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# Alkoxide, phenoxide and hydrido-phenoxide compounds of tantalum bearing the pentamethylcyclopentadienyl ligand

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## Abstract

$(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{PMe}_3)(\text{H})_2(\eta^2\text{-CHPMe}_2)$  (**1**) reacts readily with alcohols at room temperature to afford the tetra-alkoxides  $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{OR})_4$  [ $\text{R} = \text{Me}$  (**2**),  $^i\text{Pr}$  (**3**) and  $\text{Ph}$  (**4**)], with the diols  $\text{HOCH}_2\text{CH}_2\text{OH}$  and  $1,2\text{-(HO)}_2\text{C}_6\text{H}_4$  to give  $\{(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{O}_2\text{C}_2\text{H}_4)_2\}_n$  (**5**) and  $\{(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{O}_2\text{C}_6\text{H}_4)_2(\text{PMe}_3)\}_n$  (**6**) respectively, and with sterically demanding phenols to give the hydrido-phenoxide complexes  $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{H})_2(\text{OAr})_2$  ( $\text{Ar} = \text{-2,6-Me}_2\text{C}_6\text{H}_3$  (**7**),  $\text{-2,4,6-Me}_3\text{C}_6\text{H}_2$  (**8**) and  $\text{-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3$  (**9**)).

We have recently shown that the unusual cyclo-metallated complex  $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{PMe}_3)(\text{H})_2(\eta^2\text{-CHPMe}_2)$  (**1**) is a useful synthon for the  $\{(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{PMe}_3)_2\}$  moiety in reactions with carbon monoxide and dihydrogen [1,2]; in the case of CO, the  $\text{PMe}_3$  ligand is regenerated by metal-to-carbon hydrogen migrations. Here, we report on reactions of (**1**) with protic oxygen-based reagents, in particular alcohols, diols and phenols, which we expected to result in displacement of the soft  $\text{PMe}_3$  ligands and to give rise to OR ligation of the  $\{(\eta\text{-C}_5\text{Me}_5)\text{Ta}\}$  fragment. This type of reactivity was noted previously [3] and was exploited further in the reaction of  $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{PMe}_3)(\text{H})_2(\eta^2\text{-CHPMe}_2)$  with water to give the unusual butterfly cluster  $(\eta\text{-C}_5\text{Me}_5)_4\text{Ta}_4\text{O}_7(\text{OH})_2$  [3].

## 1. Results and discussion

### 1.1. Reaction of (**1**) with ROH ( $\text{R} = \text{Me}, ^i\text{Pr}, \text{Ph}$ )

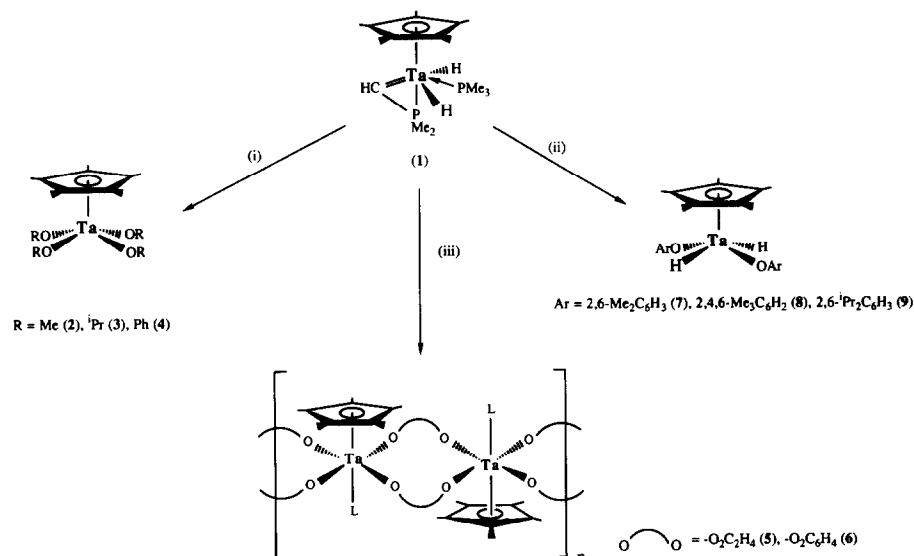
Complex **1** was found to react smoothly at room temperature with MeOH and  $^i\text{PrOH}$  (4 equiv.) in benzene to afford  $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{OR})_4$  ( $\text{R} = \text{Me}$  (**2**),  $^i\text{Pr}$  (**3**)) (Scheme 1). Both products were characterised by comparison of their  $^1\text{H}$  NMR data with those of authentic samples [4 \*]. Monitoring of the reactions by  $^1\text{H}$  NMR spectroscopy revealed that two equivalents of  $\text{PMe}_3$

