_2.



Scheme 2.

complexes $HTa(CO)_4p_2$ are formed. For $n > 2$, there is a tendency to lose a further CO ligand in solution, to yield $HTa(CO)_3p_n$. Depending on the nature of p_n, mixtures of the tetra- and tri-carbonyl complexes are obtained. Complete conversion into $HTa(CO)_3p_n$ is achieved if a THF solution is kept for several hours to days.

The tetracarbonyl complexes exhibit four bands in the CO stretching region of the IR spectra (Table 2). In a few cases the three absorptions at lower wave numbers overlap to form a very broad band. The pattern is characteristic of a *cis* arrangement of the two coordinated phosphorus functions, presumably [3] in an octahedral array of the $Ta(CO)_4p_n$ moiety. $HTa(CO)_3cp_3^*$ gives rise to two $\nu(CO)$ bands at 1910 and 1820 cm^{-1}. Since the tripod phosphine cp_3^* can occupy only *facial* (*fac*-) positions, these two absorptions are assigned to *fac*-$\{Ta(CO)_3p_n\}$. Most other complexes $HTa(CO)_3p_n$ show 5 $\nu(CO)$ bands, indicative of mixtures of *facial* and *meridional* (*mer*-) isomers, the bands at 1920–1935, $\approx$ 1850 and $\approx$ 1800 cm^{-1} being associated with *mer*-$\{Ta(CO)_3p_n\}$. The ligands p_3^* and bdmpi form *meridional* species only.

The presence of *mer*- and *fac*-isomers was confirmed by ^1H NMR spectroscopy (Table 3). In the case of *mer*- and *fac*-[$HTa(CO)_3$bdepm], for example, the less intense resonance is a doublet of triplets, which we assign to the *facial* isomer. The more intense signal at higher field, a quartet (triplet of doublets with almost identical coupling constants), belongs to the *meridional* isomer. The basis for these assignments is the assumption (considered in detail elsewhere, e.g. [2], [3] and [6]) that the basic structure is an octahedron $\{Ta(CO)_{6-n}p_n\}$ with the hydride migrating between all those faces which are not edge-spanned by the carbon back-bone of the oligodentate phosphine (see Scheme 3, in which the "allowed" positions for H^- are shown hatched). In a *facial* arrangement, there are 5 allowed faces for H^-. If we label the P atoms A (terminal) and B (central), and indicate the positions relative to H^- as *c* ("*cis*" or "close") and *t* ("*trans*" or "far"), then there are 4 A*c* and 6 A*t*, 1 B*c*, and 4 B*t*. In a *meridional* arrangement, there are 4 allowed faces, 4 A*c* and 4 A*t*, and 4 B*t*. If it is further assumed that *t* coupling is smaller than *c* coupling, $J(^1H-^{31}P)$ should be smaller in *fac*- than in *mer*-[$HTa(CO)_3$bdepm]. This model, although qualitatively in accord with the observed coupling constants,

Table 2

CO stretching frequencies for hydridotantalum complexes

Complex [a]	ν(CO) (cm^{-1}), in THF	Configuration [b]
$HTaCO_4p_n$		*cis*
$p_n =$ pepe	1990s 1850vs,br	
dcpe	1980s 1890vs 1870vs 1845vs	
pmip	1990s 1850vs,br	
dppm	1995s 1920vs 1860vs 1820sh	
bdmpi	1985s 1850vs,br	
cp_3^*	1990s 1880sh 1850vs 1840sh	
bdepm	1985s 1880sh 1850vs 1840sh	
tdep	1990s 1850vs,br	
$HTa(CO)_3p_n$		
$p_n = p_3^*$	1935s 1860m 1810s	*mer*
cp_3^*	1910s 1820m	*fac*
bdmpm	1935m 1860m 1795s	*mer*
	1920m 1830s	*fac*
bdepm	1925m 1840m 1800vs	*mer*
	1910s 1810s	*fac*
bdmpi	1920m 1800vs,br	*mer*
tdep	1925m 1855m 1995vs	*mer*
	1910m 1810vs	*fac*
$HTa(CO)_2p_n$		*trans*
$p_n =$ 2 dppe	1765 [c]	
2 pepe	1755	
p_4^*	1765	

[a] For abbreviations, see Scheme 1. [b] Assuming an octahedral arrangement of the ligands p_n and CO. [c] From ref. 3.

does not account for the extent by which the H–P^A couplings in the two isomers differ (5.5 Hz in the *fac*-, 36 Hz in the *mer*-isomer).

As in the case of the anionic complexes, the tetracarbonylhydrides formed with tri- and tetradentate phosphines may be present as mixtures of bond isomers, depending on whether the central (bridge-head) phosphorus does or does not participate in coordination to tantalum. This is evident from the ^{31}P as well as the ^{1}H NMR spectra (see Table 3), and is shown in Scheme 2 for the complexes **3** and **4** formed from the tetradentate tripod ligand tdep.

