Reactions of Unisolable Homoleptic Aryls of Niobium and Tantalum with PMe$_2$Ph and Bu^{t}NC. Crystal Structures of M(2,5-Me$_2$C$_6$H$_3$)$_2$(η^2-2,5-Me$_2$C$_6$H$_2$)(PMe$_2$Ph)$_2$, M = Nb or Ta, and Ta(η^2-PhCNBu^t)(η^2-Ph$_2$CNBu^t)$_2$(CNBu^t) †

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The tetraaryls, MR$_4$, M = Nb or Ta, R = 2-MeC$_6$H$_4$ or 2,5-Me$_2$C$_6$H$_3$, made *in situ* by interaction of MCl$_4$ and LiR or MgRBr react with PMe$_2$Ph to give the η^2-aryne compounds MR$_2$(η^2-aryne)(PMe$_2$Ph)$_2$. From the reaction of TaCl$_5$ and LiPh in Et$_2$O in the presence of PMe$_3$ the similar tantalum(IV) benzyne, TaPh$_2$(η^2-C$_6$H$_4$)(PMe$_3$)$_2$, is obtained. Interaction of a green solution probably of TaPh$_5$ with Bu^{t}NC produces the tantalum(V) compound, Ta(PhCNBu^t)(Ph$_2$CNBu^t)$_2$(CNBu^t), *via* multiple insertion reactions of Bu^{t}NC into the Ta–C bonds. The X-ray structures of M(2,5-Me$_2$C$_6$H$_3$)$_2$(η^2-2,5-Me$_2$C$_6$H$_2$)(PMe$_2$Ph)$_2$ (M = Nb or Ta) and Ta(η^2-PhCNBu^t)(η^2-Ph$_2$CNBu^t)(CNBu^t) have been determined. The isostructural arynes can be regarded as having a square-pyramidal structure with the C–C aryne bond occupying the axial site. The tantalum(V) compound contains one η^2-iminoacyl and two η^2-imine ligands.

The tetra[2-methylphenyl (*o*-tolyl)] and in some cases other tetraaryls of Cr, Mo, W, Re, Os, Ru and their structures are known;[1] those of Mo, W[2a] and Re[2b] react with tertiary phosphines, losing toluene and giving aryne (*o*-phenylene) complexes of formula MR$_2$(η^2-aryne)(PR$_3$)$_2$ (R = aryl).

We have attempted to make the *o*-tolyl compounds of Nb^{IV} and Ta^{IV} in solution and the *in situ* reaction with PMe$_2$Ph gives rise to the aryne derivatives MR$_2$(η^2-aryne)(PMe$_2$Ph)$_2$ which have been characterised by X-ray diffraction. We also report the isolation of a tantalum(IV) benzyne from the interaction of TaCl$_5$, LiPh and PMe$_3$ in Et$_2$O and an insertion reaction of pentaphenyltantalum, made *in situ*, with Bu^{t}NC which gives Ta(PhCNBu^t)(Ph$_2$CNBu^t)$_2$(NBu^t) whose X-ray structure has been determined.

Results and Discussion

Niobium- and Tantalum-(IV) *Compounds.*—The dark blue solutions formed on reaction of VCl$_4$ and LiPh in Et$_2$O were considered to contain VPh$_4$;[3] they decompose to yield biphenyl and other products but with alcohols react to give isolable VPh$_2$(OR)$_2$ species.[4] Although we have observed the formation of dark blue solutions in Et$_2$O from *o*-tolyllithium and VCl$_4$ at −78 °C we could not obtain evidence for trapping of any tetraaryl in reactions with PMe$_3$, Bu^{t}NC, CO, 2,2′-bipyridine (bipy), pyridine (py) *etc.*, all of which led to decomposition and intractable products.

The interaction of NbCl$_4$(thf)$_2$ (thf = tetrahydrofuran) or TaCl$_4$ in Et$_2$O at −78 °C with 4 equivalents of MgRBr or LiR, R = 2-MeC$_6$H$_4$ or 2,5-Me$_2$C$_6$H$_3$, also gives dark blue solutions that rapidly decompose at room temperature to give dark brown suspensions of intractable material; the biaryls can be sublimed out after evaporation of the solutions. Attempts to isolate stable products from what are probably the tetraaryls in solution on reactions with NO, NO$_2$, CO and Bu^{t}NC were unsuccessful. However, interaction with PMe$_2$Ph (PMe$_3$ reacts similarly but the products tend to be oily and difficult to crystallise) leads to mononuclear aryne complexes (Table 1) similar to those made for other elements.[2] The best procedure is to arylate the halide in Et$_2$O to generate the tetraaryls *in situ* which then react on addition of phosphine [equation (1)]; on work-up dark green (Nb) or orange-brown (Ta) crystals can be isolated.

$$\mathrm{MCl_4 + M'R \longrightarrow [MR_4] \xrightarrow{2PMe_2Ph} MR_2(aryne)(PMe_2Ph)_2} \quad (1)$$

$$\mathrm{M = Nb\ or\ Ta;\ M' = Li\ or\ MgBr}$$

The aryne compounds are paramagnetic having solution magnetic moments (Evans' method in toluene at 20 °C) characteristic for one unpaired electron, μ_B = *ca.* 1.7 in all cases. The EPR spectra in toluene at 293 K of the niobium(IV) compounds consist of sharp, thirty-line patterns centred at $g \approx 2$ due to coupling of the unpaired electron with the two ^{31}P nuclei, $a_P \approx$ 60 G, and with the ^{93}Nb nucleus ($I = \frac{9}{2}$, 100%), $a_{Nb} \approx 190$ G. The tantalum compounds showed no phosphorus coupling but had an eight-line pattern, centred on $g \approx 2$, $a_{Ta} \approx 100$ G from ^{181}Ta ($I = \frac{7}{2}$, 99.99%).

