

Preliminary communication

TRANSITION-METAL COMPLEXES OF TWO VALENCE TAUTOMERS OF A BULKY PHENOXIDE, 2,6-Bu-t₂-4-MeC₆H₂O⁻ (ArO⁻); PREPARATION AND CRYSTAL AND MOLECULAR STRUCTURE OF A PHENOXYTITANIUM(III) AND A CYCLOHEXADIENONYLRHODIUM(I) COMPLEX, [Ti(η-C₅H₅)₂OAr] AND [Rh(ArO-η⁵)(PPh₃)₂]*

B. ÇETINKAYA, P.B. HITCHCOCK**, M.F. LAPPERT**, S. TORRONI,
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, (Great Britain)
 J.L. ATWOOD**, W.E. HUNTER and M.J. ZAWOROTKO
Department of Chemistry, The University of Alabama, University, Alabama 35486 (U.S.A.)
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Summary

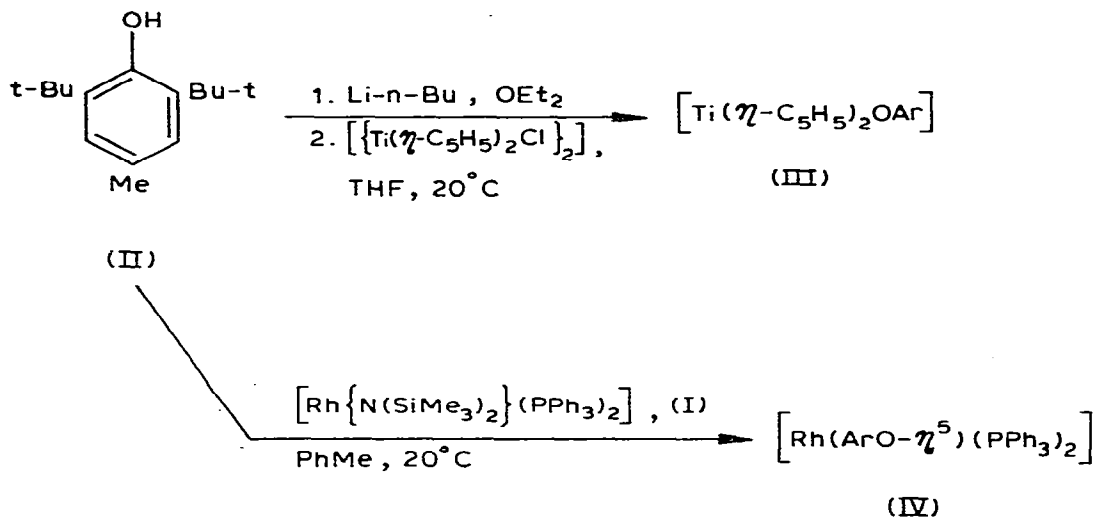
The 2,6-di-*t*-butyl-4-methylphenoxy ligand (ArO⁻) is ambidentate, giving rise to the O-bonded 15-electron *d*¹ [Ti(η-C₅H₅)₂OAr] and the η⁵-[C(2)—C(6)]-bonded 18-electron *d*⁸ complex [Rh(ArO-η⁵)(PPh₃)₂], obtained from [{Ti(η-C₅H₅)₂Cl}₂]-LiOAr and [Rh{N(SiMe₃)₂}(PPh₃)₂]-ArOH, respectively; the average Ti—C(η) distance is 2.362(10) Å, Ti—O 1.892(2) Å, and O—C(of Ar) 1.352(3) Å, and TiOC 142.3(2)^o; in the Rh^I complex, C(2)—C(6) are coplanar (with C—C(av.) 1.38(2) Å), C(1)—O 1.28 Å, and Rh to C(2)—C(6) bond lengths are in the range 2.19—2.65 Å.

We report the preparation (see Scheme 1; for the amide (I), see reference [1]) and single crystal X-ray characterisation of two transition-metal complexes derived from the anion of the phenol (II), which is thus shown to be capable of behaving as an ambidentate nucleophile. The Ti^{III} complex (III) has the 2-electron-O-centred aryloxy structure, whereas the Rh^I complex (IV) contains the 6-electron-η⁵-C-centred cyclohexadienonyl ligand. Some data are in Table 1.