are displaced and  $\text{H}_2$  is liberated ( $\delta$  4.46 ppm). No intermediates were detected, suggesting that any hydrido-alkoxo or tertiaryphosphine-alkoxo species are short-lived under the reaction conditions. The presence of an excess of  $\text{PMe}_3$  was found to retard the reaction, indicating that loss of  $\text{PMe}_3$  is rate-limiting, as found for reactions of **1** with phosphines and carbon monoxide [2].

Compound **1** also reacts smoothly with four equivalents of phenol in toluene to afford colourless crystals of the previously unreported complex  $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{OPh})_4$  (**4**) in ca. 80% isolated yield; the reaction also proceeds in the solid state with evolution of gas (assumed to be dihydrogen). PhOH reacts notably faster than either MeOH or  $^i\text{PrOH}$  with **1** and no intermediates can be detected (by  $^1\text{H}$  NMR spectroscopy). Since the oxygen atom of PhOH would be expected to be less basic than those in either MeOH or  $^i\text{PrOH}$ , the rapidity of the phenol reaction may indicate a protonation mechanism, either at the metal hydride or methine carbon sites rather than initial  $\text{PMe}_3$  displacement; this would also be consistent with the greater acidity of PhOH ( $\text{p}K_a = 9.99$ ) over MeOH ( $\text{p}K_a = 15.5$ ) and  $^i\text{PrOH}$  ( $\text{p}K_a = 16.5$ ) [6], and the fact that hydrogen atoms coordinated to  $d^0$  early transition metals are commonly hydridic in character, and direct protonation

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\* Reference number with an asterisk indicates a note in the list of references.



Scheme 1. Reactions at room temperature of  $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{PMe}_3)(\text{H})_2(\eta^2\text{-CHPMe}_2)$  (1) with ROH reagents. (i) ROH (4 equiv.); (ii) ArOH (2 equiv.), 24 h; (iii)  $\text{HO}_2\text{C}_2\text{H}_4$  (2 equiv.), 24 h, L = vacant site;  $(\text{HO})_2\text{C}_6\text{H}_4$  (2 equiv.), 24 h, L =  $\text{PMe}_3$ .

is possible [4b]. **4** is freely soluble in aromatic and moderately soluble in aliphatic hydrocarbon solvents. Its infrared spectrum shows  $\nu(\text{Ta}-\text{O})$  vibrations at  $515\text{ cm}^{-1}$ , within the range found for other tantalum phenoxide complexes [5]. An ion at  $m/e$  596 in the mass spectrum corresponds to protonated  $[(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{OPh})_3]$ ; no parent ion was observed. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data show sharp, well resolved signals for both the  $(\eta\text{-C}_5\text{Me}_5)$  and phenyl ligands and are consistent with a single, presumably monomeric, species in solution.

### 1.2. Reaction of (1) with $\text{HOCH}_2\text{CH}_2\text{OH}$ and 1,2- $(\text{HO})_2\text{C}_6\text{H}_4$

In a similar manner to the reactions with alcohols and phenol, **1** reacts smoothly with the diols,  $\text{HOCH}_2\text{CH}_2\text{OH}$  and 1,2- $(\text{HO})_2\text{C}_6\text{H}_4$  under ambient conditions to give  $[(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{O}_2\text{C}_2\text{H}_4)_2]_n$  (**5**) and  $[(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{O}_2\text{C}_6\text{H}_4)_2(\text{PMe}_3)]_n$  (**6**) respectively (Scheme 1). The compounds separate from the reaction mixtures as white (**5**) or yellow (**6**) solids in good yields. In contrast to compounds **2–4**, both **5** and **6** possess low solubility in common organic solvents, possibly indicating dimeric or oligomeric structures. Consistently, mass spectrometry revealed ions assignable to dimeric units in both compounds. Unfortunately, neither **5** nor **6** were soluble enough in suitable solvents for molecular weight determinations and we were unsuccessful in obtaining crystals suitable for X-ray diffraction analysis. Moreover,  $^1\text{H}$  NMR spectroscopy (benzene- $d_6$ ) is not particularly informative: compound **5** displays broad bands centred at  $\delta$  4.30 and  $\delta$  4.11