The arynes are thermally stable in the solid state but rapidly decompose on refluxing in hexane or toluene; they react with NO, NO$_2$, CO, O$_2$, Bu^{t}NC and Bu^{t}NCO but no well defined products could be isolated. Cyclic voltammetry data are collected in Table 2; both reversible and irreversible processes were observed for both niobium and tantalum compounds. Attempts to isolate reduced species by chemical reduction using sodium dihydronaphthylide in thf were unsuccessful.

The mechanism of formation of the arynes is doubtless similar to that proposed previously.[2b] The instability of the proposed intermediate tetraaryl is not too surprising, though some alkyls[5] and aryls[1,5] with sufficiently bulky ligands of Group 4 and 5 elements are stable in solution at room temperature. Some aryne complexes of the Group 5 elements

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† *Supplementary data available:* see Instructions for Authors *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: G = 10^{-4} T.

Table 1 Analytical and physical data for new compounds

Compound	Colour	M.p./°C	Analysis (%) C	Analysis (%) H
1 $Ta(2,5\text{-}Me_2C_6H_3)_2(\eta^2\text{-}2,5\text{-}Me_2C_6H_2)(PMe_2Ph)_2$	Orange-brown	189–190	61.3 (62.2)	6.2 (6.2)
2 $Nb(2,5\text{-}Me_2C_6H_3)_2(\eta^2\text{-}2,5\text{-}Me_2C_6H_2)(PMe_2Ph)_2$	Dark green	172–175	68.7 (70.2)	7.0 (7.0)
3 $Ta(2\text{-}MeC_6H_4)_2(\eta^2\text{-}2\text{-}MeC_6H_3)(PMe_2Ph)_2$	Orange-brown	157–160	60.2 (60.9)	5.8 (5.8)
4 $Nb(2\text{-}MeC_6H_4)_2(\eta^2\text{-}2\text{-}MeC_6H_3)(PMe_2Ph)_2$	Dark green	138–140	69.0 (69.2)	6.5 (6.5)
5 $Ta(\eta^2\text{-}PhCNBu^t)_2(\eta^2\text{-}Ph_2CNBu^t)(CNBu^t)$ *	Red	146–150 (decomp.)	65.3 (66.8)	6.7 (6.8)

* N, 6.3 (6.2%).

Table 2 Cyclic voltammetry of aryne compounds *

Compound	$E_{\frac{1}{2}}$/V
1	−2.26 (−0.82)
2	−2.34 (−0.84)
4	−2.38 (−1.07) (−0.43)

* On a OE-PP2 instrument in thf at 20 °C with 0.1 mol dm^{-3} $NBu^n{}_4PF_6$ as supporting electrolyte; platinum working, tungsten auxiliary and silver pseudo-reference electrodes. Sweep rate 50 mV s^{-1}. Values in parentheses indicate one-electron irreversible processes (E_p). Internal reference ferrocene–ferrocenium (0.000 V).

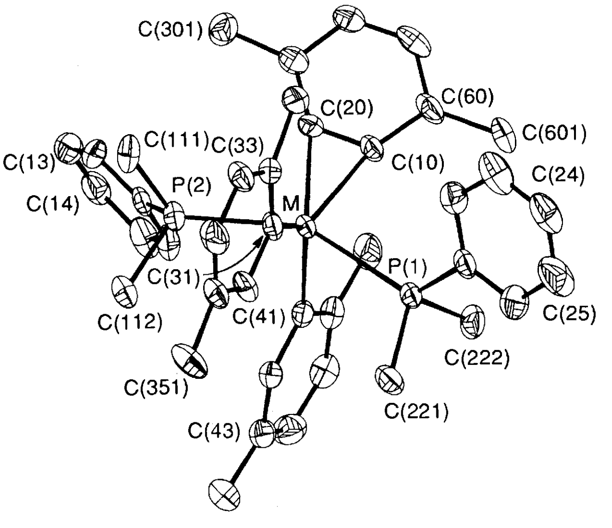


Fig. 1 The structure of the isomorphous niobium- and tantalum-(IV) compounds $M(2,5\text{-}Me_2C_6H_3)_2(\eta^2\text{-}2,5\text{-}Me_2C_6H_2)(PMe_2Ph)_2$

stabilised by cyclopentadienyl ligands are known and have a diverse reaction chemistry with small molecules.[6] Non-cyclopentadienyl compounds are rare, notably an η^2-benzyne of a bulky aryloxide of Ta^V formed as an intermediate in an intramolecular C–H activation,[7] and the 'polyphenylate' complexes of Nb and Ta shown to be bis(benzyne) species by X-ray structural determination.[8]