The preference for O-bonding in the 15-electron complex III but η⁵-C-bonding for the 18-electron IV is attributed to the greater stability associated with the chosen central metal electron configuration (cf., the alternative 19-electron Ti^{III} or 14-electron Rh^I tautomers), the superior matching of the

*No reprints available.

**Authors to whom correspondence should be addressed.



SCHEME 1. Preparation of a Ti^{III} and a Rh^{I} complex derived from the anion of 2,6-Bu- t_2 -4-MeC $_6$ H $_2$ OH (ArOH)

hard ligand ArO^- with Ti^{3+} and the softer $(\text{ArO}-\eta^5)^-$ with Rh^+ , and steric constraints.

Alkoxides or aryloxides of the 4d and 5d metals of Group VII, VIII, or I are exceedingly rare [2]. However, analogues of III are well-known, although generally dimeric, as in $[\{\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{OR}\}_2]$ ($\text{R} = \text{Me, Et, or Ph}$) [3]. π -Phenoxo complexes, " $\text{RuH}(\eta^6\text{-PhO})(\text{PPh}_3)_2$ " and some solvated analogues, as well as " $\text{Rh}(\eta^6\text{-PhO})(\text{PPh}_3)_2 \cdot 2\text{PhOH}$ ", have been described [4]. The possibility was recognised of a η^5 -cyclohexadienonyl bonding mode, and preliminary X-ray data on " $\text{RuH}(\eta^6\text{-PhO})(\text{PPh}_3)_2 \cdot \text{MeOH}$ " were cited [5]. η^5 -Cyclohexadienyl analogues are authenticated, as in $[\text{Mn}(\text{CO})_3(\eta^5\text{-C}_6\text{H}_7)]$ [6] (V) and a cyclohexa-2,4-dienone (L)-complex $[\text{Fe}(\text{CO})_3\text{L}]$ has been described [7] (and L may be regarded as the keto-tautomer of phenol).

Crystal data for compound III: $M = 397.4$, monoclinic, space group $P2_1/c$, a 8.010(6), b 15.919(8), c 17.640(8) Å, β 98.15(5)°, U 2226.5 Å³, D_c 1.19 g cm⁻³ for $Z = 4$, $\mu(\text{Mo-K}\alpha)$ 4.1 cm⁻¹. Data were collected on an Enraf-Nonius CAD-4 diffractometer in a manner similar to that previously described [8], and were refined by full-matrix least-squares techniques. The final R values were $R = 0.032$ and $R' = 0.032$ for 1901 independent reflections with $I > 3\sigma(I)$.

TABLE 1

DATA FOR $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{OC}_6\text{H}_2\text{Me-4-Bu-}t_2\text{-2,6})]$ (III) AND $[\text{Rh}(2,6\text{-Bu-}t_2\text{-4-MeC}_6\text{H}_2\text{O-}\eta^5)(\text{PPh}_3)_2]$ (IV)

Complex ^a	Colour	Yield (%)	M.p. (θ_c /°C)	IR ^b (1500–1600 cm ⁻¹)
III ^c	Deep-purple	50	167–169	1592m, 1583(sh), 1550vw, 1505vw
IV ^d	Red-brown	72	123–124	1585w, 1570m, 1548s, 1540(sh), 1530vw

^aSatisfactory microanalytical data were obtained. ^bNujol[†] mulls; s = strong, m = medium, w = weak, vw = very weak, (sh) = shoulder. ^cMonomer by cryoscopy in C₆H₆; $\epsilon_{\text{av}} = 1.9795$ at 20°C in PhMe (singlet). ^dMonomer by cryoscopy in cyclohexane; ¹H NMR in C₆H₆ at 30°C shows Bu- t protons at τ 8.4 and Me protons at τ 7.93.