( $\Delta_{1/2}$  ca. 200 Hz) due to the glycolate methylene hydrogens and a broadened absorption at  $\delta$  2.09 ( $\Delta_{1/2}$  ca. 8 Hz) that can be assigned to the  $(\eta\text{-C}_5\text{Me}_5)$  hydrogens. A fluxional dimeric or oligomeric structure in solution is consistent with these observations. Compound **6** is unusual in that it has retained one equivalent of  $\text{PMe}_3$ , as indicated by elemental analysis, IR spectroscopy ( $960\text{ cm}^{-1}$ ,  $\rho(\text{CH}_3)$ ) and mass spectrometry. The  $^1\text{H}$  NMR spectrum (THF- $d_8$ ) revealed at least seven  $(\eta\text{-C}_5\text{Me}_5)$  signals between  $\delta$  2.28–1.93 with associated  $\text{PMe}_3$  resonances appearing between  $\delta$  1.7–1.4 suggesting a complex mixture of compounds in solution possibly involving oligomeric, catechol-bridged species (possible structures for **5** and **6** are shown in Scheme 1). Two mono-cyclopentadienyl niobium catecholate complexes have been described recently,  $(\eta\text{-C}_5\text{H}_5)\text{NbCl}_2(\text{O}_2\text{C}_6\text{H}_4)$  and  $\{(\eta\text{-C}_5\text{H}_5)\text{NbCl}\}_2(\mu\text{-O})(\mu\text{-O}_2\text{C}_6\text{H}_4)_2$  and the latter has been shown to have a structure containing two bidentate, bridging catecholate ligands and a linear  $\mu$ -oxo ligand [7].

### 1.3. Reaction of 1 with ArOH (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> and 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)

Although intermediate hydrido-alkoxo or tertiaryphosphine-alkoxo species are not observed in the reactions described above, we envisaged that more sterically demanding reagents such as 2,6-disubstituted phenols might be better able to stabilise products with fewer than four phenoxide groups coordinated to tantalum. Complex **1** reacted readily within minutes at room temperature with HO-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (2 equiv.) to afford a single product as indicated by  $^1\text{H}$  NMR spec-

TABLE 1.  $^1\text{H}$  NMR data (benzene- $d_6$ , 298 K).

| Compound | Shift | Rel. Int. | Multiplicity | $J(\text{Hz})$                   | Assignment                        |
|----------|-------|-----------|--------------|----------------------------------|-----------------------------------|
| 7        | 11.54 | 2         | s            |                                  | M-H                               |
|          | 7.05  | 4         | d            | $^3J(\text{H-H})$ 7.3            | Ar- $H_m$                         |
|          | 6.76  | 2         | t            | $^3J(\text{H-H})$ 7.3            | Ar- $H_p$                         |
|          | 2.44  | 12        | s            |                                  | Ar- $\text{CH}_3$                 |
|          | 2.08  | 15        | s            |                                  | $\text{C}_5(\text{CH}_3)_5$       |
| 8        | 11.54 | 2         | s            |                                  | M-H                               |
|          | 6.85  | 4         | s            |                                  | Ar- $H_m$                         |
|          | 2.46  | 12        | s            |                                  | Ar- $\text{CH}_3(\textit{ortho})$ |
|          | 2.23  | 6         | s            |                                  | Ar- $\text{CH}_3(\textit{para})$  |
|          | 2.12  | 15        | s            |                                  | $\text{C}_5(\text{CH}_3)_5$       |
| 9        | 16.09 | 2         | s            |                                  | M-H                               |
|          | 7.07  | 4         | d            | $^3J(\text{H}_m-\text{H}_p)$ 7.3 | Ar- $H_m$                         |
|          | 6.90  | 2         | t            | $^3J(\text{H}_m-\text{H}_p)$ 7.3 | Ar- $H_p$                         |
|          | 3.47  | 4         | sept         | $^3J(\text{H-H})$ 6.8            | $\text{CH}(\text{CH}_3)_2$        |
|          | 2.04  | 15        | s            |                                  | $\text{C}_5(\text{CH}_3)_5$       |
|          | 1.24  | 24        | d            | $^3J(\text{H-H})$ 6.8            | $\text{CH}(\text{CH}_3)_2$        |