The two compounds studied by X-ray crystallography, $M(2,5\text{-}Me_2C_6H_3)_2(\eta^2\text{-}2,5\text{-}Me_2C_6H_2)(PMe_2Ph)_2$, M = Nb or Ta, are isostructural. A diagram of the niobium complex as representative is shown in Fig. 1; selected bond lengths and angles for both compounds are given in Table 3. Although actually six-co-ordinate (4C, 2P) it is most convenient to describe the geometry as square pyramidal with the midpoint of the C–C bond of the aryne occupying the axial site. The orientation of the ring places the aryne C–C bond closely parallel to the P–M–P plane. The arynes are almost symmetrically bound with the M–C distances equal within the experimental error. The aryne C–C distances seem to be slightly longer than those in other bis(aryne) compounds[8] although the high estimated standard deviations (e.s.d.s), especially in the tantalum compound, make meaningful comparisons difficult. The Nb–C and Ta–C aryl distances are very similar although the Nb–P bonds are slightly longer than the Ta–P bonds.

Table 3 Selected bond lengths (Å) and angles (°) for $M(2,5\text{-}Me_2C_6H_3)_2(\eta^2\text{-}2,5\text{-}Me_2C_6H_2)(PMe_2Ph)_2$ (M = Nb or Ta)

	M = Nb	M = Ta
P(1)–M	2.640(6)	2.621(8)
P(2)–M	2.626(6)	2.608(8)
C(41)–M	2.225(9)	2.202(18)
C(31)–M	2.184(11)	2.163(19)
C(10)–M	2.099(11)	2.076(18)
C(20)–M	2.113(12)	2.093(19)
C(20)–C(10)	1.317(14)	1.381(26)
P(2)–M–P(1)	151.2(1)	150.3(2)
C(41)–M–P(1)	85.8(3)	85.4(5)
C(41)–M–P(2)	80.0(4)	80.2(5)
C(31)–M–P(1)	82.1(3)	82.0(6)
C(31)–M–P(2)	86.8(4)	86.2(6)
C(31)–M–C(41)	127.3(5)	127.2(8)
C(10)–M–P(1)	121.8(4)	124.1(6)
C(10)–M–P(2)	86.9(4)	85.6(7)
C(10)–M–C(41)	114.7(5)	114.4(6)
C(10)–M–C(31)	115.2(4)	115.0(7)
C(20)–M–P(1)	85.5(4)	85.6(7)
C(20)–M–P(2)	123.3(4)	124.1(7)
C(20)–M–C(41)	119.5(5)	119.7(7)
C(20)–M–C(31)	110.4(4)	110.2(8)
C(20)–M–C(10)	36.4(4)	38.7(7)
C(11)–P(1)–M	119.7(3)	118.5(6)
C(101)–P(1)–M	115.5(4)	115.7(8)
C(102)–P(1)–M	114.9(5)	115.9(8)
C(201)–P(2)–M	116.9(5)	116.1(8)
C(202)–P(2)–M	112.3(5)	114.0(8)
C(21)–P(2)–M	121.0(3)	120.8(8)
C(42)–C(41)–M	116.5(8)	117.5(14)
C(46)–C(41)–M	124.6(8)	123.0(14)
C(10)–C(20)–M	71.2(7)	70.0(11)
C(20)–C(10)–M	72.3(7)	71.3(11)
C(60)–C(10)–M	162.9(8)	171.3(15)
C(30)–C(20)–M	162.9(8)	163.8(16)
C(32)–C(31)–M	127.8(8)	127.5(15)
C(36)–C(31)–M	117.8(7)	117.2(13)

Reactions involving Pentavalent Species.—We have attempted to isolate pentaaryls of Mo, Nb and Ta since $Ta(CH_2Ph)_5$ is reasonably stable at room temperature[9a] although homoleptic niobium alkyls are less so.[9b] Homoleptic unstable $TaPh_5$ has been mentioned[10] as a possible intermediate in the interaction

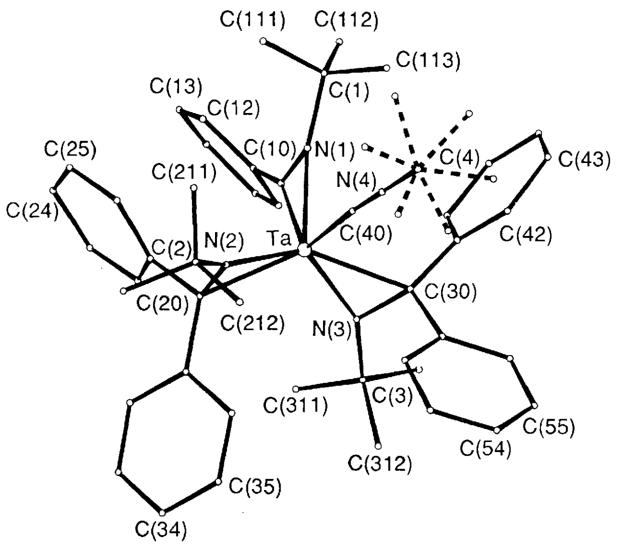


Fig. 2 The structure of $\mathrm{Ta(\eta^2\text{-}PhCNBu^t)_2(\eta^2\text{-}Ph_2CNBu^t)(CNBu^t)}$