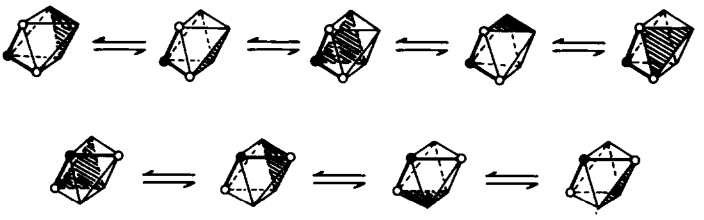
The solid state structure of a hydridotantalum complex has been elucidated in the case of $HTa(CO)_2(dppe)_2$. The compound was synthesized by UV irradiation of a THF solution of $HTa(CO)_4$dppe. Crystal data and some experimental data are shown in Table 4. Table 5 presents selected bonding parameters and Table 6 the fractional atom coordinates. A SCHAKAL plot of the molecule is given in Fig. 1. The compound crystallizes in the monoclinic space group $C2/c$ with (statistically) half a molecule of crystal THF per complex molecule. The $Ta(CO)_2p_4$ moiety is distorted octahedral, with tantalum and the four phosphorus atoms in a distorted tetragonal plane and the almost ideally linear OC–Ta–CO axis perpendicular to this plane. This is strikingly different from the structure of $HTa(CO)_2(dmpe)_2$, in which the disposition of one of the CO ligands from the octahedral axis has been put forward as an argument for the hydride-capping of one of the octahedral faces

Table 3

NMR data for hydridotantalum complexes

Complex [a]	Configuration [b]	^{31}P NMR data [c]				^{1}H NMR data [c] (hydride region)		
		Spin system [d]	δ_A	$\delta_{A'/B}$	$J_{AA'/B}$	Spin system [d]		J(HP)
$HTa(CO)_4p_n$	*cis*							
p_n = pepe		AA′	37.6(d)	44.6(d)	8.3	AA′M	−3.7(dd)	22.6, 19.1
dcpe		A_2	51.9			A_2M	−4.3(t)	19.2
pmip						AA′M	−3.9(dd)	22.2, 18.2
2 pmip [e]						A_2M	−4.1(t)	25
dppm						A_2M	−2.98(t)	18.3
bdmpi						A_2M	−4.10(t)	23.5
						ABM	−4.08(dd)	23.7, 23.1
cp_3^*		$A_2(X)$	1.0			A_2M	−3.33(6)	22.7
bdepe		$A_2(Y)$	−9.3			A_2M	−4.10(t)	23.6
		AB(X)	1.5(d)	−6.3(d)	16.4	ABM	−4.07(dd)	25.6, 22.6
tdep		$A_2(XY)$	−9.3			A_2M	−4.1(t)	23.6
		$AB(X_2)$	−0.5(d)	−6.4(d)	14.3	ABM	−3.8(dd)	30.1, 15.9
$HTa(CO)_3p_n$								
p_n = p_3^* [f]	*mer*	A_2B	45.2(d)	72.7(t)	1.9	A_2BM	−2.33(td)	37, 18
cp_3^*	*fac*	A_3	1.04			A_3M	−4.01(q)	22.3
bdmpm	*fac*					A_2BM	−2.12(dt)	15.4, 5.7
	mer	A_2B	−25.7(d)	−31.9(t)	34.5	A_2BM	−2.76(td)	42.6, 20.1
bdepm	*fac*	A_2B	1.4(d)	−23.9(t)	17.1	A_2BM	−2.01(dt)	14.1, 5.5
	mer	A_2B	1.5(d)	−33(t)	33	A_2BM	−2.6(td)	36.5, 36.2
bdmpi	*mer*	A_2B	−26.2(d)	−5.8(t)	30	A_2BM	−4.1(t) [g]	23.5 [g]
tdep	*mer*	$A_2B(X)$	−1.5(d)	−15.2(t)	16.5	A_2BM	−3.2(td)	42.8, 16
$HTa(CO)_2p_n$	*trans*							
p_n = 2 dppe [f]		[h]				$A_2A'_2M$ [i]	−3.24(tt)	96, 17
2 pepe						$A_2A'_2M$	−4.55(tt)	89, 16
p_4^*		A_2B_2	78.9(d)	64.1(d)	15.2	A_2B_2M	−1.17(tt)	70.1, 12

[a] For abbreviations of p_n see Scheme 1. [b] Assuming an octahedral arrangement in the $\{Ta(CO)_mp_n\}$ moiety. [c] In THF at ambient temperature if not indicated otherwise. [d] Labelling for the phosphorus functions is as follows: Coordinated terminal P: A and A′, coordinated central P: B, dangling P: X (terminal), Y (central). M stands for the hydride ligand. [e] Coordinated through P^iPr. [f] From ref. 3. [g] Poorly resolved pseudo-triplet. [h] The 220 K spectrum shows two inequivalent sets of two PPh_2 groups with $\delta(^{31}P) = 44.2$ and 64.1 ppm [3]. [i] 210 K.