troscopy (Table 1). The ( $\eta\text{-C}_5\text{Me}_5$ ) hydrogens resonate at  $\delta$  2.08 whilst the presence of two equivalent O-2,6- $\text{Me}_2\text{C}_6\text{H}_3$  ligands is indicated by a singlet at  $\delta$  2.44 (Me) and an AX<sub>2</sub> pattern assignable to the aryl hydrogens at  $\delta$  7.05 ( $H_{\textit{meta}}$ ) and 6.76 ( $H_{\textit{para}}$ ) respectively. Furthermore, a high frequency singlet resonance, integrating to two hydrogens, is observed at  $\delta$  11.54. This shift is characteristic of metal hydride ligands coordinated to formally electron-deficient,  $d^0$  transition metal centres (*cf.*  $\text{TaHCl}_2(\text{CHCMe}_3)(\text{PMe}_3)_3$ ,  $\delta$  10.00 [8]). On the basis of the above data, the complex may be formulated as ( $\eta\text{-C}_5\text{Me}_5$ )Ta(H)<sub>2</sub>(O-2,6- $\text{Me}_2\text{C}_6\text{H}_3$ )<sub>2</sub> (7) (Scheme 1). Two equivalents of  $\text{PMe}_3$  are liberated and no free dihydrogen is observed in the reaction mixture (by  $^1\text{H}$  NMR). Similar, rapid reactions occur between 1 and HO-2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$  and HO-2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$  to afford the analogous complexes 8 and 9 respectively, for which the  $^1\text{H}$  NMR data are summarised in Table 1.

Attempts to isolate 7 led to decomposition to unidentified products, and 9 was obtained only as an oil containing the uncomplexed phenol, as indicated by both IR and  $^1\text{H}$  NMR spectroscopy. However, a broad IR absorption at  $1800\text{ cm}^{-1}$ , with a shoulder at  $1780\text{ cm}^{-1}$ , is consistent with the presence of metal hydride ligands (*cf.* ( $\eta\text{-C}_5\text{Me}_5$ )Ta( $\text{PMe}_3$ )(H)<sub>2</sub>( $\eta^2\text{-CHPMe}_2$ ),  $\nu(\text{M-H}) = 1710(\text{s}), 1650(\text{s, br})\text{ cm}^{-1}$  [2]). Although structural information is not available, we favour a monomeric, four-legged piano-stool geometry for 7–9 in which the phenoxide ligands occupy the sterically more amenable *trans* positions as illustrated in the Scheme. Compounds containing both [M-H] and [M-OR] moieties (R = alkyl, phenyl, hydrogen) remain quite rare yet are of interest for the modelling of, for

example, water splitting reactions (such as ( $\eta\text{-C}_5\text{Me}_5$ )<sub>2</sub>Hf(H)(OH) [9] and {W( $\text{PMe}_3$ )<sub>4</sub>(H)<sub>2</sub>(OH)<sub>2</sub>}(BF<sub>4</sub>)<sub>2</sub> [10]), methanol synthesis under Fischer-Tropsch conditions (*e.g.* W( $\text{PMe}_3$ )<sub>4</sub>(H)<sub>3</sub>(OMe) [11] and ( $\eta\text{-C}_5\text{Me}_5$ )Ir(PPh<sub>3</sub>)(OEt)(H) [12]), and more recently in hydrogenation catalysis, for example by Ta(O-2,6- $\text{C}_6\text{H}_3$ )<sub>2</sub>(H)<sub>3</sub>( $\text{PMe}_2\text{Ph}$ )<sub>2</sub> [13].

## 2. Experimental details

All reactions and manipulations were carried out under dry nitrogen by standard Schlenk and vacuum-line techniques. Solvents were pre-dried over either sodium wire, calcium chloride or 4 Å molecular sieves before reflux, distilled from sodium/benzophenone (THF, THF- $d_8$ , 40–60°C petroleum ether), sodium metal (toluene) or calcium hydride ( $\text{CH}_2\text{Cl}_2$ ) under argon and were deoxygenated before use. Elemental analyses were performed by the Microanalytical Laboratory in this department. Infrared spectra were recorded as Nujol mulls between KBr windows on Perkin-Elmer 577 and 457 Grating Spectrophotometers; absorptions are abbreviated as s (strong), m (medium), w (weak), sp (sharp), br (broad). Mass spectra were recorded on a VG 7070E mass spectrometer. NMR spectra were recorded on a Bruker AC 250 instrument at ambient temperature in benzene- $d_6$  (dried by vacuum distillation from phosphorus (V) oxide) unless stated otherwise; chemical shifts are reported as  $\delta$  in ppm and were referenced internally using the residual solvent resonance ( $^1\text{H}$  and  $^{13}\text{C}$ ) relative to tetramethylsilane at 0 ppm. MeOH,  $^i\text{PrOH}$ , ArOH and HOCH<sub>2</sub>CH<sub>2</sub>OH were distilled and degassed prior to use, PhOH and 1,2-(HO)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> were commercial samples and used without further purification.

( $\eta\text{-C}_5\text{Me}_5$ )Ta( $\text{PMe}_3$ )(H)<sub>2</sub>( $\eta^2\text{-CHPMe}_2$ ) was prepared as described previously [2].

### 2.1. Reaction of 1 with ROH (R = Me, $^i\text{Pr}$ )

A benzene- $d_6$  solution of ( $\eta\text{-C}_5\text{Me}_5$ )Ta( $\text{PMe}_3$ )(H)<sub>2</sub>( $\eta^2\text{-CHPMe}_2$ ) (20 mg) was treated with ROH (4 equiv) in a 5 mm NMR tube. The samples were then flame-sealed under an atmosphere of nitrogen and the progress of reaction monitored by  $^1\text{H}$  NMR spectroscopy at ambient temperature during 48 h.

### 2.2. Reaction of 1 with PhOH. Synthesis of ( $\eta\text{-C}_5\text{Me}_5$ )Ta(OPh)<sub>4</sub> 4

Phenol (0.12 g, 1.3 mmol) was added to a toluene solution (30 cm<sup>3</sup>) of ( $\eta\text{-C}_5\text{Me}_5$ )Ta( $\text{PMe}_3$ )(H)<sub>2</sub>( $\eta^2\text{-CHPMe}_2$ ) (0.15 g 0.32 mmol) in a nitrogen-filled dry box. After 2 h stirring at room temperature, the volatiles were removed under reduced pressure to give a pale

yellow oil, which was washed with cold ( $-60^{\circ}\text{C}$ ) light petroleum ether ( $2 \times 5 \text{ cm}^3$ ) to afford a white solid. Recrystallisation from light petroleum ether ( $40 \text{ cm}^3$ ) afforded colourless crystals. Yield, 0.18 g (82%). Elemental analysis. Found: C, 58.98; H, 5.22.  $\text{C}_{34}\text{H}_{35}\text{O}_4\text{Ta}$  calcd.: C, 59.30; H, 5.13%. IR ( $\text{cm}^{-1}$ ): 3055 (w), 3015 (w), 1588 (s), 1288 (s), 1250 (s, br), 1161 (m), 1153 (m), 1069 (m), 1022 (m), 1000 (m, sp), 881 (s, br), 860 (s), 852 (s), 827 (m), 757 (s), 734 (m), 692 (s), 630 (s), 600 (m), 585 (m), 515 (m), 435 (m).  $^1\text{H}$  NMR: 7.04 [dd, 8H,  $J(\text{H}_o-\text{H}_m)$  8,  $J(\text{H}_p-\text{H}_m)$  7, Ph- $\text{H}_m$ ], 6.83 [d, 8H,  $J(\text{H}_o-\text{H}_m)$  8, Ph- $\text{H}_o$ ], 6.69 [t, 4H,  $J(\text{H}_p-\text{H}_m)$  7, Ph- $\text{H}_p$ ], 2.12 [s, 15H,  $\text{C}_5\text{Me}_5$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR: 163.84 [s,  $\text{C}_{\text{ipso}}$ ], 129.29 [s,  $\text{C}_m$ ], 124.64 [s,  $\text{C}_5\text{Me}_5$ ], 120.94 [s,  $\text{C}_p$ ], 119.94 [s,  $\text{C}_o$ ], 11.54 [s,  $\text{C}_5\text{Me}_5$ ]. Mass spectrum ( $m/e$ , CI, isobutane carrier gas): 596 [ $\text{M}-\text{OPh} + \text{H}$ ] $^+$ , 519 [ $\text{M}-\text{OPh}-\text{Ph} + \text{H}$ ] $^+$ , 426 [ $\text{M}-2\text{OPh}-\text{Ph} + \text{H}$ ] $^+$ .

### 2.3. Reaction of 1 with $\text{HOCH}_2\text{CH}_2\text{OH}$ . Synthesis of 5

$\text{HOCH}_2\text{CH}_2\text{OH}$  (0.07 g 1.07 mmol) was added from a syringe to a vigorously stirred solution of  $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{PMe}_3)(\text{H})_2(\eta^2\text{-CHPMe}_2)$  (0.25 g 0.53 mmol) in light petroleum ether ( $30 \text{ cm}^3$ ) at room temperature. A white, flocculent precipitate was observed after ca. 1 h. After 24 h stirring the product was filtered off, washed with light petroleum ether ( $2 \times 10 \text{ cm}^3$ ), and dried *in vacuo*. Yield, 0.14 g (60%). Elemental analysis. Found: C, 38.16; H, 5.48.  $\text{C}_{14}\text{H}_{23}\text{O}_4\text{Ta}$  calcd.: C, 38.54; H, 5.32%. IR ( $\text{cm}^{-1}$ ): 1278 (m), 1235 (w), 1162 (s), 1142 (s), 1120 (m), 1100 (m), 1082 (m), 1040 (m), 925 (m), 895 (m), 630 (w), 580 (w), 550 (w), 473 (m), 460 (m, br). Mass spectrum ( $m/e$ , CI isobutane carrier gas): 873 [ $\text{M}_2 + \text{H}$ ] $^+$ , 829 [ $\text{M}_2 - \text{OC}_2\text{H}_4 + \text{H}$ ] $^+$ , 437 [ $\text{M} + \text{H}$ ] $^+$ , 348 [ $(\eta\text{-C}_5\text{Me}_5)\text{TaO}_2$ ] $^+$ .

### 2.4. Reaction of 1 with 1,2-(HO) $_2\text{C}_6\text{H}_4$ . Synthesis of 6

Light petroleum ether ( $40 \text{ cm}^3$ ) was added to a solid mixture of  $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{PMe}_3)(\text{H})_2(\eta^2\text{-CHPMe}_2)$  (0.25 g 0.53 mmol) and 1,2-(HO) $_2\text{C}_6\text{H}_4$  (0.12 g 1.07 mmol) at room temperature. Stirring for 30 min resulted in dissolution of the catechol and precipitation of a yellow solid. After 24 h the product was filtered off, washed with light petroleum ether ( $2 \times 10 \text{ cm}^3$ ), and dried *in vacuo*. Yield, 0.28 g (86%). Elemental analysis. Found: C, 49.37; H, 5.72.  $\text{C}_{25}\text{H}_{32}\text{O}_4\text{PTa}$  calcd.: C, 49.34; H, 5.31%. IR ( $\text{cm}^{-1}$ ): 3045 (w), 1587 (w), 1345 (m), 1339 (w), 1291 (m), 1277 (s), 1264 (s), 1255 (s), 1215 (m), 1100 (m), 1095 (m), 1040 (m), 1020 (m), 1013

(m), 985 (w), 960 (m), 820 (m), 809 (s), 756 (s), 732 (s), 650 (m), 629 (s), 600 (m), 529 (m), 515 (m), 489 (w). Mass spectrum ( $m/e$ , EI 70 eV): 961 [ $\text{M}_2 - (\text{HO})_2\text{C}_6\text{H}_4 - \text{PMe}_3 - \text{C}_4\text{H}_4(\text{OH})$ ] $^+$ , 532 [ $(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{O}_2\text{C}_6\text{H}_4)_2$ ] $^+$ .

### 2.5. Reaction of 1 with $\text{ArOH}$ ( $\text{Ar} = -2,6\text{-Me}_2\text{C}_6\text{H}_3$ , $-2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ and $-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$ )

$(\eta\text{-C}_5\text{Me}_5)\text{Ta}(\text{PMe}_3)(\text{H})_2(\eta^2\text{-CHPMe}_2)$  (20 mg) was dissolved in benzene- $d_6$  solvent in a 5 mm NMR tube and treated with  $\text{ArOH}$  (2 equiv.) at ambient temperature. The samples were then flame-sealed under nitrogen and the progress of the reactions monitored by  $^1\text{H}$  NMR spectroscopy.

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