Table 4 Selected bond lengths (Å) and angles (°) for $\mathrm{Ta(\eta^2\text{-}PhCNBu^t)(\eta^2\text{-}Ph_2CNBu^t)_2(CNBu^t)}$

N(3)–Ta	1.974(10)	N(1)–Ta	2.133(11)
N(2)–Ta	1.961(11)	C(10)–Ta	2.131(13)
C(20)–Ta	2.267(13)	C(30)–Ta	2.261(13)
C(40)–Ta	2.183(15)	C(30)–N(3)	1.465(15)
C(10)–N(1)	1.250(15)	C(20)–N(2)	1.415(15)

N(1)–Ta–N(3)	119.2(4)	N(2)–Ta–N(3)	126.5(5)
N(2)–Ta–N(1)	111.3(4)	C(10)–Ta–N(3)	100.9(5)
C(10)–Ta–N(1)	34.1(4)	C(10)–Ta–N(2)	111.9(5)
C(20)–Ta–N(3)	101.6(5)	C(20)–Ta–N(1)	114.3(5)
C(20)–Ta–N(2)	38.3(4)	C(20)–Ta–C(10)	93.3(5)
C(30)–Ta–N(3)	39.7(4)	C(30)–Ta–N(1)	105.9(5)
C(30)–Ta–N(2)	136.7(4)	C(30)–Ta–C(10)	111.3(5)
C(30)–Ta–C(20)	135.8(4)	C(40)–Ta–N(3)	114.3(5)
C(40)–Ta–N(1)	85.5(5)	C(40)–Ta–N(2)	85.0(5)
C(40)–Ta–C(10)	119.6(5)	C(40)–Ta–C(20)	123.1(5)
C(40)–Ta–C(30)	76.5(5)	C(10)–N(1)–Ta	72.9(7)
C(1)–N(1)–Ta	153.9(8)	C(1)–N(1)–C(10)	133.2(10)
C(2)–N(2)–Ta	148.8(7)	C(2)–N(2)–C(20)	128.1(10)
C(20)–N(2)–Ta	82.6(7)	C(3)–N(3)–Ta	152.5(7)
C(3)–N(3)–C(30)	126.4(10)	C(30)–N(3)–Ta	80.8(7)
N(1)–C(10)–Ta	73.0(8)	C(11)–C(10)–Ta	152.3(8)
C(11)–C(10)–N(1)	134.7(10)	N(2)–C(20)–Ta	59.1(6)
C(21)–C(20)–Ta	114.0(8)	C(21)–C(20)–N(2)	119.4(11)
C(31)–C(20)–Ta	124.8(9)	C(31)–C(20)–N(2)	115.1(10)
C(31)–C(20)–C(21)	113.9(10)	N(3)–C(30)–Ta	59.5(6)
C(41)–C(30)–Ta	112.9(8)	C(41)–C(30)–N(3)	120.5(10)
C(51)–C(30)–Ta	123.4(8)	C(51)–C(30)–N(3)	114.3(10)
C(51)–C(30)–C(41)	115.2(10)	N(4)–C(40)–Ta	175.9(10)

Table 5 Crystal data, details of intensity measurements and crystal refinement

Formula	$C_{40}H_{48}NbP_2$	$C_{40}H_{48}P_2Ta$	$C_{50}H_{61}N_4Ta$
M	683.475	771.717	899.01
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/a$	$P2_1/n$
a/Å	10.640(1)	10.641(2)	10.960(1)
b/Å	33.387(4)	33.451(7)	21.462(2)
c/Å	11.026(1)	11.025(3)	18.866(3)
α/°	90	90	90
β/°	113.14(1)	113.18(2)	91.91(2)
γ/°	90	90	90
U/Å^3	3601.80	3607.57	4435.26
Z	4	4	4
D_c/g cm^{-3}	1.261	1.421	1.346
F(000)	1436	1564	1848
μ/cm^{-1}	4.51	30.66	22.82
Total no. of reflections	12 581	5608	6576
No. of unique reflections	5864	5002	6154
No. of observed reflections $[F_o > 3\sigma(F_o)]$	3472	3287	3881
No. of refined parameters	388	388	500
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0.006 172	0.001 073	0.000 594
Final R	0.0676	0.0526	0.0484
Final R'	0.0701	0.0528	0.0456

of excess of LiPh and $\mathrm{TaCl_2(OC_6H_3Me_2\text{-}2,6)_3}$ which gives dark decomposition products. Although some $\mathrm{2\text{-}MeC_6H_4}$ complexes are more stable than C_6H_5 ones[1] the only identifiable product from interaction of MCl_5, M = Nb or Ta, with *o*-tolyllithium in Et_2O has been bitolyl arising from aryl group coupling and reduction of the metal. Since interaction of $MoCl_5$ with *o*-tolyllithium gave low yields of $\mathrm{Mo(C_6H_4Me\text{-}2)_4}$[11a] we also carried out this reaction in the presence of PMe_3 in the hope that a $\mathrm{Mo(C_6H_4Me\text{-}2)_5}$ intermediate might be trapped as a molybdenum(v) aryne, but on work-up the orange crystalline product proved to be only $\mathrm{MoCl_2(PMe_3)_4}$.[11b]