Scheme 3.

[7]. Although in $HTa(CO)_2(dppe)_2$, the hydride ligand has not been located explicitly, a face-capped octahedron is unlikely to be the molecular structure in this case. Rather, the unusually wide angle P3–Ta–P4 (116.7(1)° (as compared to P1–Ta–P2 = 91.1(1)°) is indicative of a hydride in the TaP_4 plane, lying between P3 and P4. Hence, the molecular structure is better described in terms of a

Table 4

Crystal data and some details of data collection and refinement for *trans*-$[HTa(CO)_2(dppe)_2] \cdot \frac{1}{2}THF$

Space group	$C2/c$
a (pm)	4839.6(10)
b (pm)	1112.9(2)
c (pm)	1859.9(3)
β (°)	97.82(2)
Z	8
V (pm^3)	$9924.3 \cdot 10^6$
Empirical formula	$C_{58}H_{53}O_{2.5}Ta$
Molecular mass (g mol^{-1})	1070.88
Density, calcd. (g cm^{-3})	1.42
Absorption coefficient (cm^{-1})	23
Scan range (°)	$4.5 < 2\theta < 28.0$
Symmetry-independent reflexes	11628
Significant ($F_o > 4\sigma(F_o)$) reflexions	8652
Refined parameters	783
R; R_w	0.0458; 0.0425
Residual electron density, max/min (e Å^{-1})	1.50/ − 2.74
Crystal dimensions (mm^3)	1.1 × 0.3 × 0.18

Table 5

Selected bond lengths (pm), bond angles (°) and best planes (deviations in pm)

Bond lengths		Angles	
Ta–C1	205.3(6)	C1–Ta–C2	177.0(3)
Ta–C2	205.3(7)	P1–Ta–P2	91.1(1)
Ta–P1	258.3(2)	P2–Ta–P3	75.9(1)
Ta–P2	261.2(2)	P3–Ta–P4	116.7(1)
Ta–P3	252.2(2)	P1–Ta–P4	76.5(1)
Ta–P4	250.7(2)	O1–C1–Ta	177.5(6)
C1–O1	118.6(8)	O2–C2–Ta	178.3(6)
C2–O2	116.5(8)		

plane P1(−9.5)–P2(9.7)–P3(−7.6)–P4(7.5)–Ta(1.9) pentagonal bipyramid, a structural type reported for $HTa(PPh_3)_2(dmpe)_2$ [8] and $HV(CO)_4dppe$ [9]. The complex is diamagnetic, as expected for a compound of composition $HTa(CO)_2(dppe)_2$, excluding an alternative formulation without H^- as an additional ligand, viz. $Ta(CO)_2(dppe)_2$, which, as a 17-electron species, should be paramagnetic. The P–metal–P chelate angle is smaller in $HTa(CO)_2(dppe)_2$ (75.9 and 76.5°) than in $V(CO)_2(dppe)_2$ (82.0°) and $HV(CO)_4(dppe)$ (81.5°), but similar to that of $HTa(CO)_2(dmpe)_2$ (75.8°).

Photo-induced reactions of hydridotantalum complexes

In contrast to the H–V bond in $HV(CO)_4dppe$, which under irradiation yields the diamagnetic $HV(CO)_2(dppe)_2$ [2] along with paramagnetic *trans*-$[V(CO)_2(dppe)_2]$ [1], the Ta–H bond is remarkably stable towards photo cleavage. Irradiation of $HTa(CO)_4p_{2/3}$ leads to the complexes $HTa(CO)_2(p_{2/3})_2$, formed in low yields only. The poor yields suggest that homolytic cleavage of the metal–hydrogen bond is also an accompanying reaction in the tantalum system, with the unstable 17-electron species undergoing rapid decomposition. Better yields of the dicarbonyl complexes are obtained from $HTa(CO)_3p_4$ (see Tables 2 and 3 for spectroscopic data). There is only one IR active $\nu(CO)$ band (Table 2), indicative of a *trans* disposition for the two CO ligands.

If irradiation is carried out in the presence of substrates, the hydride is replaced (Cl^-) or transferred (pentafulvenes, alkenes). These reactions cannot be carried out thermally. IR data for the reaction products are summarized in Table 7. Irradiation of a mixture of $HTa(CO)_4dppe$ and $[Et_4N]Cl$ leads, with loss of 2 CO, to the seven-coordinate chloro complex $ClTa(CO)_2(dppe)_2$. In solution, there is only one $\nu(CO)$ band, indicating a *trans* disposition of the two CO groups. In the solid state, two $\nu(CO)$ indicate *cis* configuration. The overall ligand arrangement is possibly that of a trigonal prism with the chloride capping the tetragonal face spanned by the P atoms, as in other hepta-coordinate halogenotantalum complexes [10–12] and in the corresponding niobium complex $ClNb(CO)_2(dppe)_2$ [13].