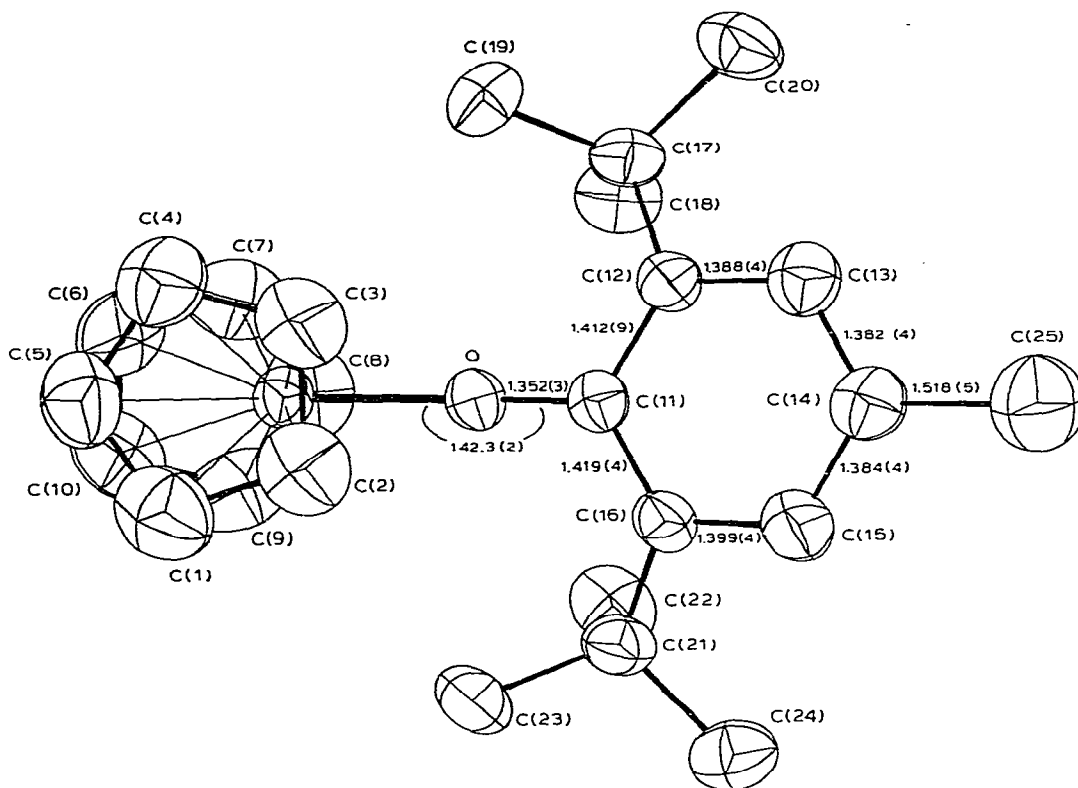


Fig. 1. A perspective view of the molecular structure of $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{OAr})]$ (III) showing selected bond lengths and the numbering system used. The $\text{Ti}-\text{C}(\eta)$ distance ranges from 2.352(4) to 2.380(4) Å and average 2.362(10) Å. The angle Cp (centroid)—Ti—Cp (centroid) is 135.5°.

The molecule is illustrated in Fig. 1. Evidence of steric effects associated with the bulky aryloxy are seen in parameters associated with the ligand itself. The $\text{Ti}-\text{O}-\text{C}$ angle, 142.3(2)°, is much larger than the 125° values found in $\text{M}(\text{OAr})_2$ ($\text{M} = \text{Ge}$ or Sn) [9], and the central carbon atoms of the *t*-butyl ligands lie 0.34 and 0.40 Å out of the plane of the phenyl group. The $\text{Ti}-\text{O}$ bond length, 1.892(2) Å, is slightly outside the range of 1.78 to 1.86 Å found in compounds with the $\text{Ti}-\text{O}-\text{Ti}$ linkage [10], but the parameters of the $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ unit appear normal for Ti in the +3 oxidation state [11].