When $TaCl_5$ was arylated similarly in the presence of PMe_3 a low yield of an unstable green crystalline complex could be isolated. The compound has an EPR spectrum (293 K, toluene) similar to that of the arynetantalum compounds described earlier and the mass spectrum shows the molecular ion corresponding to $\mathrm{TaPh_2(\eta^2\text{-}C_6H_4)(PMe_3)_2}$ together with peaks indicating sequential loss of PMe_3. This suggests that a one-electron reduction of an initially pentavalent species has occurred. In an attempt to confirm the formation of $TaPh_5$ by trapping, a similar arylation of $TaCl_5$ using 5 equivalents of LiPh in Et_2O was carried out at −78 °C followed by slow warming to −10 °C, to give a deep green solution. This colour was also noted[8] in the reaction of $TaCl_5$ and excess of LiPh in thf which on warming led to $\mathrm{[TaPh_4(\eta^2\text{-}C_6H_4)_2\{Li(thf)\}_2]^-}$. Addition of $\mathrm{Bu^tNC}$ to the green solution and work-up led to a diamagnetic compound having a ^1H NMR spectrum showing three sets of CMe_3 resonances (δ 1.39, 1.08, and 1.00; ratio 1:1:2). The IR spectrum shows stretching frequencies for isocyanide (2175 cm^{-1}) and iminoacyl (1589 cm^{-1}) ligands.

X-Ray diffraction study confirms that the compound is an insertion product derived from $TaPh_5$ of formula $\mathrm{Ta(\eta^2\text{-}PhCNBu^t)(\eta^2\text{-}Ph_2CNBu^t)_2(CNBu^t)}$. A diagram of the molecule is shown in Fig. 2; selected bond lengths and angles are given in Table 4. The compound contains one η^2-iminoacyl and two η^2-imine groups, the latter formed by a double insertion of $\mathrm{Bu^tNC}$ into two $\mathrm{Ta\text{–}C_6H_5}$ bonds, and a co-ordinated $\mathrm{Bu^tNC}$ group. The formation of η^2-imine groups by a double migration of phenyl groups has only recently been observed in the reaction of $\mathrm{Bu^tNC}$ and the tantalum compound $\mathrm{TaPh_3(OC_6H_3Me_2\text{-}2,6)_2}$;[12] the resulting η^2-iminoacyl η^2-imine, $\mathrm{Ta(\eta^2\text{-}PhCNBu^t)(\eta^2\text{-}Ph_2CNBu^t)(OC_6H_3Me_2\text{-}2,6)_2}$ was characterised only spectroscopically. The insertion of $\mathrm{Bu^tNC}$ into $\mathrm{V(C_6H_2Me_3\text{-}2,4,6)_3(thf)}$ gives $\mathrm{V(\eta^2\text{-}2,4,6\text{-}Me_3C_6H_2CNBu^t)_3}$ which has been characterised by a recent X-ray study.[13]

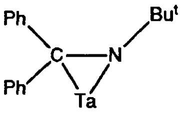
It is convenient to consider that the η^2-imine, $\mathrm{R_2C{=}NBu^t}$, groups co-ordinate as 2e dianionic ligands as in **I**, with single M–C, M–N and N–C bonds; the arylimino ligand $\mathrm{RCNBu^t}$ is considered as a 3e ligand as in **II**. Thus the tantalum atom can be assigned the v oxidation state; with $\mathrm{Bu^tNC}$ acting as a 2e donor an 18e count for Ta would require p_π–d_π donation from two imino nitrogen atoms as in **III**. The bond lengths for N–Ta seem to imply that N(2) and N(3) behave in this way.

Table 6 Fractional atomic coordinates (× 10^4) for $Nb(2,5-Me_2C_6H_3)_2(\eta^2-2,5-Me_2C_6H_2)(PMe_2Ph)_2$

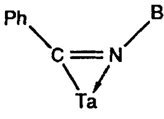
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Nb	1248(1)	1345.7(3)	2483(1)	C(32)	3100(8)	1309(3)	5628(9)
P(1)	−451(2)	1776(1)	3164(2)	C(33)	3346(9)	1189(4)	6892(9)
P(2)	2141(2)	654(1)	2015(2)	C(34)	2540(10)	907(4)	7191(10)
C(10)	2729(8)	1613(3)	1937(8)	C(35)	1432(10)	753(4)	6145(10)
C(20)	2133(8)	1901(3)	2334(9)	C(36)	1184(8)	874(3)	4882(9)
C(30)	2505(10)	2304(3)	2443(10)	C(41)	−611(8)	1130(3)	814(8)
C(40)	3595(12)	2388(4)	2069(11)	C(42)	−1504(8)	870(3)	1132(10)
C(50)	4209(10)	2093(4)	1596(11)	C(43)	−2738(9)	725(4)	150(12)
C(60)	3805(9)	1687(4)	1491(9)	C(44)	−3042(11)	839(4)	−1100(13)
C(11)	−1569(8)	2147(3)	2008(9)	C(45)	−2168(10)	1090(4)	−1475(10)
C(12)	−1726(10)	2532(3)	2351(11)	C(46)	−937(9)	1234(4)	−512(9)
C(13)	−2651(10)	2787(4)	1482(12)	C(301)	1921(12)	2649(4)	2986(11)
C(14)	−3381(10)	2666(4)	147(13)	C(601)	4454(10)	1358(4)	923(11)
C(15)	−3228(10)	2274(4)	−213(12)	C(111)	330(10)	2043(4)	4751(10)
C(16)	−2311(9)	2020(4)	705(10)	C(112)	−1739(10)	1488(4)	3518(11)
C(21)	3904(9)	495(3)	2930(9)	C(211)	1880(10)	544(4)	278(10)
C(22)	4806(9)	771(4)	3760(11)	C(221)	1215(9)	225(4)	2341(11)
C(23)	6193(11)	647(5)	4499(13)	C(321)	4057(10)	1633(4)	5436(10)
C(24)	6593(11)	265(5)	4333(13)	C(351)	567(12)	429(5)	6456(13)
C(25)	5699(12)	0(5)	3521(16)	C(431)	−3688(12)	474(5)	545(14)
C(26)	4321(11)	124(4)	2814(14)	C(461)	−36(12)	1497(4)	−924(11)
C(31)	1972(8)	1158(3)	4544(9)				

Table 7 Fractional atomic coordinates (× 10^4) for $Ta(2,5-Me_2C_6H_3)_2(\eta^2-2,5-Me_2C_6H_2)(PMe_2Ph)_2$

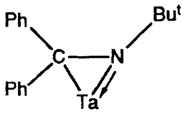
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ta	1248(1)	1346.6(7)	2475(1)	C(32)	3088(17)	1322(7)	5615(17)
P(1)	−445(5)	1768(2)	3159(5)	C(33)	3399(20)	1196(6)	6898(20)
P(2)	2124(5)	657(2)	2023(5)	C(34)	2557(22)	897(7)	7161(20)
C(10)	2729(17)	1592(5)	1914(17)	C(35)	1446(21)	750(7)	6117(19)
C(20)	2120(19)	1896(5)	2334(16)	C(36)	1158(17)	864(5)	4849(19)
C(30)	2479(19)	2321(7)	2416(18)	C(41)	−596(16)	1137(5)	822(17)
C(40)	3574(24)	2396(9)	2020(21)	C(42)	−1492(17)	880(5)	1126(21)
C(50)	4206(21)	2088(7)	1546(21)	C(43)	−2731(20)	723(6)	176(25)
C(60)	3797(17)	1701(6)	1485(18)	C(44)	−3026(21)	849(8)	−1146(29)
C(11)	−1554(16)	2138(6)	1975(17)	C(45)	−2173(24)	1099(7)	−1479(21)
C(12)	−1731(20)	2503(7)	2352(25)	C(46)	−913(19)	1247(5)	−506(19)
C(13)	−2627(24)	2789(7)	1394(31)	C(301)	4043(20)	1640(6)	5430(20)
C(14)	−3370(22)	2657(9)	109(23)	C(601)	4410(21)	1372(9)	918(23)
C(15)	−3233(22)	2265(8)	−208(23)	C(111)	334(21)	2047(7)	4721(19)
C(16)	−2290(19)	2015(7)	682(19)	C(112)	−1727(19)	1484(7)	3509(22)
C(21)	3920(18)	503(7)	2936(19)	C(211)	1857(21)	555(7)	295(19)
C(22)	4816(19)	782(9)	3800(20)	C(221)	1199(21)	223(6)	2313(22)
C(23)	6170(22)	649(11)	4499(27)	C(351)	574(24)	438(8)	6400(24)
C(24)	6595(24)	270(9)	4358(25)	C(321)	1919(25)	2648(7)	2935(22)
C(25)	5683(22)	6(8)	3543(27)	C(431)	−3692(22)	463(8)	519(29)
C(26)	4328(22)	118(6)	2821(27)	C(461)	−31(24)	1512(8)	−961(21)
C(31)	1972(17)	1159(6)	4515(16)				



I



II



III

The models described by formalisms **I** and **II** are also consistent with other geometrical features. Thus the C–N distances in the three-membered rings are 1.42(2), 1.47(2) Å for ligands N(2)–C(20) and N(3)–C(30) (type **I**) and 1.25(2) Å for N(1)–C(10) (type **II**). The Ta–C(40) distance of 2.18(2) Å is long as expected for a d^0 tantalum compound.

Experimental

The general methods and techniques have been described;[14] all operations were carried out under purified N_2 or Ar or in vacuum. Microanalyses were by Pascher, Remagen.

The starting materials were prepared as described: $NbCl_4(thf)_2$[15] $TaCl_4(PMe_2Ph)_2$,[16] $Li(C_6H_4Me-2)$ and $Li(C_6H_3Me_2-2,5)$.[17] IR spectra were recorded in KBr disks.

$Ta(2,5-Me_2C_6H_3)_2(\eta^2-2,5-Me_2C_6H_2)(PMe_2Ph)_2$ **1**.—To a stirred solution of $TaCl_4(PMe_2Ph)_2$ (0.7 g, 1.2 mmol) in Et_2O (40 cm^3) was added 4 equivalents of $Li(C_6H_3Me_2-2,5)$ (0.52 g, 4.7 mmol) in Et_2O (30 cm^3) and 2 equivalents of PMe_2Ph (0.3 cm^3) at −78 °C. After slow warming to room temperature with stirring for 24 h, removal of solvent left a brown oil that was dissolved in toluene (40 cm^3). After passage through a column of neutral Al_2O_3 (1 × 3 cm), which was then washed with

Table 8 Fractional atomic coordinates (× 10^4) for $Ta(\eta^2\text{-}PhCNBu^t)(\eta^2\text{-}Ph_2CNBu^t)_2(CNBu^t)$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ta	10 740.6(4)	1 189.8(2)	2 494.3(2)	C(43)	9 434(13)	3 536(6)	2 398(10)
N(3)	8 995(7)	1 222(4)	2 717(4)	C(44)	9 569(13)	3 628(7)	3 136(10)
N(1)	11 994(8)	1 789(4)	3 051(5)	C(45)	9 485(11)	3 107(7)	3 582(8)
N(2)	11 589(8)	498(4)	2 043(5)	C(46)	9 295(10)	2 500(6)	3 306(7)
N(4)	11 393(9)	2 024(5)	1 040(5)	C(51)	8 286(10)	1 721(5)	1 567(6)
C(10)	11 566(9)	1 426(5)	3 497(6)	C(52)	8 577(12)	1 286(6)	1 058(6)
C(20)	11 151(11)	160(5)	2 627(6)	C(53)	7 809(15)	1 180(7)	464(8)
C(30)	9 054(11)	1 771(5)	2 258(6)	C(54)	6 813(17)	1 568(8)	349(9)
C(40)	11 210(11)	1 719(5)	1 554(7)	C(55)	6 524(14)	2 015(7)	845(9)
C(11)	11 752(11)	1 336(5)	4 275(5)	C(56)	7 244(13)	2 110(7)	1 454(8)
C(12)	12 919(12)	1 233(6)	4 587(6)	C(1)	12 906(10)	2 318(6)	3 104(7)
C(13)	13 002(12)	1 140(6)	5 315(7)	C(2)	12 262(11)	249(5)	1 409(7)
C(14)	11 989(13)	1 181(7)	5 740(7)	C(3)	7 875(10)	957(6)	3 028(6)
C(15)	10 833(14)	1 273(7)	5 435(7)	C(4)	11 628(13)	2 384(6)	397(6)
C(16)	10 730(11)	1 345(5)	4 688(6)	C(111)	14 124(12)	2 025(7)	2 990(10)
C(21)	12 008(11)	13(5)	3 244(6)	C(112)	12 866(15)	2 640(6)	3 855(8)
C(22)	11 541(11)	−172(5)	3 882(6)	C(113)	12 531(11)	2 793(6)	2 540(8)
C(23)	12 326(13)	−332(6)	4 463(7)	C(211)	13 444(13)	634(7)	1 336(8)
C(24)	13 632(13)	−296(6)	4 398(8)	C(212)	11 460(13)	330(6)	730(6)
C(25)	14 069(12)	−77(6)	3 774(8)	C(213)	12 602(12)	−456(5)	1 510(7)
C(26)	13 300(11)	75(5)	3 202(7)	C(311)	8 274(11)	421(6)	3 515(6)
C(31)	10 260(11)	−365(5)	2 435(6)	C(312)	6 958(11)	693(6)	2 452(8)
C(32)	10 285(11)	−944(5)	2 770(7)	C(313)	7 202(11)	1 462(7)	3 467(7)
C(33)	9 467(12)	−1 417(6)	2 562(8)	C(411)	10 657(23)	2 898(12)	336(14)
C(34)	8 589(13)	−1 325(6)	2 020(9)	C(41B)	11 781(41)	3 077(21)	625(24)
C(35)	8 573(12)	−748(7)	1 688(8)	C(412)	12 949(25)	2 603(13)	455(15)
C(36)	9 376(12)	−270(6)	1 874(8)	C(42B)	12 690(43)	2 087(21)	83(25)
C(41)	9 137(10)	2 404(5)	2 569(7)	C(413)	11 445(24)	1 961(11)	−238(14)
C(42)	9 207(11)	2 923(5)	2 130(8)	C(43B)	10 565(51)	2 256(25)	−81(30)

toluene (40 cm^3), the combined solution was evaporated and the residue extracted with hexane (2 × 30 cm^3), reduced to 10 cm^3 and cooled (−20 °C) to give orange-brown crystals. Yield: 0.55 g, 56%. IR: 3010s, 2980s, 2900s, 1427w, 1362s, 1321m, 1290w, 1026m, 908s, 903m, 626w, and 606w cm^{-1}

$Nb(2,5\text{-}Me_2C_6H_3)_2(\eta^2\text{-}2,5\text{-}Me_2C_6H_2)(PMe_2Ph)_2$ **2**.—This was obtained as for compound **1** from $NbCl_4(thf)_2$ (1.0 g, 2.64 mmol), $(C_6H_3Me_2\text{-}2,5)MgBr$ (9.6 cm^3 of a 1.1 mol dm^{-3} solution in thf) and PMe_2Ph (0.7 cm^3) in thf (70 cm^3) at −78 °C. The final hexane extract (15 cm^3) gave green crystals on cooling. Yield: 1.0 g, 56%. IR: 2960s, 2924s, 2855s, 1437w, 1384s, 1261s, 1100s, 1026s, 942w, 923m, 908w, 795s, 744m, 739m, 695m and 621w cm^{-1}

$Ta(2\text{-}MeC_6H_4)_2(\eta^2\text{-}2\text{-}MeC_6H_3)(PMe_2Ph)_2$ **3**.—As for compound **1**, from $TaCl_4(PMe_2Ph)_2$ (0.4 g, 0.67 mmol) in Et_2O (30 cm^3), $Li(C_6H_4Me\text{-}2)$ (0.26 g, 2.7 mmol) in Et_2O (20 cm^3) and PMe_2Ph (0.17 cm^3) at −78 °C. The work-up as above led to a hexane solution (10 cm^3) which gave brown-orange crystals on cooling. Yield: 0.2 g, 40%. IR: 3012s, 2980s, 2940s, 1929w, 1880w, 1550w, 1426m, 1390m, 1300s, 1210m, 1192m, 1056w, 1074w, 957s and 916s cm^{-1}.

$Nb(2\text{-}MeC_6H_4)_2(\eta^2\text{-}2\text{-}MeC_6H_3)(PMe_2Ph)_2$ **4**.—As for compound **1**, from $NbCl_4(thf)_2$ (0.5 g, 1.32 mmol) in thf (50 cm^3), $Mg(C_6H_4Me\text{-}2)Br$ (7.0 cm^3 of a 0.76 mol dm^{-3} solution in thf) and PMe_2Ph (0.32 cm^3). Work-up as before to give a final hexane solution (20 cm^3) led to green crystals (two crops). Yield: 0.35 g 40%. IR: 3033s, 2961s, 2910s, 2852m, 1951w, 1931w, 1881w, 1810w, 1561s, 1488s, 1434s, 1378m, 1290s, 1274s, 1236m, 1210w, 1157m, 1099m, 1074w, 943s, 907s, 868m, 786s, 739s, 696s, 670m, 484s and 402m cm^{-1}.

$Ta(\eta^2\text{-}PhCNBu^t)_2(\eta^2\text{-}Ph_2CNBu^t)(CNBu^t)$ **5**.—To a stirred suspension of $TaCl_5$ (0.25 g, 0.7 mmol) in Et_2O (30 cm^3) at −78 °C was added LiPh (3.2 cm^3 of 1.1 mol dm^{-3}) and the mixture allowed to warm slowly to −10 °C (0.5 h with stirring). Addition of Bu^tNC (0.4 cm^3, 3.5 mmol) produced a light red solution which was stirred at room temperature (0.5 h) and evaporated. Extraction of the residue into toluene (20 cm^3) and passage of the latter through Al_2O_3 followed by evaporation of the solution and extraction of the residue into hexane (2 × 15 cm^3) gave red crystals after concentration (12 cm^3) and cooling. Yield: 0.39 g, 63%. IR: 2175s, 1589s cm^{-1} and aromatic bands as for other compounds. ^1H NMR ($CDCl_3$): δ 7.22(s), 7.17(d), 7.01(m), 6.73(m) (aromatic); 1.39 (s, 9 H, $CNBu^t$), 1.08 (s, 9 H, $PhCNBu^t$), and 1.00 (s, 18 H, Ph_2CNBu^t).

$TaPh_2(\eta^2\text{-}C_6H_4)(PMe_3)_2$ **6**.—To a stirred solution of $TaCl_5$ (0.2 g, 0.56 mmol) in Et_2O (30 cm^3) at −78 °C was added LiPh (2.5 cm^3 of 1.1 mol dm^{-3} solution in Et_2O) and PMe_3 (0.2 cm^3). After warming and stirring (2 h), evaporation of the solution, extraction of the residue in hexane (30 cm^3) and concentration and cooling of the latter (5 cm^3, −20 °C) a green-beige powder was obtained. Recrystallisation twice from hexane gave green crystals. Yield: 5%. Mass spectrum: *m*/*z* 563 (M^+), 487 ($M^+ - PMe_3$) and 411 ($M^+ - 2PMe_3$).

X-Ray Crystallography.—Crystals of the three compounds were sealed under argon in thin-walled glass capillaries. Cell dimension and intensity data were recorded as previously described using a CAD-4 diffractometer[18] for the two tantalum complexes and a FAST TV Area detector diffractometer[19] for the niobium complex. The structures were solved and developed *via* the heavy-atom method and refined by full-matrix least squares. The non-hydrogen atoms were refined anisotropically; no hydrogen atoms were included. The Bu^t group on the *tert*-butyl isocyanide ligand in the tantalum(V) compound is disordered over two sites with 68/32% occupancies. Absorption corrections were made using the DIFABS[20] procedure in each case. Crystal data and experimental details are collected in Table 5. Final fractional atomic coordinates are given in Tables 6–8.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal paremeters and remaining bond lengths and angles.

Acknowledgements

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