Chloro complexes were also prepared by reductive carbonylation with Al of $TaCl_4$ in the presence of a phosphine. An example is $ClTa(CO)_3bdmpm$.

2-Methyl-2-butene reacts with $HTa(CO)_4pepe$ under photo-chemical conditions to form an isomeric mixture of two σ-alkyl complexes, the *anti*-Markovnikov adduct $pepe(CO)_4Ta{-}CH(Me)CHMe_2$ (**5**), and the Markovnikov adduct $pepe(CO)_4Ta{-}CMe_2CH_2Me$ (**6**) (Scheme 2). As expected, **5** is the main product in this "hydrotantalation" reaction. The IR pattern (Table 4) clearly differs from that of $HTa(CO)_4pepe$ (1990s, 1850vs,br cm^{-1}). The ^{31}P resonances ($\delta(^{31}P) = 34.4$ [PEt_2] and 41.6 ppm [PPh_2]) are shifted to high magnetic field by *ca.* 3 ppm relative to $HTa(CO)_4pepe$. The two isomers show distinctive ^{13}C NMR data: there are two broad plateau-like resonances, indicative of carbon coupling to the ^{181}Ta nucleus (nuclear spin $I = 7/2$) at $\delta(^{13}C) = 37.5$ (**5**) and 29.3 ppm (**6**). From the overall width at half height (78 Hz), a coupling constant $^1J(^{181}Ta{-}^{13}C)$ 9.8(5) Hz is obtained.

If it is assumed that coupling is completely conserved, the resonance involves eight components arising from the interaction of the nuclei ^{13}C and ^{181}Ta (spin 7/2), broadened to the extent at which the individual components are not resolved. Division of $W_{1/2}$ by 8 then provides an estimate for the upper limit of $J(C{-}Ta)$.

Table 6

Fractional coordinates and isotropic temperature factors for the non-hydrogen atoms

Atom	x	y	z	U_{eq}
Ta	0.3620(1)	0.3294(1)	0.4568(1)	0.032(1)
CO1	0.3603(1)	0.1600(6)	0.4997(4)	0.046(6)
O1	0.3597(1)	0.0640(4)	0.5270(3)	0.067(6)
CO2	0.3617(1)	0.5006(6)	0.4156(3)	0.045(6)
O2	0.3610(1)	0.5969(4)	0.3908(3)	0.068(6)
P1	0.4117(1)	0.3284(2)	0.5278(1)	0.040(1)
P2	0.3808(1)	0.2544(2)	0.3395(1)	0.043(2)
P3	0.3186(1)	0.2955(1)	0.3677(1)	0.037(1)
P4	0.3553(1)	0.4121(1)	0.5786(1)	0.037(1)
C1	0.4077(1)	0.3249(7)	0.6251(4)	0.051(7)
C2	0.3540(2)	0.3005(6)	0.2647(3)	0.051(7)
C3	0.3261(1)	0.2531(7)	0.2755(3)	0.049(7)
C4	0.3886(1)	0.4255(6)	0.6411(3)	0.047(6)
C11	0.3329(1)	0.3282(6)	0.6340(3)	0.042(6)
C12	0.3332(2)	0.3560(6)	0.7072(3)	0.054(7)
C13	0.3168(2)	0.2897(8)	0.7491(4)	0.072(9)
C14	0.3003(2)	0.1978(7)	0.7197(4)	0.068(9)
C15	0.2999(2)	0.1710(7)	0.6469(4)	0.060(8)
C16	0.3155(2)	0.2351(6)	0.6039(3)	0.051(7)
C21	0.3413(2)	0.5653(5)	0.5804(3)	0.045(6)
C22	0.3579(2)	0.6603(6)	0.5628(4)	0.066(9)
C23	0.3473(3)	0.7775(7)	0.5586(5)	0.089(13)
C24	0.3207(3)	0.8003(7)	0.5715(5)	0.088(14)
C25	0.3042(2)	0.7075(8)	0.5865(4)	0.076(10)
C26	0.3137(2)	0.5889(7)	0.5920(4)	0.056(8)
C31	0.2965(1)	0.1704(6)	0.3900(3)	0.041(5)
C32	0.2708(2)	0.1881(7)	0.4150(4)	0.057(7)
C33	0.2565(2)	0.0901(8)	0.4384(5)	0.074(10)
C34	0.2671(2)	−0.0225(8)	0.4362(5)	0.076(10)
C35	0.2914(2)	−0.0421(6)	0.4113(4)	0.063(9)
C36	0.3069(2)	0.0531(6)	0.3893(4)	0.052(7)
C41	0.4122(2)	0.3152(7)	0.3080(4)	0.058(8)
C42	0.4184(2)	0.4349(8)	0.3205(4)	0.071(9)
C43	0.4410(2)	0.4894(10)	0.2951(5)	0.090(12)
C44	0.4581(2)	0.4253(13)	0.2586(7)	0.106(15)
C45	0.4546(3)	0.2985(17)	0.2485(8)	0.163(26)
C46	0.4293(2)	0.2488(11)	0.2707(6)	0.108(14)
C51	0.3833(2)	0.0927(6)	0.3206(4)	0.049(7)
C52	0.3753(2)	0.0421(7)	0.2523(4)	0.065(9)
C53	0.3760(2)	−0.0808(8)	0.2415(5)	0.081(11)
C54	0.3852(2)	−0.1570(8)	0.2990(6)	0.088(12)
C55	0.3930(2)	−0.1083(7)	0.3669(5)	0.072(10)
C56	0.3920(2)	0.0159(7)	0.3773(4)	0.057(7)
C61	0.4375(1)	0.4510(6)	0.5295(4)	0.045(6)
C62	0.4300(2)	0.5582(6)	0.4948(4)	0.056(8)
C63	0.4483(2)	0.6539(7)	0.4986(5)	0.074(10)
C64	0.4746(2)	0.6431(8)	0.5371(6)	0.077(11)
C65	0.4820(2)	0.5378(9)	0.5707(5)	0.073(10)
C66	0.4642(2)	0.4409(7)	0.5678(4)	0.060(8)
C71	0.2935(1)	0.4211(5)	0.3504(3)	0.041(6)
C72	0.2749(2)	0.4275(7)	0.2864(4)	0.054(7)
C73	0.2566(2)	0.5232(8)	0.2733(4)	0.064(9)

Table 6 (continued)

Atom	x	y	z	U_{eq}
C74	0.2551(2)	0.6093(7)	0.3254(5)	0.065(9)
C75	0.2729(2)	0.6026(7)	0.3888(4)	0.063(9)
C76	0.2920(2)	0.5112(7)	0.4013(3)	0.051(7)
C81	0.4337(1)	0.1979(6)	0.5171(4)	0.049(7)
C82	0.4313(2)	0.0925(7)	0.5568(5)	0.065(9)
C83	0.4465(2)	−0.0097(8)	0.5413(6)	0.081(12)
C84	0.4629(2)	−0.0083(10)	0.4897(7)	0.095(14)
C85	0.4659(2)	0.0959(9)	0.4488(6)	0.082(11)
C86	0.4511(2)	0.1987(6)	0.4628(5)	0.063(9)

Table 7

Selected spectroscopic data for chloro-, alkyl- and cyclopentadienyl-tantalum complexes, THF solutions

Compound	
$ClTa(CO)_3bdmpm$	$\nu(CO)$ 1930 1830 1805 cm^{-1}
$ClTa(CO)_2(dppe)_2$	$\nu(CO)$ 1730 cm^{-1}
η^5-$(C_5H_4CHMe_2)Ta(CO)_3dppm$	$\nu(CO)$ 1930s 1830,1805vs cm^{-1}
	$\delta(P_A)$ 25.5d, $\delta(P_X)$ −25.4d; $J = 51$ Hz
cis-$[\eta^5$-$(C_5H_4CHMe_2)Ta(CO)_2dppe]$	$\nu(CO)$ 1830s 1760s cm^{-1}
cis-$[\eta^5$-$(C_5H_4CHRR')Ta(CO)_2p_3^*]$ [a]	$\nu(CO)$ 1860s 1785s cm^{-1}
	$\delta(P_A)$ 82.0d, $\delta(P_B)$ 65.4dd, $\delta(P_X)$ −11.3d ppm
	J_{AB} 10, J_{BX} 31 Hz
cis-$[\eta$-$C_5H_{11}Ta(CO)_4pepe]$ [b]	$\nu(CO) = 1925$m, 1829sh, 1818vs cm^{-1}
	$\delta(PPh_2)$ 41.6, $\delta(PEt_2)$ 34.4 ppm

[a] IR data for R = R′ = Me, Ph and for R = H, R′ = NMe_2; ^{31}P NMR data for R = H, R′ = NMe_2.

[b] See Scheme 2, compounds **5** and **6**, for the alkyl ligand.

Hydride transfer also takes place when the hydridotantalum complexes $HTa(CO)_{6-n}p_n$ are irradiated in the presence of pentafulvenes. As with hydridovanadium complexes [14], ring-substituted η^5-cyclopentadienyl complexes are formed (eq. 1). Di- and tri-tertiary phosphines (dppe and p_3^*) yield the *cis*-dicarbonyl species $Cp'Ta(CO)_2p_n$. With p_n = dppm, the tricarbonyl complex $(C_5H_4CHMe_2)Ta(CO)_3dppm$ is obtained, formation of a strained four-membered

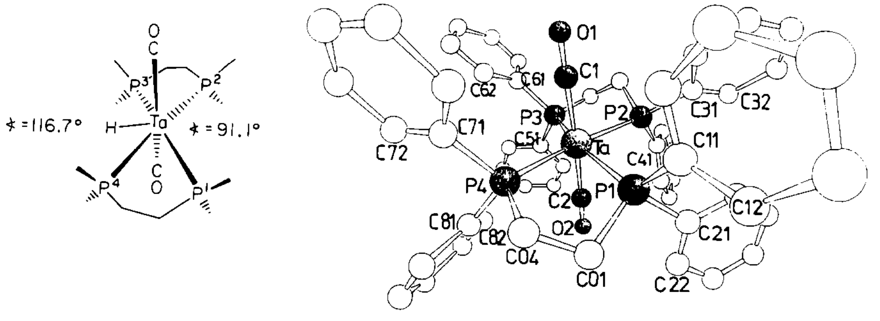
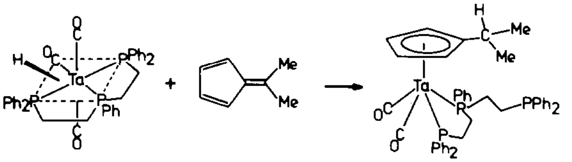


Fig. 1. Schematic representation of $HTa(CO)_2(dppe)_2$ and SCHAKAL perspective drawing of the $Ta(CO)_2P_4$ moiety (the hydride ligand has not been localized explicitly).

chelate ring thus being avoided. Support for the view that the reaction described by eq. 1 is in fact a hydride transfer from the metal to the *exo* carbon of the fulvene is provided by the formation of η^5-$\{C_5H_4CDMe_2\}Ta(CO)_2$dppe with $DTa(CO)_4$dppe. The deuterido complex was generated in a suspension of *tert*-butyl chloride and carbonylphosphinetantalate in hexane/D_2O, a reaction originally described for the preparation of $HV(CO)_4$dppe by Ellis *et al.* [15].



(1)

Experimental

General

All operations were conducted under inert gas in dry, oxygen-free solvents.

Irradiations with a high pressure mercury lamp (HPK 125, Philips) were carried out either "internally" (A) or "externally" (B). A: For internal irradiation, a 150 ml DEMA irradiation vessel (Mangels, Bonn) equipped with a water-cooled quartz immersion well was used. To agitate the solution and to carry off carbon monoxide evolved during irradiation, N_2 was continuously passed through a filter plate in the bottom of the vessel. B: for external irradiation a Duran Schlenk tube of 20–50 ml capacity with a gas inlet equipped with a filter plate at the bottom to allow passage of N_2 was used. In this case, the immersion well carrying the mercury lamp was placed close to the Schlenk tube. The advantage of the latter arrangement is the smaller probe volume and the fact that short-wave UV ($\lambda < 360$ nm) is filtered out, preventing damage to the phosphines. Reaction times are usually longer with arrangement B.

Silica gel (Kieselgel 60 reinst., 70–230 mesh ASTM, Merck) was activated under high vacuum for 2 h and stored under nitrogen.

IR spectra were obtained on a Perkin–Elmer 577 spectrometer as THF solutions in 0.1 mm KBr cuvettes or, if only sparingly soluble, as KBr pellets or in Nujol suspensions between KBr plates. ^1H NMR spectra (5 mm diameter vials, THF-d_8) were recorded on Bruker AM 360 and MSL 300 spectrometers, and $^{31}P\{^1H\}$ NMR spectra (10 mm vials, THF/THF-d_8 2/1) on a Bruker AM 360 instrument at 145.8 MHz.

X-ray structure analyses were undertaken on a Syntex $P2_1$ diffractometer (Mo-K_α irradiation, graphite monochromator) at room temperature in the $\theta/2\theta$ scan mode. The programs SHELXS-86, PATSEE and MITHRIL [16–18], and SHELXS-76 [19] were used for the solution and refinement of the structures. H atoms were refined as rotors riding on the pivot C atoms with a common isotropic thermal factor for all H atoms. No absorption corrections were carried out. Suitable crystals grew within days at room temperature at the interface of THF solutions layered with heptane.

Hexacarbonyltantalate was prepared from freshly sublimed $TaCl_5$ by reductive carbonylation with lithium naphthalide in DME (normal pressure synthesis according to Ellis *et al.* [20]; yield: 15%), or with Mg–Zn in pyridine (high pressure synthesis according to Calderazzo *et al.* [21]; yield: 26%) and converted into stable $[Et_4N][Ta(CO)_6]$ [3]. Phosphines were purchased (dmpe, dcype, pepe and phenylated phosphines) or prepared by published procedures: bdepe, bdmpm, bdepm, tdep, tdmp [22], bdmpi and pmpi [1].

Preparation of complexes

Tetracarbonylphosphinetantalate(–I). 479 mg (1 mmol) of $[Et_4N][Ta(CO)_6]$ and an equivalent amount of the phosphine p_n were dissolved in 150 mL (A) or 20 mL (B) of THF and irradiated for 45 min (A) or 2 h (B). The colour changed from yellow through orange to dark red. The reaction was monitored by IR spectroscopy and the irradiation terminated when the IR bands characteristic of unsubstituted (ν(CO) = 1849 cm^{-1}) and monosubstituted carbonyltantalate (ν(CO) = 1960w-m) had disappeared. Concentration to *ca.* 10 mL and treatment with *ca.* 15 mL of pentane with vigorous stirring yielded viscous oils of compositions *cis*-$[Et_4N][Ta(CO)_4p_n]$. These were washed once with 5 mL of pentane. The viscous oils solidified upon drying under high vacuum, yielding red powders when finely ground. Yields were between 61 and 83%.

Carbonylhydridophosphinetantalum(I). A solution of 0.7 mmol of $[Et_4N]$ $[Ta(CO)_4p_n]$ in 10 mL of THF was placed on a column filled with silica gel (dimensions: 6 × 8 cm). Elution with 150 mL of THF for 20 min afforded orange coloured solutions containing the hydrido complexes. Concentration to 15 mL and treatment with 30 mL of pentane yielded the hydrido complexes as orange-red powders in yields of about 75%: $HTa(CO)_4p_n$ (p_n = dppm, dppp, dppb, dcype, pepe, pmip, bdepm, bdepe, bdmpi); $HTa(CO)_3p_n$ (p_n = cp_3^*, p_3^*, p_4^*, tdep, tdmp, bdmpm; see also ref. 3 for p_3^* and p_4^*).

Small amounts of $[Et_4N][Ta(CO)_5p_n]$ (and sometimes also $[Et_4N][Ta(CO)_6]$), which remains unconverted at the top of the column, can be extracted with acetonitrile.

The complexes *trans*-$[HTa(CO)_2p_n]$ (p_n = p_4^*, 2 pepe, 2 dppe; for the dppe complex see also ref. 3) were obtained by 1 h irradiation of a THF solution containing 0.55 mmol of $HTa(CO)_3p_4^*$ (method A), $HTa(CO)_4$dppe (method A), or $HTa(CO)_4$pepe (method B). The originally light-red solutions became dark-red during irradiation. After filtration and evaporation to dryness, the complexes were obtained as dark-red to black-red powders in 50% yields.

$DTa(CO)_4$dppe. A mixture of 0.78 mL (890 mg = 9.6 mmol) of freshly distilled *tert*-butyl chloride and 0.71 g (0.86 mmol) of $[Et_4N][Ta(CO)_4$dppe$]$ [3] with 4 mL of heptane was stirred at room temperature for 10 min. 11.7 mL of D_2O were then added and stirring continued for 90 min. The suspension was cooled to 0°C, and the residue ($DTa(CO)_4$dppe) filtered off. The orange-red powder was washed with three 5 mL portions of D_2O and dried under high vacuum. Yield: 67%.

$ClTa(CO)_2$(dppe)$_2$. A solution of 400 mg (0.57 mmol) of $HTa(CO)_4$dppe and 100 mg (0.58 mmol) of $[Et_4N]Cl$ in 40 mL of THF was irradiated for 45 min (method B). After filtration to remove small amounts of decomposition products, the solution was evaporated to dryness to yield 310 mg (0.42 mmol = 74%) of the dark-red chloro complex.

$ClTa(CO)_3$bdmpm. A suspension of 465 mg (1 mmol) of $TaCl_4 \cdot 2THF$ (prepared by reduction with Al of $TaCl_5 \cdot 2MeCN$ in THF) and 252 mg (1 mmol) of bdmpm in 50 mL of THF was treated with 0.5 mL of sodium amalgam (1%) and

stirred for 12 h while a slow CO stream was passed over the reaction mixture. After about 1 h, CO stretching bands began to grow in the IR spectrum. The solution was decanted from a black precipitate and filtered through 1 cm of pretreated (degassed) Celite. The dark-brown solution thus obtained was concentrated to 5 mL and treated with 20 mL of hexane. The solution was kept for several days at 0°C and 82 mg (0.15 mmol = 15% yield) of red-brown, powdery $ClTa(CO)_3$bdmpm then isolated.

$C_5H_{11}Ta(CO)_4$pepe. A solution of 300 mg (0.5 mmol) of $HTa(CO)_4$pepe and 1 g (14.3 mmol) of 2-methyl-2-butene in 20 mL of THF was irradiated for 3 h (method B). The yellow-orange solution turned dark red. The solution was filtered and the filtrate evaporated to dryness and washed with three 10 mL portions of hexane. After 2 h drying under high vacuum, $C_5H_{11}Ta(CO)_4$pepe was obtained as a brown-red, viscous oil, consisting of a mixture of *anti*-Markovnikov (main component) and Markovnikov adduct. Yield 230 mg (0.35 mmol = 69%).

Reactions of hydrido complexes with pentafulvenes. A solution of 0.8 g (0.98 mmol) of $HTa(CO)_3p_3^*$ and an equimolar amount of the fulvene in 40 mL of THF was irradiated (method B) for 1 h (6,6-dimethylfulvene), 2 h (6-dimethylaminofulvene) and 3 h (6,6-diphenylfulvene). The red solutions were concentrated to 10 mL, and the products precipitated with pentane, filtered off, and dried *in vacuo*. Yields of $Cp'Ta(CO)_2p_3^*$: 57% ($Cp' = C_5H_4CHMe_2$), 35% ($Cp' = C_5H_4$-CH_2NMe_2) and 42% ($Cp' = C_5H_4CHPh_2$). The reaction of $HTa(CO)_4$dppm with 6,6-dimethylfulvene (irradiation time 20 min) gave a red-brown solution, which was passed through a short column of silica gel. Concentration of the eluate to 5 ml yielded a precipitate of 0.55 g (0.76 mmol = 38%) of red-brown η^5-$C_5H_4CHMe_2Ta(CO)_3$dppm. Small amounts of a dicarbonyl complex were recovered from the mother liquor.

A solution of 400 mg (0.58 mmol) $DTa(CO)_4$dppe and 60 mg (0.57 mmol) 6,6-dimethylfulvene in 40 mL of THF was irradiated for 30 min. The THF was removed and the residue dried under high vacuum. 400 mg (0.53 mmol = 93%) of *cis*-[η^5-$C_5H_4CDMe_2Ta(CO)_2$dppe] (degree of deuteration *ca.* 80%; by ^1H NMR) were thus obtained.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (Re 431/6-3) and the Fonds der Chemischen Industrie.

References

1 D. Rehder, F. Süßmilch, W. Priebsch and M. Fornalczyk, J. Organomet. Chem., 411 (1991) 357.
2 D. Rehder, P. Oltmanns, M. Hoch, C. Weidemann and W. Priebsch, J. Organomet. Chem., 308 (1986) 19.
3 D. Rehder, M. Fornalczyk and P. Oltmanns, J. Organomet. Chem., 331 (1987) 207.
4 D. Rehder and U. Puttfarcken, J. Organomet. Chem., 184 (1980) 343.
5 K. Bachmann and D. Rehder, J. Organomet. Chem., 276 (1984) 177.
6 U. Puttfarcken and D. Rehder, J. Organomet. Chem., 185 (1980) 219; Z. Naturforsch., Teil B, 37 (1982) 348.
7 P. Meakin, L.J. Guggenberger, F.N. Tebbe and J.P. Jesson, Inorg. Chem., 13 (1974) 1025.
8 P.J. Domaille, B.M. Foxman, T.J. McNeese and S. Wreford, J. Am. Chem. Soc., 102 (1980) 4114.

9 T. Greiser, U. Puttfarcken and D. Rehder, Transition Met. Chem., 4 (1979) 168.
10 M.L. Luetgens, Jr., D.J. Santure, J.C. Huffman and A.P. Sattelberger, J. Chem. Soc., Chem. Commun., (1985) 552.
11 S. Datta and S.S. Wreford, Inorg. Chem., 16 (1977) 1134.
12 L.D. Brown, S. Datta, J.K. Kouba, L.K. Smith and S.S. Wreford, Inorg. Chem., 17 (1978) 729.
13 C. Felten, J. Richter, W. Priebsch and D. Rehder, Chem. Ber., 122 (1989) 1617.
14 D. Wenke and D. Rehder, J. Organomet. Chem., 273 (1984) C43; ibid., 348 (1988) 205.
15 A. Davison and J.E. Ellis, J. Organomet. Chem., 36 (1972) 131.
16 G.M. Sheldrick, SHELXS-86, Programs for Crystal Structure Solution, University of Göttingen, 1986.
17 E. Egert, PATSEE, Fragment Search by Integrated Patterson and Direct Methods, University of Göttingen, 1984.
18 C.J. Gilmore, MITHRIL, Integrated Direct-Methods Computer Program, J. Appl. Crystallogr., 17 (1984) 42.
19 G.M. Sheldrick, SHELXS-76, Programs for Crystal Structure Determination, University of Cambridge, 1974.
20 C.J. Dewey, J.E. Ellis, K.L. Fjare, K.M. Pfahl and G.F.P. Warnock, Organometallics, 2 (1983) 388.
21 F. Calderazzo, U. Englert, G. Pampaloni, G. Pelizzi and R. Zamboni, Inorg. Chem., 22 (1983) 1865.
22 M. Antberg, C. Prengel and L. Dahlenburg, Inorg. Chem., 23 (1984) 4170.