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Preparation, characterization, and reactions of 16-electron Ta(η^5-C_5Me_5)(η^3-1-phenylallyl)$_2$

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Abstract

Treatment of Cp*TaCl$_4$ with 4 equiv of phenylallylMgBr in THF afforded Cp*Ta(1-phenylallyl)$_2$ (**2**), whose structure was characterized by a single crystal X-ray study as 16-electron two legged piano stool with two allyl moieties in supine-supine geometry. In this reaction, the starting Ta^V complex was reduced to a Ta^{III} species accompanying the formation of reductive allyl-coupling products, diphenyl-1,5-hexadiene derivatives **3**. π-Donor molecules such as carbon monoxide, tert-butyl isocyanide, isocyanates and isothiocyanates induced the coupling reaction of two phenylallyl groups on tantalum to give 1,6-diphenyl-1,5-hexadiene (**3a**). The intermediate Cp*Ta(tert-BuNC)$_2$(η^2,η^2-1,6-diphenyl-1,5-hexadiene) (**5**) was characterized by ^{1}H NMR spectroscopy. Complex **2** was the catalyst precursor for the selective dimerization of isocyanates. Oxygen donor molecules such as DMSO and pyridine-*N*-oxide reacted with **2** to afford 1:1 adducts. One-electron oxidation of **2** with ferrocenium cation resulted in the formation of 1-phenyl-1-propene. The Ta^{IV} complexes, [Cp*Ta(1-phenylallyl)$_2$][oxidant], were obtained by the reaction of **2** with TCNQ and DDQ.

1. Introduction

Allyl complexes of transition metals have been typical examples of organometallic complexes and have been found to play the key role in a number of organic reactions [1–3]. The homoleptic allyl complexes of Nb and Ta, M(C_3H_5)$_4$, have been reported to be thermally unstable above −30°C and therefore their chemistry has not been developed [1,4]. The introduction of a Cp ligand generally stabilizes these otherwise unstable allyl species [5–9]. Some attempts to synthesize CpTa(C_3H_5)$_2$ were made without success. In general, the use of Cp* remarkably improved the efficiency of synthesis of many of the organic derivatives of Nb and Ta, *e.g.* Cp*M(diene)$_2$ (M = Nb and Ta) [10]. Recently, progress in the chemistry of mono(pentamethylcyclopentadienyl) complexes of Group 5 metals has been reviewed [11]. Here, we report the preparation, structure, and some reactions of the mono(pentamethylcyclopentadienyl)tantalum-bisallyl complex.

2. Results and discussion

2.1. *Synthesis and structure of Cp*Ta(1-phenylallyl)$_2$ (2)*

The reaction of Cp*TaCl$_4$ (Cp* = η^5-C_5Me_5) with 4 equiv of C_3H_5MgCl produced a dark green compound of the empirical formula Cp*Ta(C_3H_5)$_2$ (**1**) in 3% yield. The structure of **1** was characterized based on ^{1}H-NMR data, and the mass spectrum suggested this to be the trimeric complex [Cp*Ta(C_3H_5)$_2$]$_3$. High air-sensitivity and low chemical yield of **1** prevented further characterization. On the other hand, treatment of Cp*TaCl$_4$ with 4 equiv of 1-phenylallylmagnesium bromide in THF afforded Cp*Ta(1-phenylallyl)$_2$ (**2**) as red-brown crystals in 56% yield. During the course of the reaction, the coupling of the allyl ligands afforded 1,6-diphenyl-1,5-hexadiene (**3a**), 1,4-diphenyl-1,5-hexadiene (**3b**), and 3,4-diphenyl-1,5-hexadiene (**3c**). A similar intramolecular coupling reaction of two pentadienyl groups coordinated to CpNb has been reported [12]. Thus, the starting Ta^V compound was reduced to Ta^{III}. Hydrolysis of **2** in benzene-d_6 resulted in the quantitative formation of a 1:1 mixture of 3-phenyl-1-propene and 1-phenylpropane. The strong oxophilic

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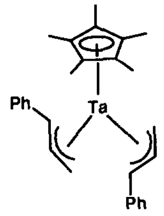
property of tantalum induced the cleavage of the H–O bond to form a hydrido-oxo-tantalum species [13], which further reduced the C–C double bond. That an intramolecular process was operative could be deduced by the formation of 3-deutero-3-phenyl-1-propene and 1,2,3-trideutero-1-phenylpropane upon deutrolysis [14*].



2

A remarkable feature of the ^{1}H NMR spectrum of 2 is that the central proton of the allyl ligand is shifted to lower field, and the terminal protons are shifted to higher field. In the ^{13}C NMR spectrum, the J(C–H) values of C1, C2, and C3 are 145, 168, and 151 Hz, respectively. Recently, the σ^3-allyl structure (tantalabicyclobutane) for Cp$_2^*$Ta(C$_3$H$_5$) has been proposed based on the high field chemical shifts and the relatively low J(C–H) coupling constants (147–149 Hz) for the terminal and central carbons of the allyl group [8]. The 1,3-σ^2-allyl structure is considered to explain the NMR spectral data of 2. Such a σ-bond nature in metallacycles gives rise to the agostic interaction at the terminal carbon of allyl moiety of 2 (*vide infra*).

The orientation of the π-allyl ligands allows for three possible isomeric structures, supine-supine, supine-prone, and prone-prone [15*]. In complex 2, variable-temperature NMR measurements showed no stereoisomerism and no fluxionality in solution with only one set of signals due to two equivalent allyl moieties being observed in the ^{1}H and ^{13}C NMR. Finally, the orientation of the π-allyl ligands in solid state was determined by X-ray analysis as supine-supine.

A view of complex 2 is shown (Fig. 1), along with the atom numbering scheme. Principal bond distances and angles are listed in Table 1. A pentamethylcyclopentadienyl ligand is bonded in the usual η^5-fashion with average Ta–C and C–C bond distances of 2.41 and 1.40 Å, respectively. The bonding description of the tantalum-allyl linkages is of particular interest. The tantalum atom is coordinated to two allyl groups in the supine-supine mode. The related isoelectronic CpZr(allyl)(butadiene) [16] and Cp*Hf(1,2,3-Me$_3$-allyl)(1,2-Me$_2$-butadiene) [17] have supine-supine and prone-prone geometry, respectively. The isostructural allyl complexes of chromium and molybdenum, CpCr(allyl)$_2$ and CpMo(allyl)$_2$, have the same geometry as that of 2 [18]. On the other hand, Cp*Zr(η^3-allyl)Cl$_2$ has its η^3-allyl group in the prone geometry [19].

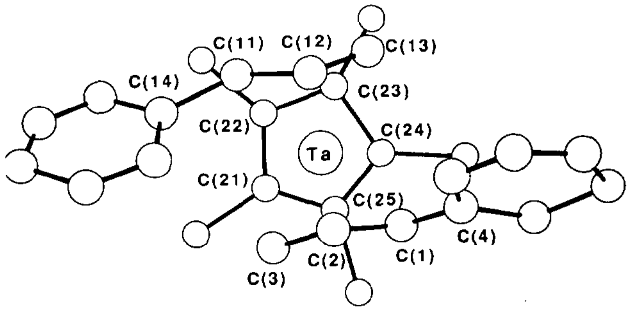


Fig. 1. The crystal structure of 2.

The structure of 2 may also be regarded as two-legged piano stool when the allyl group is considered as a ligand. Another example of a tantalum complex with two-legged piano stool geometry is (η^6-C$_6$Et$_6$)Ta(DIPP)$_2$ (DIPP = 2,6-diisopropylphenoxide) [20].

In most transition metal allyl compounds, the distance between the metal and the central carbon in allyl moiety is generally shorter than the average distance between the metal and the terminal carbons in the same allyl moiety [21,22]. In contrast, some early transition metals complexes such as CpZr(allyl)(butadiene) [16], Cp*Hf(1,2,3-Me$_3$-allyl)(1,2-Me$_2$-butadiene) [17], CpMo(allyl)$_2$ [18a], and lanthanide metal complexes such as Cp$_2^*$Sm(allyl) [23] and Cp*U(methallyl)$_3$ [24] have a geometrical arrangement in which the distance metal–central carbon in allyl is longer than that of metal–terminal carbon atoms. In the present case, metal–central carbon distances, Ta–C(2) (2.25(3) Å) and Ta–C(12) (2.27(3) Å), are comparable with that of the averaged Ta–C(terminal) bond lengths (2.25 and

TABLE 1. Selected bond distances (Å) and angles (deg) for 2

Ta–C(1)	2.32(2)	Ta–C(2)	2.25(3)
Ta–C(3)	2.17(2)	Ta–C(11)	2.27(2)
Ta–C(12)	2.27(3)	Ta–C(13)	2.29(2)
Ta–C(21)	2.41(1)	Ta–C(22)	2.46(3)
Ta–C(23)	2.45(2)	Ta–C(24)	2.37(2)
Ta–C(25)	2.37(3)		
C(1)–C(2)	1.46(3)	C(2)–C(3)	1.49(3)
C(11)–C(12)	1.41(4)	C(12)–C(13)	1.28(4)
C(1)–C(2)–C(3)	114(2)	C(2)–C(1)–C(4)	121(2)
C(11)–C(12)–C(13)	123(2)	C(12)–C(11)–C(14)	129(2)

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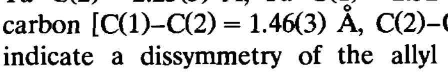
* Reference number with asterisk indicates a note in the list of references.

2.28 Å). In the allyl moiety [C(1)–C(3)], increasing tantalum–carbon bond distances [Ta–C(3) = 2.17(2) Å, Ta–C(2) = 2.25(3) Å, Ta–C(1) = 2.32 Å] and carbon–carbon [C(1)–C(2) = 1.46(3) Å, C(2)–C(3) = 1.49(3) Å] indicate a dissymmetry of the allyl group having a tendency of conversion η^3–η^1, a feature previously pointed out for the structure of CpZr(allyl)$_3$ [25]. The hydrogen atoms attached to C(1) and C(11) are fairly close (2.50 Å, r_{bp} [26] = 1.1) to the tantalum atom. The Ta–C(1 or 11)–H angles (91–96°) and the small coupling constant J(C–H) (145 Hz) also indicate an agostic interaction [27]. The 16-e species is thus stabilized by this unique interaction. The phenyl group on the allyl may also help in this case.

2.2. *Reactions of 2 with CO, tert-BuNC, RNCS, and RNCO*

The most prominent feature of the reactivity of **2** is the reductive elimination of the allyl groups. Treatment of **2** with donor molecules such as carbon monoxide, isocyanide, isocyanate and isothiocyanate induces the coupling reaction of phenylallyl groups to afford 1,6-diphenyl-1,5-hexadiene (**3a**) in modest yield.



(1)

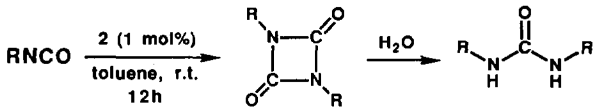
Carbonylation of **2** in toluene afforded **3a** in 87% yield along with the carbonylated tantalum complex Cp*Ta(CO)$_4$ (13% yield) and a cluster complex with the formula, Cp$^*_3$Ta$_3$(CO)$_n$ [28,29]. Insertion of CO into the Ta–C bond was not detected [30]. Compound **3a** may be formed selectively via an intermediate, Cp*Ta(CO)$_n$(η^1-3-phenylallyl)$_2$ (**4**), which undergoes reductive elimination to give **3a** and the above carbonyltantalum complexes.

In the case of the reaction of **2** with tert-butyl isocyanide, we detected the intermediate Cp*Ta(tert-BuNC)$_2$(η^2,η^2-1,6-diphenyl-1,5-hexadiene) (**5**). Monitoring of the reaction of **2** with 0.5 equiv of tert-butyl isocyanide in benzene-d_6 by ^{1}H NMR suggested the formation of an 18 electron complex **5**, together with the starting complex **2** and the decomposed products. The ^{1}H NMR spectrum of **5** displayed two singlets attributable to two tert-butyl groups at δ 1.17 and 1.27 and a singlet at δ 1.82 ppm due to Cp*. Furthermore, four signals were observed at δ 1.38, 1.64, 4.78, and 5.60 ppm, which were tentatively assigned to the protons H3, H3′, H1, and H2, respectively, of a 1,6-diphenyl-1,5-hexadiene moiety coordinated to tantalum via η^2-coordination of two double bonds. However, we could not determine the coordination mode of the hexadiene moiety, *i.e.* whether prone or supine.

^{1}H NMR data of a reported mononuclear η^2,η^2-hexadiene molybdenum complex, Mo(CO)$_4$(η^2,η^2-1,5-hexadiene) (**6**) [31], prepared by the reaction of Mo$_2$(μ^2-η^3-allyl)$_2$(η^3-allyl)$_2$ with carbon monoxide support the above assignment of the structure of **2**. In complex **6**, the allylic methylene protons are observed at δ 1.16 and 1.77 and the olefin proton H2 at δ 4.46 ppm.

Attack by a π-donor (L) is reported to induce the reductive coupling of allyl groups of CpCr(allyl)$_2$ to give paramagnetic 17-electron chromium complexes, CpCr(η^2,η^2-1,5-hexadiene) (L) (**7**), in which hexadiene coordinates to chromium in the supine mode [18b]. Complex **5** is too unstable to be isolated, and all attempts to isolate **5** resulted in decomposition to **3a** and unidentified tantalum complexes. In the presence of excess tert-butyl isocyanide, complex **2** afforded **3a** in 78% yield.

Complex **2** is the catalyst precursor for the dimerization of phenylisocyanate. In the presence of **2** (1 mol%) a toluene solution of PhNCO at room temperature afforded the dimer (83% yield) with a trace of trimer. The allyl coupling product **3a** was isolated in 73% yield. Thus, the tantalum(I) species is considered catalytically active. Dimerization of ethyl isocyanate, tert-butyl isocyanate, and cyclohexyl isocyanate in the presence of **2** (1 mol%) afforded the corresponding urea derivatives in 69–90% yields upon hydrolysis of the cyclic dimer as shown in (2).



(2)

Similarly, the reaction of **2** with excess isothiocyanates such as PhNCS, EtNCS, and c-C$_6$H$_{11}$NCS gave **3a** in 81–92% yield, but the catalytic dimerization of isothiocyanate was not detected.

Thus, the coordination of sterically less crowded donor molecules induces the intramolecular coupling reaction of allyl moieties to afford 18-electron species such as **5**. The further coordination of donor molecules releases **3a** and tantalum(I) species result. In contrast, no interaction of **2** was observed with sterically more crowded donor molecules such as trialkylphosphine and pyridine. It is interesting that the less crowded donor molecules such as DMSO and pyridine-N-oxide can also interact with tantalum (*vide infra*). Thus, the shape of donor molecules is crucial for their ability to coordinate to the tantalum atom of **2**, since the tantalum atom is partially shielded by Cp* and phenylallyl ligands.

2.4. *Reaction of 2 with DMSO and pyridine-N-oxide*

Tantalum is generally regarded as an oxophilic element. Interaction of **2** with oxygen donor molecules such as dimethylsulfoxide and pyridine-N-oxide was therefore studied. Treatment of **2** with dimethylsulfoxide in toluene at room temperature resulted in the rapid formation of orange precipitates of Cp*Ta(1-phenylallyl)$_2$(DMSO) (**8**). The poor solubility of **8** in organic solvents prevented characterization except for elemental analysis. The reaction of **8** with 2 equiv of pinacol afforded the colourless bis(pinacolate) complex Cp*Ta(OCMe$_2$CMe$_2$O)$_2$ (**9**) and 3-phenylpropene in quantitative yield (by NMR). Similarly, the reaction of pyridine-*N*-oxide with **2** afforded a 1:1 adduct, whose further reaction with 2 equiv of pinacol also gave **9** and 3-phenylpropene. The mass spectrum indicated that complex **9** is monomeric. This finding is in sharp contrast to the report that the complex [Cp*Ta(OCH$_2$CH$_2$O)$_2$]$_n$ has a dimeric or oligomeric structure [32].

2.5. Oxidation of 2 with oxidants

When a solution of **2** in benzene-d_6 was exposed to oxygen, 3-phenyl-1-propene was formed (48% yield) together with unidentified tantalum residue. This is the oxidative elimination of an allyl group. The reaction of the d^0-metallocene dialkyl complexes of titanium and zirconium with one-electron oxidants to give products arising from alkyl radical expulsion or alkyl elimination has recently been reported [33]. The C–H bond activation of a methyl group of Cp* is known to give a hydride tantalum species [34]. Therefore, hydrogen is migrating from one of the methyl groups during the elimination of the allyl ligand to give 3-phenyl-1-propene.

Monitoring of the treatment of **2** with 2 equiv of ferrocenium cation in benzene-d_6 indicated complete disappearance of **2** within a few minutes and the formation of 1-phenyl-1-propene in 46% yield and 2 equiv of ferrocene. The corresponding 1:1 reaction afforded 1-phenyl-1-propene in 43% yield and ferrocene (1 equiv). The tantalum moiety must be oxidized to Ta^{V} and Ta^{IV} in each case, but we found only decomposed tantalum complexes.

In contrast, treatment of **2** in THF with the weaker one-electron oxidants DDQ and TCNQ gave the tantalum(IV) complexes, [Cp*Ta(1-phenylallyl)$_2$][DDQ] (**10a**) (dark red microcrystalline solid, 64% yield) and [Cp*Ta(1-phenylallyl)$_2$][TCNQ] (**10b**) (deep red microcrystalline solid, 90% yield). The presence of the TCNQ anion radical of **10b** was confirmed by the comparison of the UV spectrum with that of the reported anion radical [35]. ESR spectra of **10** in the solid state displayed a signal assignable to radical anions of DDQ and TCNQ [36], but no signal due to Ta^{IV}, d^1, was detected. Mononuclear paramagnetic Ta^{IV} complexes such as TaCl$_2$H$_2$(PMe$_3$)$_4$ [37] and Cp*TaCl$_3$(PMe$_3$) [38] showed ESR spectra with g values around 1.95–1.99. Thus, we believe that the signal of Ta^{IV} is superimposed on that of anion radicals.

3. Experimental section

3.1. General

All manipulations of air- and moisture-sensitive compounds were carried out by the use of standard Schlenk techniques under argon atmosphere. All solvents were purified by distillation under argon after drying over calcium hydride or sodium benzophenone ketyl. Cp*TaCl$_4$ was prepared according to the literature [39].

Nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were measured on a JEOL JNM-EX-270 and a JEOL JNM-GSX-400 spectrometers. Mass spectra were recorded on a JEOL SX-102 spectrometer. Elemental analyses were performed at the Elemental Analysis Center of Osaka University. All melting points were measured in sealed tubes and were not corrected.

3.2. Preparations

3.2.1. [Cp*Ta(C_3H_5)$_2$]$_3$

To a solution of Cp*TaCl$_4$ (1.81 g, 3.95 mmol) in dry THF (30 ml) cooled at −78°C was added allyl Grignard reagent (18.1 mmol) in ether (18 ml). The reaction mixture initially turned to deep reddish violet and then to green. All volatiles were removed under reduced pressure, and the resulting residue was then extracted with hexane (70 ml). The solution was concentrated to *ca.* 10 ml and cooled to −20°C overnight to give **1** (41 mg, 3% yield) as dark green powder, mp. 104–107°C; mass spectrum (^{181}Ta) m/z; 1197 (M$^+$); UV (THF) λ_{max} 580 nm. ^{1}H NMR (C_6D_6) for a major isomer (70 ~ 80%): δ 4.62 (m, H$_2$), 1.86 (s, Cp*), 0.93 (m, H$_{1syn}$), −0.79 (m, H$_{1anti}$); ^{13}C NMR (C_6D_6): δ 12.01 ($C_5\mathit{Me}_5$), J(C–H) = 127 Hz), 54.05 (C$_1$, J(C–H) = 149 Hz), 73.56 (C$_2$, J(C–H) = 170 Hz), 101.28 (C_5Me$_5$).

3.2.2. Cp*Ta(1-phenylallyl)$_2$ (2)

To a solution of Cp*TaCl$_4$ (1.21 g, 2.64 mmol) in dry THF (20 ml) cooled at −78°C, was added a solution of 1-phenylallyl Grignard reagent (10.7 mmol) in ether (70 ml) via a syringe. The mixture was slowly warmed to room temperature and stirred overnight. During this period, the solution changed from deep orange to green, and finally to deep brown. The volatiles were then removed under reduced pressure, and the residue was extracted with a mixture of toluene and hexane (40 ml). The extract was filtrated through a pad of Celite and the filtrate was concentrated to *ca.* 5 ml under reduced pressure to afford **2** as red-brown microcrystals in 56% yield, mp 150–153°C; ^{1}H NMR (C_6D_6): δ 6.87–7.23 (aromatic protons), 5.64 (ddd, H_2, $J(1,2) = 9.6$ Hz, $J(2,3_{syn}) = 9.4$ Hz, $J(2,3)_{anti} = 9.5$ Hz), 1.74 (s, Cp*), 0.72 (dd, H_1, $J(1,3_{anti} = 1.9$ Hz), 0.07 (ddd, H_{3syn}, $J(3_{syn},3_{anti}) = 6.4$ Hz), −0.27 (ddd, H_{3anti}; ^{13}C NMR (C_6D_6): d 124.0, 127.8, 127.9, and 128.6 (aromatic carbons), 143.5 (C_5Me_5), 76.71 (C_2, J(C–H) = 168 Hz), 73.69 (C_1, 145 Hz), 62.91 (C_3, 151 Hz), 11.71 (C_5Me_5, 126 Hz); mass spectrum (^{181}Ta) m/z; 550 (M^+); UV(THF) λ_{max} 757 nm. Anal. Calcd. for $C_{28}H_{33}Ta$: C, 61.09; H, 6.09. Found: C, 61.19; H, 6.16%.

From the supernatant solution, a mixture of three isomers (8 : 1 : 4 ratio), *i.e.* *(E,E)*-1,6-diphenyl-1,5-hexadiene (**3a**), (*E*)-1,4-diphenyl-1,5-hexadiene (**3b**), 3,4-diphenyl-1,5-hexadiene (**3c**), was isolated in 42% yield by preparative TLC (Merck silica gel 60 F_{254}).

(*E,E*)-1,6-diphenyl-1,5-hexadiene [40,41]: m.p. 79°C (lit. [41] 79.0–79.5°C); ^{1}H NMR ($CDCl_3$) δ 2.38 (m, H3), 6.25 (m, H2), 6.43 (d, H1, $J(1,2) = 15.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 32.0 (C3), 128.8 (C2), 129.5 (C1). (*E*)-1,4-diphenyl-1,5-hexadiene: ^{1}H NMR ($CDCl_3$) δ 2.63 (ddd, H3, $J(1,3) = 1.2$ Hz, $J(2,3) = J(3,4) = 7.2$ Hz), 3.42 (dt, H4, $J(4,5) = 7.4$ Hz), 5.0–5.1 (m, H6a and H6b), 6.02 (m, H5), 6.11 (dt, H2, $J(1,2) = 15.6$ Hz), 6.34 (d, H1); ^{13}C NMR ($CDCl_3$) δ 38.0 (C3), 49.0 (C4), 113.6 (C6), 127.5 (C2), 130.5 (C1), 140.4 (C5). 3,4-diphenyl-1,5-hexadiene [41]: ^{1}H NMR ($CDCl_3$) δ 3.63 (m, H3), 4.78 (dd, H1a, $J(1a,2) = 17.1$ Hz and $J(1a,1b) = 1.2$ Hz), 4.85 (dd, H1b, $J(1b,2) = 10.1$ Hz), 5.86 (m, H2); ^{13}C NMR ($CDCl_3$) δ 54.5 (C3), 114.7 (C1), 139.1 (C2). Signals due to aromatic protons and carbons are omitted.

3.3. Reactions

3.3.1. Reaction of 2 with carbon monoxide

A solution of **2** (0.57 g, 1.03 mmol) in toluene (10 ml) was placed in an autoclave and CO (50 atm) introduced. The reaction mixture was stirred at room temperature overnight. The solution changed from dark brown to red brown. All volatiles were removed under reduced pressure, and the residue sublimed to give $Cp^*Ta(CO)_4$ (60 mg, 13% yield), the residual oily products were dissolved in toluene (2 ml) and the solution concentrated to 1 ml and cooled to −30°C to give colourless crystals of 1,6-diphenyl-1,5-hexadiene. The supernatant solution contained $Cp^*Ta(CO)_4$ and an unknown cluster compound having the empirical formula $Ta_3Cp_3^*(CO)_n$. Spectral data of $Cp^*Ta(CO)_4$ were superimposed on those from the literature [28]. Spectral data of $Cp_3^*Ta_3(CO)_n$: ^{1}H-NMR (C_6D_6, 30°C): δ 1.60 (s), 1.69 (s) relative intensity 1 : 2; IR (nujol): 1977w, 1943s, 1861s cm^{-1}; FAB MS (M.B. matrix) m/z 1123 ($M^+ - 21$, $n = 7$).

Another trial for carbonylation of **2** (0.17 g, 0.31 mmol) in toluene afforded **3a** (64 mg, 87% yield) under the same conditions. The complex was isolated by preparative TLC (silica gel 60).

3.3.2. Hydrolysis of 2

To a solution of **2** (3.7 mg, 6.7×10^{-3} mmol) in benzene-d_6 (0.5 ml) was added water (6 μl, 3.4×10^{-1} mmol) via a syringe. 3-Phenyl-1-propene and 1-phenylpropane were obtained in 49 and 48% yields, respectively, based on ^{1}H NMR spectrum.

To a solution of **2** (22.8 mg, 4.2×10^{-5} mol) dissolved in benzene-d_6 was added $HBF_4 \cdot OEt_2$ (0.015 g, 9.3×10^{-5} mol) via a syringe. The solution turned pale yellow. ^{1}H NMR spectrum indicated the formation of 1-phenyl-1-propene in 90% yield.

3.3.3. Reaction of 2 with $[Cp_2Fe][BF_4]$

To a solution of **2** (22.8 mg, 4.2×10^{-5} mol) in benzene-d_6 (0.5 ml) was added $[Cp_2Fe]BF_4$ (8.8 mg, 4.2×10^{-5} mol). After 1 h, equiv of ferrocene and 1-phenyl-1-propene (43%) were detected.

To a solution of **2** (54.8 mg, 10.7×10^{-5} mol) dissolved in benzene-d_6 (0.8 ml) was added ferrocenium cation (64.2 mg, 0.235 mmol). The solution changed to orange within 30 min. ^{1}H NMR spectrum exhibited signals due to ferrocene (2 equiv) and 1-phenyl-1-propene (46% yield).

3.3.4. Reaction of 2 with tert-butyl isocyanide

To a solution of **2** (60 mg, 0.10 mmol) in toluene (2 ml) was added excess tert-butyl isocyanide (1.2 ml). After the reaction mixture was stirred for 1 h, all volatiles were removed under reduced pressure. From the resulting residue, **3a** was isolated in 78% yield.

3.3.5. Dimerization of phenyl isocyanate catalyzed by 2

Phenyl isocyanate (1.4 ml, 12.8 mmol) was added to a stirred solution of **2** (66 mg, 0.13 mmol) in toluene (2 ml) at room temperature. After the reaction mixture was stirred at this temperature overnight, the solution turned black and a colourless solid precipitated. The resulting solid was filtered and dried *in vacuo* to give colourless PhNCO dimer (1.25 g, 83% yield), which was contaminated with trace amounts of the trimer. From the supernatant solution, **3a** (22 mg) and colourless PhNCO trimer (21 mg) were obtained by preparative TLC (Merck silica gel 60 F_{254}).

1,3-Diphenyl uretidenedione: mp. 178°C (lit. [42] 176.2°C); IR (nujol) 1769s, 1748s cm^{-1}; mass spectrum m/z; 238 (M^+). 1,3,5-Triphenyl isocyanurate: mp. 279°C (lit. [43] 280–281°C); IR (nujol) 1693s cm^{-1}; mass spectrum m/z; 357 (M^+).

3.3.6. *Dimerization of ethyl isocyanate catalyzed by* **2**

Ethyl isocyanate (0.7 ml, 9.08 mmol) was added to a stirred solution of **2** (52 mg, 0.09 mmol) in toluene (2 ml) at room temperature. After the reaction mixture was stirred at room temperature for 12 h, the solution turned dark in colour. After evaporation of all volatiles, the resulting residues were separated by preparative TLC to give 1,6-diphenyl-1,5-hexadiene (65 mg, 83% yield) and diethylurea (0.12 g, 63% yield). Diethylurea: mp 75°C (lit. [44] 75–75.3°C); IR (nujol) 3308s, 1613s cm^{-1}; mass spectrum m/z; 116 (M^+).

Similarly, the dimerization of cyclohexyl isocyanate and of tert-butyl isocyanate was catalyzed by **2** in toluene to give dicyclohexylurea and di(tert-butyl)urea in 89 and 90% yields, respectively, upon hydrolysis. Each reaction afforded **3a** in 59 and 81% yields, respectively.

Dicyclohexylurea: mp 228°C (lit. [45] 227–228°C); IR (nujol) 3308s, 1641s cm^{-1}; mass spectrum m/z; 224 (M^+). Di(tert-butyl)urea: mp 240°C (lit. [46] 242°C); ^1H NMR ($CDCl_3$) δ 1.33 (s, tert-Bu), 3.92 (bs, NH); IR (nujol) 3326s, 1621s cm^{-1}; mass spectrum m/z; 172 (M^+).

3.3.7. *Reaction of* **2** *with RNCS*

A mixture of **2** (0.05 g, 0.10 mol) with excess PhNCS (1.1 ml) in toluene (2 ml) was stirred at room temperature. After 12 h, all volatiles were removed under reduced pressure. The produce was separated by preparative TLC. Elution with toluene affords **3a** in 81% yield. Similarly, treatment of **2** with ethyl isothiocyanate and cyclohexyl isothiocyanate gave **3a** in 85 and 92% yields, respectively.

3.3.8. *Reaction of* **2** *with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone*

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (63 mg, 0.28 mmol) was added to a stirred solution of **2** (150 mg, 0.28 mmol) in 15 ml of THF at room temperature for 2 h. The resulting solid was filtered, washed with hexane, and dried *in vacuo* to give a dark brown powder of $[Ta(C_5Me_5)(1\text{-phenylallyl})_2][DDQ]$ [47] in 64% yield. mp > 280°C; ESR $g = 2.0037$ (solid, 25°C); Anal. Calcd. for $C_{36}H_{33}Cl_2N_2O_2Ta(H_2O)_2$: C, 53.15; H, 4.58; N, 3.44. Found: C, 52.75; H, 4.65; N, 3.39%.

3.3.9. *Reaction of* **2** *with 7,7,8,8-Tetracyanoquinodimethane*

7,7,8,8-Tetracyanoquinodimethane (TCNQ) (40 mg, 0.19 mmol) was added to a stirred solution of **2** (106.5 mg, 0.19 mmol) in 30 ml of THF. After 2 h $[Ta(C_5Me_5)(1\text{-phenylallyl})_2][TCNQ]$ was obtained in 90% yield. mp > 280°C; ESR $g = 2.0030$ (solid, 25°C); Anal. Calcd. for $C_{40}H_{37}N_4Ta(H_2O)_4$: C, 58.11; H, 5.49; N, 6.78. Found: C, 58.12; H, 5.15; N, 6.96%.

3.3.10. *Reaction of* **2** *with DMSO*

Thoroughly dried dimethylsulfoxide (170 mg, 2.14 mmol) was added to a solution of **2** (393 mg, 0.714 mmol) in 15 ml of toluene at room temperature and stirred for 2 h. The resulting solid was filtered, washed with hexane, and dried *in vacuo* to give an orange powder of $Ta(C_5Me_5)(1\text{-phenylallyl})_2(Me_2SO)$ (0.23 g, 51% yield). Anal. Calcd. for $C_{30}H_{39}OSTa$: C, 57.32; H, 6.25. Found: C, 56.94; H, 5.85%.

To a suspension of $Ta(C_5Me_5)(1\text{-phenylallyl})_2(Me_2SO)$ (0.23 g, 0.37 mmol) in toluene (10 ml) at room temperature was added pinacol (87 mg, 0.73 mmol). Stirring for 1 h at ambient temperature made the precipitate dissolve and the colour change from orange to pale yellow. The solvent was removed under reduced pressure to give $Ta(C_5Me_5)(C_6H_{12}O_2)_2$ as colourless powder in 60% yield, together with 3-phenylpropene in quantitative yield. Recrystallization of the product from a mixture of toluene and hexane gave colourless crystals of $Ta(C_5Me_5)(C_6H_{12}O_2)_2$. m.p. > 300°C. ^1H NMR (C_6D_6, 30°C) δ 2.11 (s, C_5Me_5), 1.53, 1.32 (s, CH_3). Mass spectrum m/z, 548 (M^+).

3.3. *Reaction of* **2** *with pyridine-N-oxide*

To a stirred solution of **2** (245 mg, 0.445 mmol) in 15 ml of toluene was added pyridine-*N*-oxide (90.7 mg, 0.954 mmol). The reaction mixture was stirred at room temperature for 2 h. The resulting solid was filtered, washed with hexane, and dried *in vacuo* to give an orange powder of $Ta(C_5Me_5)(1\text{-phenylallyl})_2(C_5H_5NO)$ (0.12 g, 41% yield), m.p. 148–150°C. To a suspension of the obtained complex (6.8 mg, 0.011 mmol) in benzene-d_6 (0.5 ml) at room temperature was added pinacol (4.9 mg, 0.041 mmol). The ^1H NMR spectrum indicated that $Ta(C_5Me_5)(C_6H_{12}O_2)_2$, pyridine-*N*-oxide, and 3-phenylpropene were present in *ca.* 1 : 1 : 2 molar ratio, suggesting the formula of $Ta(C_5Me_5)(1\text{-phenylallyl})_2(C_5H_5NO)$.

3.4. *X-ray structure determination of* **2**

The X-ray study (Table 2) was carried out with a Rigaku AFC-5R automatic diffractometer. Intensity data were obtained by θ–2θ scans with Mo Kα radiation ($\lambda = 0.71069$). Lattice parameters were obtained by a least-squares analysis of 20 reflections scattered in reciprocal space, obtained from the automatic centering routine. Intensities of three standard reflections were monitored after every 100 data points. Background was measured before and after each peak. The solution and refinement of the structure were carried out on a VAX computer using the TEXSAN package,

TABLE 2. Crystal data and data collection parameters for complex **2**

Formula	$C_{28}H_{33}Ta$
Formula weight	550.52
Crystal system	monoclinic
Space group	*Cc*
a, Å	21.996(5)
b, Å	8.995(4)
c, Å	16.863(5)
β, deg	135.85(1)
Z	4
V, Å^3	2324(2)
d_{calcd}, g cm^{-3}	1.573
Diffractometer	Rigaku AFC 5R
Radiation	Mo Kα (λ = 0.71069 Å)
Reflections measd	±h, ±k, +1
Crystal size, mm	0.3 × 0.4 × 0.5
Abs. coeff, cm^{-1}	46.84
Scan mode	$2\theta-\omega$
Temp, °C	25
Scan speed, deg/min	5
Scan width, deg	$1.2+0.5\tan\theta$
Bkgd count, sec	5
$2q_{max}$, deg	65
Data collected	3613
Unique data ($I > 3\sigma(I)$)	2753
No. of variables	260
R	0.026
R_w	0.029
GOF	1.16
Δ, e Å^{-3}	1.22 (max.) −0.54 (min.)

which includes subroutines for direct methods, difference Fourier maps, least squares refinements, and distance and angle calculations. The data were corrected for Lorentz and polarization effects. Absorption correction was made by standard method using azimuthal scan of a reflection having near 90°.

A Patterson map revealed the positions of the tantalum atom, and subsequent least-squares refinements (full-matrix) and difference Fourier maps gave the positions of all non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. Hydrogens were included in the last refinement at the positions determined by difference maps (hydrogen atoms of allyl moieties) and at calculated positions, but were not refined.

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References and notes

1 G. Wilke, B. Bogdanović, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter and H. Zimmermann, *Angew. Chem., 78* (1966) 157; *Angew. Chem., Int. Ed. Engl., 5* (1966) 151.

2 J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, Univ. Sci. Press, California, 1987.

3 C. Elschenbroich and A. Salzer, *Organometallics*, VCH, Weinheim, 1992.

4 T. Kruck and H.-U. Hempel, *Angew. Chem., 83* (1971) 437; *Angew. Chem., Int. Ed. Engl., 10* (1971) 408.

5 A. van Baalen, C.J. Groenenboom and H.J. de Liefde Meijer, *J. Organomet. Chem., 74* (1974) 245.

6 P.R. Brown, F.G.N. Cloke and M.L.H. Green, *J. Chem. Soc., Chem. Commun.*, (1980) 1126; M.J. Bunker, A. de Cian, M.L.H. Green, J.J.E. Moreau and N. Siganporia, *J. Chem. Soc., Dalton Trans.*, (1980) 2155; M.L.H. Green and A.K. Hughes, *J. Chem. Soc., Dalton Trans.*, (1992) 527.

7 H. Yasuda, T. Arai, T. Okamoto and A. Nakamura, *J. Organomet. Chem., 361* (1989) 161.

8 V.C. Gibson, G. Parkin and J.E. Bercaw, *Organometallics, 10* (1991) 220.

9 J.M. Mayer, C.J. Curtis and J.E. Bercaw, *J. Am. Chem. Soc., 105* (1983) 2651.

10 H. Yasuda, K. Tatsumi, T. Okamoto, K. Mashima, K. Lee, A. Nakamura, Y. Kai, N. Kanehisa and N. Kasai, *J. Am. Chem. Soc., 107* (1985) 2410; T. Okamoto, H. Yasuda, A. Nakamura, Y. Kai, N. Kanehisa and N. Kasai, *J. Am. Chem. Soc., 110* (1988) 5008.

11 R. Poli, *Chem. Rev., 91* (1991) 509 and references cited therein; L. Messerle, *Chem. Rev., 88* (1988) 1229.

12 E. Melendez, A.M. Arif, A.L. Rheingold and R.D. Ernst, *J. Am. Chem. Soc., 110* (1988) 8703.

13 A. van Asselt, B.J. Burger, V.C. Gibson and J.E. Bercaw, *J. Am. Chem. Soc., 108* (1986) 5347.

14 The structure of 3-deutero-3-phenyl-1-propene and 1,2,3-trideutero-1-phenylpropane was determined by mass and NMR spectra.

15 We have used the designation, supine/prone, to distinguish the direction of diene coordinated to Group 5 metals [10].

16 G. Erker, K. Berg, C. Krüger, G. Müller, K. Angermund, R. Benn and G. Schroth, *Angew. Chem., 96* (1984) 445; *Angew. Chem., Int. Ed. Engl., 23* (1984) 455.

17 T.J. Prins, B.E. Hauger, P.J. Vance, M.E. Wemple, D.A. Kort, J.P. O'Brien, M.E. Silver and J.C. Huffman, *Organometallics, 10* (1991) 979.

18 (a) P.W. Jolly, C. Krüger, C.C. Romão and M.J. Romão, *Organometallics 3* (1984) 936; (b) K. Angermund, A. Döhring, P.W. Jolly, C. Krüger and C.C. Romão, *Organometallics, 5* (1986) 1268; (c) O. Andell, R. Goddard, S. Holle, P.W. Jolly, C. Krüger and Y.H. Tsay, *Polyhedron, 8* (1989) 203; (d) M.C. Azevedo, T.H. Brock, P.W. Jolly, A. Rufinska and G. Schroth, *Polyhedron, 10* (1991) 459.

19 P.J. Vance, T.J. Prins, B.E. Hauger, M.E. Silver, M.E. Wemple, L.M. Pederson, D.A. Kort, M.R. Kannisto, S.J. Geerligs, R.S. Kelly, J.J. McCandless, J.C. Huffman and D.G. Peters, *Organometallics, 10* (1991) 917.

20 P.A. Wexler, D.E. Wigley, J.B. Koerner and T.A. Albright, *Organometallics, 10* (1991) 2319.

21 G. Wilkinson, F.G.A. Stone and E.W. Abel, *Comprehensive Organometallic Chemistry*, Pergamon Press, 1982.

22 Recent examples of early transition metals: K.-B. Shiu, K.-S. Liou, C.P. Cheng, B.-R. Fang, Y. Wang, G.-H. Lee and W.-J. Vong, *Organometallics, 8* (1989) 1219; D.J. Wink, N.-F. Wang and J.P. Springer, *Organometallics, 8* (1989) 259; F. Iczek, P.W. Jolly and C. Krüger, *J. Organomet. Chem., 382* (1990) C11; P. Betz, P.W. Jolly, C. Krüger and U. Zakrzewski, *Organometallics, 10* (1991) 3520; L.M. Atagi, S.C. Critchlow and J.M. Mayer, *J. Am. Chem. Soc., 114* (1992) 1483; R. Krämer, E. Lippmann, K. Noisternig, M. Steimann, U. Nagel and W. Beck, *Chem. Ber., 126* (1993) 927.

23 W.J. Evans, T.A. Ulibarri and J.W. Ziller, *J. Am. Chem. Soc., 112* (1990) 2314.

24 T.H. Cymbaluk, R.D. Ernst and V.W. Day, *Organometallics, 2* (1983) 963.

25 G. Erker, K. Berg, K. Angermund and C. Krüger, *Organometallics, 6* (1987) 2620.

26 R.H. Crabtree, E.M. Holt, M. Lavin and S.M. Morehouse, *Inorg. Chem., 24* (1985) 1986.

27 M. Brookhart, M.L.H. Green and L.-L. Wong, *Prog. Inorg. Chem., 36* (1988) 1.

28 W.A. Herrmann, W. Kalcher, H. Biersack, I. Bernal and M. Creswick, *Chem. Ber., 114* (1981) 3558.

29 W.A. Herrmann and H. Biersack, *J. Organomet. Chem., 191* (1980) 397; W.A. Herrmann, M.L. Ziegler, K. Weidenhammer and H. Biersack, *Angew. Chem., Int. Ed. Engl.*, 18 (1979) 960; W.A. Herrmann, H. Biersack, M.L. Ziegler, K. Weidenhammer, R. Siegel and D. Rehder, *J. Am. Chem. Soc., 103* (1981) 1692; J.N. Lewis and K.G. Caulton, *Inorg. Chem., 19* (1980) 3201; V.C. Gibson, T.P. Kee and W. Clegg, *J. Organomet. Chem., 353* (1988) C23.

30 J. Arnold, T.D. Tilley, A.L. Rheingold, S.J. Geib and A.M. Arif, *J. Am. Chem. Soc., 111* (1989) 149; T.Y. Meyer, L.R. Garner, N.C. Baenziger and L. Messerle, *Inorg. Chem., 29* (1990) 4045.

31 R.J. Blau and U. Siriwardane, *Organometallics, 10* (1991) 1627.

32 V.C. Gibson and T.P. Kee, *J. Organomet. Chem., 444* (1993) 91.

33 W. Tumas, D.R. Wheeler and R.H. Grubbs, *J. Am. Chem. Soc., 109* (1987) 6182; R.F. Jordan, R.E. LaPointe, C.S. Bajgur, S.F. Echols and R. Willett, *J. