Mono- and Bis-η-cyclopentadienyl Derivatives of Niobium and Tantalum: Improved Synthetic Routes *via* Trialkyl(cyclopentadienyl)tin Reagents

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The compounds $[SnBu^n{}_3(\sigma\text{-}C_5H_4R)]$ (R = H or Me) have been used to prepare the species $[MCl_4(C_5H_4R)]$ (M = Nb or Ta, R = H or Me), $[TaX_2(\eta\text{-}C_5H_5)_2]$ (X = Cl or Br), and $[NbCl_2(\eta\text{-}C_5H_4Me)_2]$ in very high yields. Using these compounds as starting materials the following products have been prepared $[NbCl_4(\eta\text{-}C_5H_4Me)L]$ [L = MeCN, PhCN, $P(OMe)_3$, or $Ph_2PCH_2CH_2PPh_2$(dppe)], $[Ta(\eta\text{-}C_5H_5)_2H_3]$, and $[Ta(\eta\text{-}C_5H_5)_2Y_2]$ where $Y_2 = (SMe)_2$ or $PhCH_2Cl$. Partial hydrolysis of $[NbCl_4(\eta\text{-}C_5H_4Me)]$ gives the compound $[\{NbCl_3(\eta\text{-}C_5H_4Me)(OH_2)\}_2O]$. Reduction of $[NbCl_4(\eta\text{-}C_5H_5)]$ with $[\{AlEtCl_2\}_2]$ in the presence of dppe gives $[NbCl_3(\eta\text{-}C_5H_5)(dppe)]\cdot PhMe$. This reduces with sodium amalgam in the presence of carbon monoxide giving $[Nb(\eta\text{-}C_5H_5)(dppe)(CO)_2]$ which protonates in acid giving $[Nb(\eta\text{-}C_5H_5)(dppe)(CO)_2H][PF_6]$. The compounds $[Pt\{Ta(\eta\text{-}C_5H_5)_2(SMe)_2\}_2][PF_6]_2$ and $[NbBr_3(\eta\text{-}C_5H_5)(dppe)]\cdot PhMe$ are also described.

WITHIN recent years there has been increasing interest in the chemistry of cyclopentadienyl derivatives of niobium and tantalum.[1-10] Although the compounds $[Ta(\eta\text{-}C_5H_5)_2H_3]$ [11] and $[NbCl_2(\eta\text{-}C_5H_5)_2]$ [12] have long been known, they have not been readily available since their syntheses are either unreliable or inconvenient. Several years ago we found an improved route to $[NbCl_2(\eta\text{-}C_5H_5)_2]$ [13] which has since been the main source of the $[Nb(\eta\text{-}C_5H_5)_2]$ system. We set out to develop improved routes to the niobium and tantalum cyclopentadienyl compounds in order to facilitate the study of these systems which we believe will have a considerable and interesting chemistry.

Abel has shown that trialkyl(cyclopentadienyl)tin reagents could act as cyclopentadienylating agents towards transition metals, *via* metathetical exchange with a transition-metal halide *e.g.* equation (1).[14] Since this

$$[MnCl(CO)_5] + [SnMe_3(\sigma\text{-}C_5H_5)] \longrightarrow [Mn(\eta\text{-}C_5H_5)(CO)_3] + SnMe_3Cl + 2CO \quad (1)$$

tin reagent is soluble in light petroleum and toluene it seemed to us that it might have advantages as a cyclopentadienylating reagent towards those metal halides which are both strong Lewis acids and prone to react with ethers such as tetrahydrofuran. Further, the product $SnMe_3Cl$ is also soluble in toluene, whilst most cyclopentadienylmetal halides are only moderately soluble in toluene.

This paper describes the use of the compounds $[SnBu^n{}_3(\sigma\text{-}C_5H_4R)]$ in the synthesis of new and known cyclopentadienyl derivatives of niobium and tantalum. The tri-n-butyltin derivatives were used instead of trimethyltin analogues since tri-n-butyltin chloride is cheap and readily available. Some of the mono(cyclopentadienyl) halides described below have been independently synthesised, as recently communicated.[15]

This paper also shows that the η-cyclopentadienyl halide derivatives of niobium and tantalum are, as would be expected, useful precursors to a variety of organometallic derivatives of these metals. Preliminary descriptions of part of this work have been published.[16-18]

RESULTS

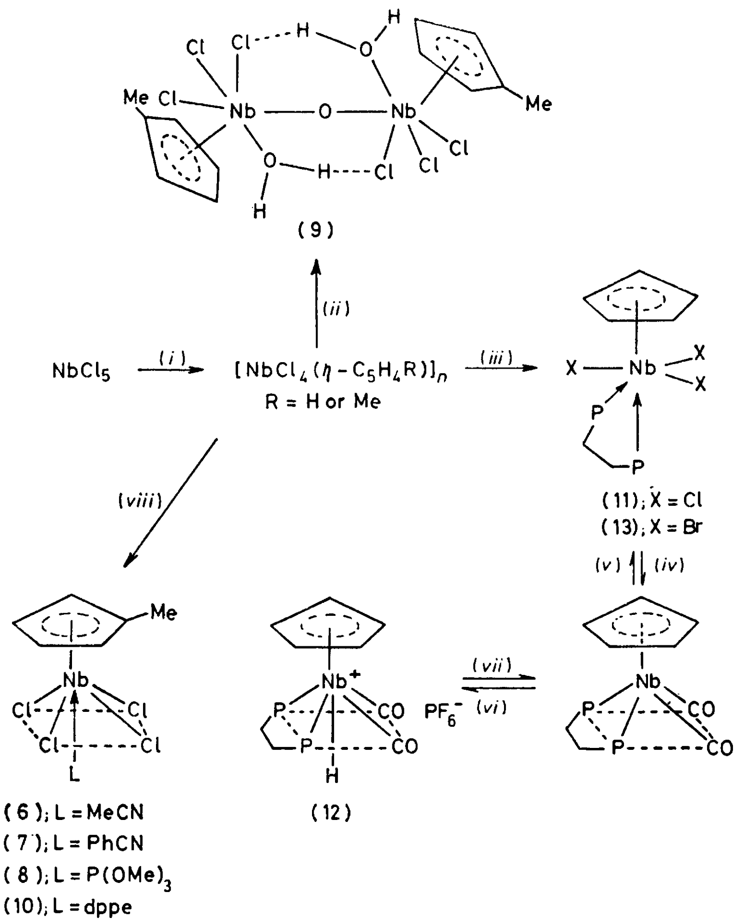
Chemical Studies.—Treatment of a toluene solution of pentachloroniobium with one mole equivalent of η-cyclopentadienyl(tri-n-butyl)tin, $[SnBu^n{}_3(\eta\text{-}C_5H_4R)]$ (1; R = H), gives almost immediate precipitation of pure red microcrystals of the compound $[NbCl_4(\eta\text{-}C_5H_5)]$, (2). In a similar manner the related compounds $[TaCl_4(\eta\text{-}C_5H_5)]$, (3), $[NbCl_4(\eta\text{-}C_5H_4Me)]$, (4), and $[TaCl_4(\eta\text{-}C_5H_4Me)]$, (5), may be prepared from the corresponding tin reagent (1; R = H or Me). The tetrahalides (2)—(5) are very sensitive to hydrolysis and on exposure to air they steadily decolourise to a white-yellow material. They are insoluble in non-polar organic solvents. However they dissolve in donor solvents such as MeCN, EtCN, PhCN, and $P(OMe)_3$. In some cases it was found possible to isolate pure 1 : 1 adducts from these solutions. For example the compounds $[NbCl_4(\eta\text{-}C_5H_4Me)L]$, were L = MeCN, (6), PhCN, (7), and $P(OMe)_3$, (8), were prepared in this way. The compounds (6)—(8) are soluble in dichloromethane or excess of the ligand but the solutions are unstable and they slowly turn from red to yellow and deposit pale material. There is little doubt that all the compounds (2)—(5) form adducts with these donor solvents but due to the decomposition we were not able to isolate analytically pure samples in most cases. However, the i.r. spectra were clearly indicative of the nature of the adducts. The solutions of the tetrahalides (2)—(5), in acetonitrile for example, could be treated with hydrogen chloride gas without rapid decomposition of the compounds. Indeed crystalline samples of the compounds together with some small quantities of decomposition material could be obtained by crystallisation of the compounds (2)—(5) from acetonitrile or other solvents saturated with hydrogen chloride gas. However, despite many attempts and although we were able to obtain crystals of excellent appearance in some cases we were unable to obtain samples which were suitable for crystal-structure determination. Thus we do not know for sure what are the structures of the compounds (2)—(5). We presume them to be dimeric.

Partial hydrolysis of (4) during one of the attempted crystallisations of (4) from dichloromethane saturated with hydrogen chloride, presumably slightly wet, gave the compound $[\{NbCl_3(\eta\text{-}C_5H_4Me)(OH_2)\}_2O]$, (9), whose crystal structure has been determined and is represented in Scheme 1. The original publication of this structure was incorrect as a hydroxyl group was shown in place of the H_2O ligand.[17]

The adduct $[NbCl_4(\eta\text{-}C_5H_4Me)(dppe)]$, (10), where dppe represents 1,2-bis(diphenylphosphino)ethane, was prepared by treatment of (4) with dppe in acetonitrile.

Treatment of (2) with dimeric ethylaluminium dichloride in toluene in the presence of dppe causes reduction to the four-valent state and bright violet crystals of the compound $[NbCl_3(\eta\text{-}C_5H_5)(dppe)]\cdot PhMe$, (11), are formed upon ethanolysis. The crystal structure has been determined[17] and is represented in Scheme 1. Compound (11) is soluble in dichloromethane and acetone. It crystallises from the latter as the acetone solvate. The e.s.r. spectrum of (11) shows the expected ten lines since ^{93}Nb has spin 9/2 with $\langle g \rangle = 2.014$ and $A_{iso.} = 133$ G.*

Reduction of (11) with sodium amalgam in the presence of 1 atm of carbon monoxide provides a convenient route to the known dicarbonyl $[Nb(\eta\text{-}C_5H_5)(dppe)(CO)_2]$. This, as would be expected, acts as a base and dissolves in dilute hydrochloric acid giving the hydrido-cation, and after addition of the PF_6^- anion, the compound $[Nb(\eta\text{-}C_5H_5)(dppe)(CO)_2H][PF_6]$, (12). The protonation is reversible and addition of base to (12) reforms the parent dicarbonyl.



SCHEME 1 Mono(cyclopentadienyl)niobium derivatives: (*i*) $[SnBu^n_3(C_5H_4R)]$ in toluene at r.t.; (*ii*) CH_2Cl_2 + traces of H_2O; (*iii*) $[\{AlEtCl_2\}_2]$ and dppe in C_6H_5Me at r.t. For X = Cl, the stereochemistry is essentially octahedral (*X*-ray) (ref. 17); (*iv*) sodium amalgam and 1 atm of CO at r.t.; (*v*) $PhCH_2X$ in C_6H_5Me; (*vi*) dilute hydrochloric acid then aqueous $[NH_4][PF_6]$, a square-planar arrangement for the $P_2(CO)_2$ ligands is envisaged; (*vii*) aqueous sodium hydroxide; (*viii*) pure MeCN, PhCN, $P(OMe)_3$, or dppe; a square-planar arrangement for the Cl atoms is envisaged

Treatment of $[Nb(\eta\text{-}C_5H_5)(dppe)(CO)_2]$ with benzyl bromide does not give a stable alkyl addition product. Rather the compound $[NbBr_3(\eta\text{-}C_5H_5)(dppe)]\cdot PhMe$, (13), is formed.

In an attempt to prepare the tantalum analogue of this compound, (3) was treated with dimeric ethylaluminium dichloride in the presence of dppe. To our surprise the product, after ethanolysis, was the known bis(η-cyclopentadienyl) derivative $[TaCl_2(\eta\text{-}C_5H_5)_2]$, (14) It was later found that the presence of dppe was not necessary for this reaction. In a further study we found that treatment of pentachlorotantalum with three mole equivalents of (1; R = H) gave the compound (14) in excellent yields. This represents a much improved synthesis of (14) compared with previous routes. In a similar manner, the compound $[TaBr_2(\eta\text{-}C_5H_5)_2]$, (15), may be prepared from (1; R = H) and $TaBr_5$.

We also found that treatment of (14) with $Na[AlH_2(OCH_2CH_2OMe)_2]$ gives the elusive trihydride $[Ta(\eta\text{-}C_5H_5)_2H_3]$, (16), in resonable yield. This reaction for niobium has been independently described by Labinger and Wong[19] who also investigated the mechanism. Treatment of (16) with n-butyl-lithium precipitates golden-yellow crystals, (17), which

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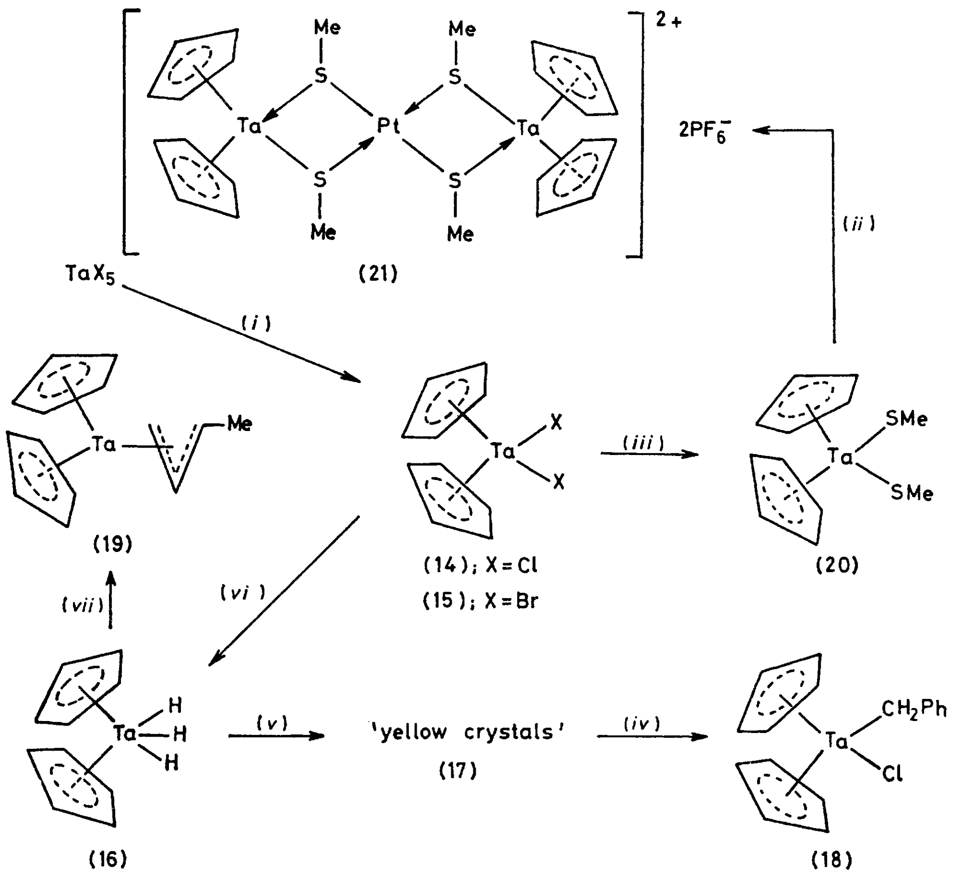
* Throughout this paper: 1 G = 10^{-4} T; 1 atm = 101 325 Pa; 1 mmHg ≈ 13.6 × 9.8 Pa.

are exceedingly sensitive to moisture and oxygen. They are insoluble in light petroleum and toluene and are decomposed by all other solvents investigated. By analogy with the compound [{Mo(η-C_5H_5)$_2$HLi}$_4$] [20] we presume that (17) contains Ta–Li bonds. In support of this proposal we observe that treatment of (17) with benzyl chloride gives the compound [TaCl(η-C_5H_5)$_2$(CH_2Ph)], (18), which is analogous to the *et al* [21] derivatives described previously by Schrock, *i.e.* [TaCl(η-C_5H_5)$_2$($CH_2C_6H_4Me$-*p*)]. The e.s.r. spectrum of (18) shows eight lines centred at $\langle g \rangle = 1.965$ with $A_{\text{iso.}} = 150$ G. We also note that treatment of (16) with butadiene gives the known [21] 1-methylallyl derivative [Ta(η-C_5H_5)$_2$(η-C_3H_4Me-1)], (19), in good yield.



SCHEME 2 Some bis(η-cyclopentadienyl)tantalum chemistry: (*i*) [$SnBu^n_3$(σ-C_5H_5)] in CH_2Cl_2, 80%; (*ii*) [$PtCl_2(NCPh)_2$] in CH_2Cl_2 then aqueous [NH_4][PF_6]; (*iii*) Na[SMe] in EtOH at r.t. for 1 h; (*iv*) $PhCH_2Cl$ at −90 °C, 60%; (*v*) $LiBu^n$ in hexane–toluene for 1 h at r.t.; (*vi*) butadiene in toluene at 80 °C for 6 h

Treatment of compound (14) with sodium methanethiolate gives red-purple [Ta(η-C_5H_5)$_2$(SMe)$_2$], (20). The niobium analogue has been described previously.[22] Compound (20) acts as a ligand and reacts with [$PtCl_2(NCPh)_2$] giving compound (21) with a diamagnetic trinuclear cation, [Pt{Ta(η-C_5H_5)$_2$(SMe)$_2$}$_2$][PF_6]$_2$.

DISCUSSION

The structures proposed for the new compounds and the new synthetic routes are shown in Schemes 1 and 2. The structures are based on the data given in the Table. As already stated, we do not know the structures of the compounds (2)—(5). Since they have Lewis-acid properties and can form adducts such as (6)—(8) they may well be dimeric with bridging chlorine ligands. The adducts (6)—(8) are mono(cyclopentadienyl) derivatives, as are the compounds (10) and (11) which are formed from compounds (4) and (2) respectively. Therefore, it seems most unlikely that the compounds (2)—(5) have a [M(η-C_5H_5)$_2$] system as, for example, in [(η-C_5H_5)$_2$$Cl_2$M–Cl–$MCl_5$]. Further, the mass spectrum of (3) shows highest bands at *m*/*e* = 351, 332, and 321 corresponding to the ions [$TaCl_3$(η-C_5H_5)]$^+$, [$TaCl_2$(η-C_5H_5)O]$^+$, and $TaCl_4^+$ respectively. Compound (3) does not sublime under vacuum so the absence of a parent-ion peak is not unexpected. We note that there are no bands assignable to fragments containing the [Ta(η-C_5H_5)$_2$] moiety. In contrast, the compounds (14), (18), and (20) all show bands assignable to the parent ions as well as many fragments containing the [Ta(η-C_5H_5)$_2$] system. We, therefore, can be reasonably confident that compound (3) does not contain this system. In which case the formation of (14) from (3) in the presence of [{$AlEtCl_2$}$_2$] is somewhat surprising since it must involve migration of a cyclopentadienyl group.

In conclusion, the above studies show that the trialkyl(cyclopentadienyl)tin reagent is clearly useful for the synthesis of η-cyclopentadienyl halides of niobium and tantalum and doubtless it will prove to be widely applicable, for example to the η-cyclopentadienyl halides of the Group 4 and 6 elements.

EXPERIMENTAL

All preparations and manipulations were carried out under dinitrogen or *in vacuo*. Solvents were carefully dried and distilled before use. Infrared spectra were obtained as mulls on a Perkin-Elmer 457 instrument. Electron spin resonance spectra were recorded on a JEOL JES-3BX instrument and were calibrated using 1,1-diphenyl-2-picrylhydrazyl. Mass spectra were measured on an A.E.I. M.S.9 instrument. Hydrogen-1 n.m.r. spectra were measured on a JEOL 60 MHz instrument. The compound $[SnBu^n_3(\sigma\text{-}C_5H_5)]$ was prepared as described. The analogues $[SnBu^n_3(\sigma\text{-}C_5H_4R)]$, where R = Me or Bu^n, were prepared in an identical manner using the salts $Na[C_5H_4R]$ instead of sodium cyclopentadienide.[22] The tin compounds were all distilled under vacuum before use and were stored under dinitrogen.

Analytical and spectroscopic data

			Analytical data (%) [a]		
	Compound	Colour	C	H	Halogen
(2)	$[NbCl_4(\eta\text{-}C_5H_5)]$	Bright red	20.15 (20.0)	1.8 (1.7)	47.1 [b] (47.3)
(3)	$[TaCl_4(\eta\text{-}C_5H_5)]$	Bright red	15.3 (15.5)	1.4 (1.3)	36.4 [c] (36.6)
(4)	$[NbCl_4(\eta\text{-}C_5H_4Me)]$	Red	23.05 (22.9)	2.3 (2.2)	43.2 (45.2)
(5)	$[TaCl_4(\eta\text{-}C_5H_4Me)]$	Red	18.05 (17.05)	1.9 (1.7)	33.35 (33.25)
(6)	$[NbCl_4(\eta\text{-}C_5H_4Me)(NCMe)]$	Red	27.3 (27.0)	3.1 (2.8)	38.75 [d] (40.0)
(7)	$[NbCl_4(\eta\text{-}C_5H_4Me)(NCPh)]$	Red	36.5 (37.4)	2.6 (2.9)	33.5 [e] (34.05)
(8)	$[NbCl_4(\eta\text{-}C_5H_4Me)\{P(OMe)_3\}]$	Red	24.5 (24.65)	3.6 (3.6)	32.5 [f] (32.4)
(9)	$[\{NbCl_3(\eta\text{-}C_5H_4Me)(OH_2)\}_2O]$	Red	23.8 (23.6)	3.3 (2.95)	
(10)	$[NbCl_4(\eta\text{-}C_5H_4Me)(dppe)]$	Red	44.8 (44.4)	3.6 (3.7)	27.2 (27.7)
(11)	$[NbCl_3(\eta\text{-}C_5H_5)(dppe)]\cdot PhMe$	Bright violet	60.3 (60.4)	5.1 (4.9)	13.7 (14.1)
(12)	$[Nb(\eta\text{-}C_5H_5)(dppe)(CO)_2H][PF_6]$	Yellow	52.3 (52.3)	4.2 [g] (4.0)	
(13)	$[NbBr_3(\eta\text{-}C_5H_5)(dppe)]\cdot PhMe$	Red-black	53.1 (51.4)	5.0 (4.2)	27.9 [h] (27.0)
(18)	$[TaCl(\eta\text{-}C_5H_5)_2(CH_2Ph)]$	Dark metallic	47.9 (46.65)	4.1 (3.9)	7.95 (8.1)
(20)	$[Ta(\eta\text{-}C_5H_5)_2(SMe)_2]$	Red-purple	35.1 (35.5)	3.6 (3.95)	
(21)	$[Pt\{Ta(\eta\text{-}C_5H_5)_2(SMe)_2\}_2][PF_6]_2$	Red-orange	21.4 (21.6)	2.5 [i] (2.7)	

[a] Calculated values are given in parentheses. [b] Nb: 31.1 (31.0) %. [c] Ta: 46.8 (46.65)%. [d] N: 4.1 (3.9)%. [e] N: 3.1 (3.35)% [f] ^1H n.m.r. data (in C_6D_6): τ 3.18, 3.72, relative intensity 4, multiplicity complex(**c**) (A_2B_2 pattern), $\eta\text{-}C_5H_4$; τ 6.19, **d** [*J*(P–H) 12 Hz), $(OMe)_3$); τ 7.5, *3*, **s**, Me; *M* (cryoscopic in benzene) 350 (439). [g] ^1H n.m.r. spectrum [in $(CD_3)_2CO$]: τ 2.45, *20*, **c**, Ph_4; τ 5.01, *5*, **s**, $\eta\text{-}C_5H_5$; τ 7.06, *4*, **c**, $(CH_2)_2$; τ 8.92, *1*, **t**, [*J*(P–H) 6.9 Hz], NbH; ν(CO) 1 970, 2 020 cm^{-1}, ν(NbH)? 1 704 cm^{-1}. [h] E.s.r. spectrum (in CH_2Cl_2): $\langle g \rangle = 2.044$, decet., $A_{iso} = 126$ G. [i] ^1H n.m.r. data [in $(CD_3)_2CO$]: τ 3.72, *20*, **s**, $4\eta\text{-}C_5H_5$; τ 6.92, *12*, **t** [*J*(Pt–H) 41 Hz], 4 Me.

Tetrachloro(η-cyclopentadienyl)tantalum, (3).—Finely ground tantalum pentachloride (17.47 g, 48.78 mmol) was dissolved in toluene (1 200 cm^3); after filtration from a small quantity of undissolved material the bright orange filtrate was treated with $[SnBu^n_3(\sigma\text{-}C_5H_5)]$ (18.2 g, 51.36 mmol), added dropwise with stirring. The mixture was stirred for a further 30 min at room temperature (r.t.) and the resulting yellow precipitate was allowed to settle whilst the mixture was cooled to 0 °C for 1 h. The supernatant liquor was decanted and the yellow solid washed with toluene and then light petroleum (b.p. 30—40 °C). The mustard-yellow product was dried *in vacuo*. The yield was 10.5 g; 56%.

Tetrachloro(η-cyclopentadienyl)niobium, (2).—Finely ground pure niobium pentachloride (26.7 g, 110 mmol) in dry, distilled dichloromethane (3 000 cm^3), was stirred at 40 °C until most of the solid had dissolved. The warm solution was filtered from a small quantity of residual solid and whilst still warm it was treated with η-cyclopentadienyl-(tri-n-butyl)tin (39 g, 110 mmol) added dropwise (15—30 min). The initially pale yellow solution developed an intense red colouration and a dark brown-maroon solid slowly separated. After stirring for a further 15 min the solution was cooled to 0 °C and stirred for a further 45 min. The solid was allowed to settle and the supernatant liquor was decanted. The residue was washed with toluene (50 cm^3) and then light petroleum (b.p. 60—80 °C, 50 cm^3) and dried *in vacuo*. The yield of the maroon microcrystalline solid was 22.8 g; 70%.

Tetrachloro(η-methylcyclopentadienyl)niobium, (4).—A filtered solution of pentachloroniobium (0.4 g, 8.9 mmol) in toluene (400 cm^3) was treated with $[SnBu^n_3(\eta\text{-}C_5H_4Me)]$ (3 cm^3, 10.5 mmol) in toluene (10 cm^3). A red precipitate settled almost immediately. The supernatant liquid was separated by filtration and the red microcrystalline residue was washed with light petroleum (b.p. 30—40 °C, 3 × 50 cm^3) and dried *in vacuo*, 1.6 g (58%). Dichloromethane can replace toluene as the reaction solvent but the yield is reduced to *ca.* 50%. Also, it is necessary to concentrate the solvent to obtain precipitation of the product. The product may not be recrystallised and its solutions steadily decompose.

Tetrachloro(η-*methylcyclopentadienyl*)*tantalum*, (5).—This was prepared in the same manner as the niobium analogue from pentachlorotantalum (4.6 g, 712.8 mmol) in dichloromethane (300 cm^3) and [SnBu$^n_3$(η-C$_5$H$_4$Me)] (3.5 cm^3, 12.3 mmol) in dichloromethane (10 cm^3). It was necessary to concentrate the reaction mixture to *ca.* 100 cm^3 to obtain precipitation of the product, 1.6 g (31%).

Tetrachloro(η-*methylcyclopentadienyl*)(*trimethyl phosphite*)-*niobium*, (8).—Pure [NbCl$_4$(η-C$_5$H$_4$Me)] (0.3 g) was dissolved in the minimum of trimethyl phosphite (*ca.* 1 cm^3) with warming (60 °C). The resulting red solution was cooled to 0 °C for 12 h giving red crystals. These were collected and recrystallised from toluene, 70%. The compound is soluble in dichloromethane and benzene. It is decomposed by water.

Benzonitriletetrachloro(η-*methylcyclopentadienyl*)*niobium*, (7).—Benzonitrile (3 cm^3) in toluene (10 cm^3) was added slowly to [NbCl$_4$(η-C$_5$H$_4$Me)] (0.3 g). The red solid dissolved and then a yellow-orange precipitate appeared. Hydrogen chloride gas was passed into the mixture giving a deep red solution. Light petroleum (b.p. 30—40 °C, 5 cm^3) was added giving a red precipitate. This was separated and washed with toluene–light petroleum (b.p. 30—40 °C), 1 : 2 (2 × 10 cm^3) and dried *in vacuo*. The compound slowly decomposed in air. It is soluble in dichloromethane but the solution shows evidence for steady decomposition.

Acetonitriletetrachloro(η-*methylcyclopentadienyl*)*niobium*, (6).—The compound [NbCl$_4$(η-C$_5$H$_4$Me)] (0.3 g) was dissolved in acetonitrile (30 cm^3) giving a red solution. This was cooled to −20 °C and after 4 h red microcrystals separated. These were collected, washed with acetonitrile (2 × 3 cm^3) then light petroleum (2 × 10 cm^3), and finally dried *in vacuo*, 41%. It was not found possible to recrystallise the compound as solutions showed slow decomposition.

1,2-*Bis*(*diphenylphosphino*)*ethanetetrachloro*(η-*methylcyclopentadienyl*)*niobium*, (10).—The compounds [NbCl$_4$(η-C$_5$H$_4$-Me)] (0.35 g) and dppe (1.0 g) were dissolved in acetonitrile (30 cm^3). The resulting red solution was filtered and cooled to 0 °C. After 6 h red microcrystals separated. These were collected and washed with acetonitrile (2 × 10 cm^3) and dried *in vacuo*, 50%. The compound dissolved in dichloromethane but the solutions showed evidence for steady decomposition.

Dichlorobis(η-*methylcyclopentadienyl*)*niobium*.—A solution of pentachloroniobium (1 g) in dichloromethane (50 cm^3) was treated with [SnBu$^n_3$(σ-C$_5$H$_4$Me)] (2.8 g) and the mixture was stirred for 3.5 h. The solvent was removed under reduced pressure and the residue was washed with light petroleum. It was then extracted with dichloromethane. The extract was filtered, concentrated under reduced pressure, and cooled giving brown crystals. These were collected, washed with light petroleum (b.p. 30—40 °C, 2 × 50 cm^3), and dried *in vacuo*, 70%.

Dichlorobis(η-*cyclopentadienyl*)*tantalum*, (14).—*Method A*. A solution of TaCl$_5$ (37.5 g, 0.105 mmol) in dichloromethane (1 500 cm^3) was treated with [SnBu$^n_3$(σ-C$_5$H$_5$)] (115 g, 0.315 mmol) at room temperature in a dropwise manner. The mixture was stirred for 15 h and the resulting deep green reaction mixture was filtered and toluene (500 cm^3) was added to the filtrate. The solution was concentrated under reduced pressure to 700 cm^3 and cooled to −20 °C. A green microcrystalline solid separated, which was collected, washed with toluene, and dried *in vacuo*, 25.2 g. The mother-liquor was further concentrated to 300 cm^3 and a further 9.6 g of green product were obtained. The total yield was 34.8 g; 87%.

Sublimation of the green crystals at 220 °C, 10^{-3} mmHg gave the brown crystalline form of [TaCl$_2$(η-C$_5$H$_5$)$_2$].

Method B. A stirred solution of [TaCl$_4$(η-C$_5$H$_5$)] (4.0 g) in dry toluene (300 cm^3) was treated with [{AlEtCl$_2$}$_2$] (30 cm^3 of a solution in toluene containing 250 g dm^{-3}). The mixture was shaken vigorously (20 min) until all the original yellow-red crystals had been replaced by a dark oil. The mixture was then cooled to −20 °C and ethanol was added dropwise with shaking until the oil had dissolved (*ca.* 10 cm^3). A brown crystalline precipitate appeared which was allowed to settle. The supernatant liquor was separated and the residue was washed with toluene (3 × 25 cm^3) and dried *in vacuo*, 1.2 g; 61%. The product was characterised by microanalysis and by the i.r. and mass spectrum as the pure compound [TaCl$_2$(η-C$_5$H$_5$)$_2$]. It is moderately stable in air and is soluble in acetone and dichloromethane giving green solutions. Treatment of the compound with ethanol, water, or tetrahydrofuran causes steady decomposition to a white material. The e.s.r. spectrum in dichloromethane showed an eight-line spectrum $\langle g \rangle = 1.94$; $A_{\text{iso.}} = 124$ G.

Dibromobis(η-*cyclopentadienyl*)*tantalum*, (15).—The procedure was essentially the same as used in method A for the dichloro-analogue starting from TaBr$_5$ (14.1 g, 25.0 mmol) in dichloromethane (500 cm^3) and [SnBu$^n_3$(σ-C$_5$H$_5$)] (25.5 g, 72 mmol). The yield was 9.6 g; 85%.

Bis(η-*cyclopentadienyl*)*trihydridotantalum*, (16).—The compound [TaCl$_2$(η-C$_5$H$_5$)$_2$] (7.22 g, 18.9 mmol) in dry toluene (100 cm^3) was treated dropwise with Na[AlH$_2$-(OCH$_2$CH$_2$OMe)$_2$] (12.2 g) in toluene (100 cm^3). The mixture was warmed to r.t. and stirred for 12 h. It was then cooled to 0 °C and water (5 cm^3) added slowly. The mixture was filtered and the residue was washed with toluene (2 × 25 cm^3). The combined filtrates were evaporated to dryness under reduced pressure and the reddish white residue was sublimed at 105 °C and 10^{-3} mmHg giving white crystals of the pure product, 2.5 g; 42%.

Bis(η-*cyclopentadienyl*)(η-1-*methylallyl*)*tantalum*, (19).—The compound [Ta(η-C$_5$H$_5$)$_2$H$_3$] (0.33 g, 1.1 mmol) in toluene (50 cm^3) was treated with butadiene (1.5 g) and the mixture was warmed to 80 °C for 6 h. The solvent was removed from the green reaction mixture under reduced pressure and the residue was extracted with light petroleum (b.p. 40—60 °C) (2 × 10 cm^3). The extract was filtered and concentrated to 10 cm^3 and cooled to −40 °C. Dark green crystals separated. These were collected, washed with cold light petroleum, and dried *in vacuo*, 0.21 g; 56%. The product was identified from the ^{1}H n.m.r. spectrum.[21] It could be sublimed at 100 °C and 10^{-3} mmHg.

Reaction between [Ta(η-C$_5$H$_5$)$_2$H$_3$] *and n-Butyl-lithium*.—A solution of [Ta(η-C$_5$H$_5$)$_2$H$_3$] (2.0 g, 1.1 mmol) in toluene (300 cm^3) was treated with n-butyl-lithium in hexane (5 cm^3 of a 1 mol dm^{-3} solution in hexane). The solution immediately became orange and after a few minutes yellow needle crystals separated. After 1 h the solution was filtered from the orange-yellow crystals which were washed with toluene (2 × 50 cm^3) and then used in the reaction described below.

Benzylchlorobis(η-*cyclopentadienyl*)*tantalum*, (18).—The yellow crystals prepared from [Ta(η-C$_5$H$_5$)$_2$H$_3$] (0.457 g, 1.5

mmol) and n-butyl-lithium, as described above, were suspended in dry toluene and the mixture was cooled to -90 °C. Excess of benzyl chloride (1.2 g) was added and the mixture was allowed to warm to r.t. The solution was filtered and the solvent was removed from the red filtrate under reduced pressure. The residue was dissolved in toluene (50 cm^3) and light petroleum (b.p. 60—80 °C, 50 cm^3) was added. The solution was then cooled to -20 °C for 12 h and dark metallic crystals separated, 0.29 g. Concentration of the mother liquors gave a further 0.15 g of the product. The combined product was washed with light petroleum (2×30 cm^3) and dried *in vacuo*, 0.44 g; 66%.

1,2-*Bis(diphenylphosphino)ethanetrichloro(η-cyclopentadienyl)niobium–Toluene* (1/1), (11).—A suspension of the compound $[NbCl_4(\eta\text{-}C_5H_5)]$ (1.86 g, 6.2 mmol) in cold toluene (0 °C, 130 cm^3) was treated with a solution of dimeric ethylaluminium dichloride in toluene (25 cm^3 of a solution of 0.226 g cm^{-3}, 48.5 mmol). The mixture was stirred for 30 min then dppe (2.47 g, 6.2 mmol) was added giving a red solution and a dark oil. After stirring for a further 10 min the mixture was then cooled to -40 °C. Ethanol at -40 °C (30 cm^3) was added and the mixture was allowed to warm to room temperature and was at the same time vigorously shaken. Bright violet crystals were formed in the mixture which was cooled to -30 °C for 4 h. The reaction mixture was filtered and the crystals were washed with ethanol (2×50 cm^3) then toluene (2×50 cm^3) and finally with light petroleum (b.p. 30—40 °C, 40 cm^3) and dried *in vacuo*, 3.49 g; 75%.

1,2-*Bis(diphenylphosphino)ethanetribromo(η-cyclopentadienyl)niobium–Toluene* (1/1), (13).—The compound $[Nb(\eta\text{-}C_5H_5)(dppe)(CO)_2]$ (0.357 g, 0.58 mmol) in toluene (80 cm^3) was treated with benzyl bromide (1 cm^3, 8.4 mmol). The mixture was heated to 60—70 °C for 6 h. Dark crystals formed together with a brown sediment. These were separated, washed with toluene and light petroleum, and dried *in vacuo*. The product was obtained as deep red-black crystals, 0.414 g; 80%.

1,2-*Bis(diphenylphosphino)ethanedicarbonyl(η-cyclopentadienyl)niobium*.—*Method A*. A suspension of $[NbCl_4(\eta\text{-}C_5H_5)]$ (0.53 g, 1.77 mmol) in toluene (100 cm^3) was treated with dppe (0.71 g, 1.77 mmol). An excess of sodium amalgam (40 g of a 1% solution, 17 mmol) was then added and the mixture was stirred under 1 atm of carbon monoxide for 1.5 days. The suspended amalgam was allowed to settle and the deep orange reaction mixture was filtered. The solvent was removed from the filtrate under reduced pressure giving an orange-red solid. This was recrystallised from diethyl ether–light petroleum at -30 °C as large red-orange crystals, yield, 0.36 g; 33%. The compound was identified from the i.r. spectrum.

Method B. The compound $[NbCl_3(\eta\text{-}C_5H_5)(dppe)]\cdot PhMe$ (1.14 g, 1.51 mmol) in toluene (100 cm^3) was treated with sodium amalgam (40 g of a 1% solution, 17 mmol). The mixture was stirred under 1 atm of carbon monoxide for 1.5 days. The product was isolated as described in method A, yield 0.60 g; 65%.

Bis(η-cyclopentadienyl)bis(methylthio)tantalum, (20).—Sodium ethoxide in ethanol, prepared by adding sodium (0.4 g) to pure, dry ethanol (40 cm^3), was cooled to -20 °C and methanethiol (2 cm^3) was added. Then $[TaCl_2(\eta\text{-}C_5H_5)_2]$ (0.7 g) was added and the mixture was stirred for 1 h at r.t. giving a deep red solution. The solvent was removed under reduced pressure and the dry residue was extracted with dichloromethane (3×50 cm^3). The red-purple extract was concentrated under reduced pressure and addition of light petroleum (b.p. 30—40 °C) separated deep red-purple crystals, 0.33 g; 45%.

The compound is air sensitive and was decomposed by water. It was soluble in dichloromethane, toluene, and acetone. The solutions show evidence for slow decomposition (hours).

Bis[bis(η-cyclopentadientyl)bis(methylthio)tantalum]platinum Bis(hexafluorophosphate), (21).—The compound $[PtCl_2(NCPh)_2]$ (0.1 g, 0.21 mmol) in dichloromethane (10 cm^3) was added to a freshly prepared solution of $[Ta(\eta\text{-}C_5H_5)_2(SMe)_2]$ (0.2 g, 0.5 mmol) in dichloromethane (10 cm^3). A red-orange precipitate separated. This was washed with dichloromethane (3×10 cm^3) and dried *in vacuo*. Analysis and the i.r. and ^{1}H n.m.r. spectra showed the product to be $[PtCl_2\{Ta(\eta\text{-}C_5H_5)_2(SMe)_2\}_2]\cdot 2H_2O$ (Found: C, 25.6; H, 3.2. Calc.: C, 25.9; H, 3.2%). The i.r. spectrum showed ν(OH) at 3 400 cm^{-1} and δ at 1 620 cm^{-1}. The compound is soluble in water and ethanol. Addition of ammonium hexafluorophosphate to the aqueous extract gave a red precipitate which was washed with water and dried *in vacuo* (70%). This compound is moderately stable in air (hours).

1,2-*Bis(diphenylphosphino)ethanedicarbonyl(η-cyclopentadienyl)hydridoniobium Hexafluorophosphate*, (12).—The compound $[Nb(\eta\text{-}C_5H_5)(dppe)(CO)_2]$ (0.56 g, 9.15 mmol) in acetone (20 cm^3) was treated with aqueous hydrochloric acid (60 cm^3 of 2 mol dm^{-3} solution). The aqueous layer rapidly developed a yellow colour. Addition of aqueous ammonium hexafluorophosphate gave a yellow precipitate which was collected, washed with water, and recrystallised from acetone–ethanol as yellow needles, yield 0.55 g; 79%.

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