Crystal data for compound IV: $\text{C}_{51}\text{H}_{53}\text{OP}_2\text{Rh}\cdot 2\text{C}_6\text{H}_6$, $M = 1003.2$, triclinic, space group $P\bar{1}$, a 11.570(3), b 19.650(4), c 13.298(5) Å, α 74.39(5)°, β 96.23(4)°, γ 113.34(3)°, U 2673.5 Å³, $Z = 2$, $\mu(\text{Cu}-K\alpha)$ 35.1 cm⁻¹. Data were collected on a Hilger and Watts Y290 diffractometer and refined by large block least squares, $R = 0.088$, $R' = 0.115$ for the 1920 reflections with $I > 3\sigma(I)$. The CO bond length (Fig. 2) is indicative of a double bond and the CC bond lengths are similar to those in the cyclohexadienyl complex V [6]. All the substituents on the ring are bent slightly away from the metal. The slight asymmetry in the metal—ring bonding, as evident from the longer $\text{Rh}-\text{C}(6)$ bond, is probably the result of minimisation of non-bonded contacts of the large *t*-Bu groups with the Ph rings on P(1).

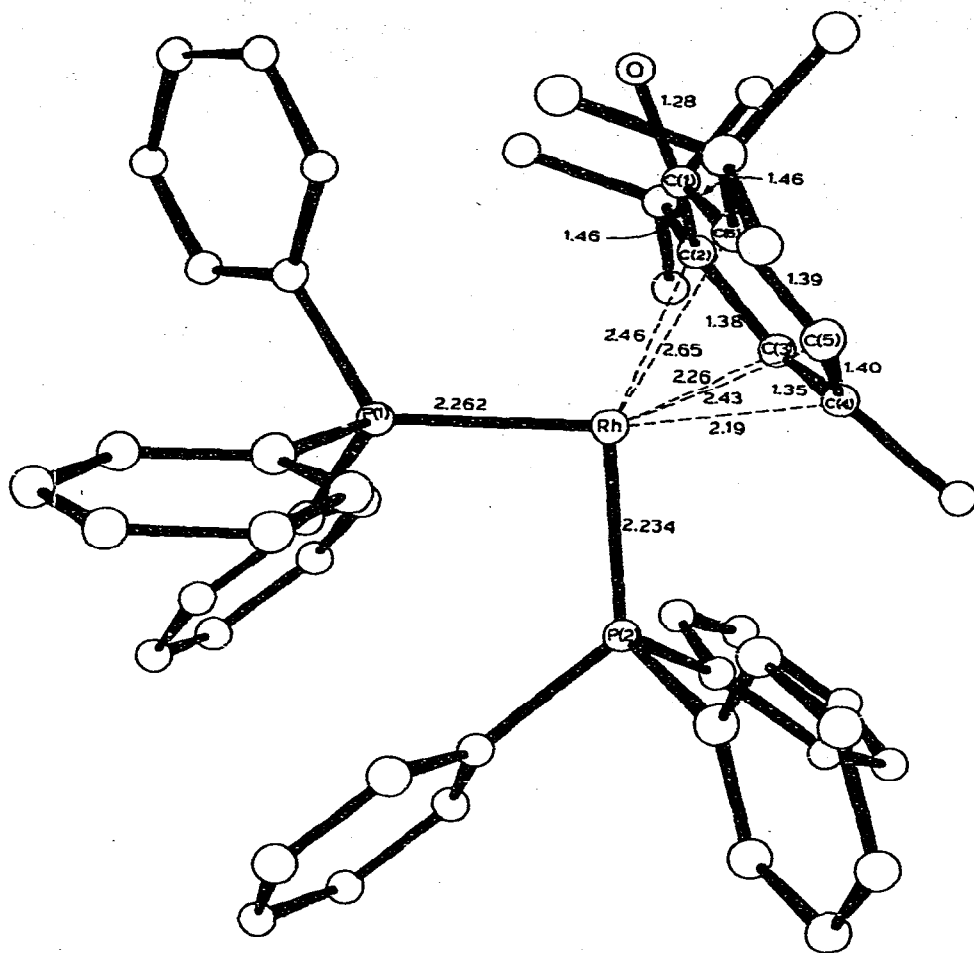


Fig. 2. A perspective view of the molecular structure of $[\text{Rh}(\text{OAr-}\eta^5)(\text{PPh}_3)_2]$ (IV) showing selected bond lengths and the numbering system used. E.s.d.'s are Rh-P 0.005, Rh-C 0.02, C-C 0.02 Å.

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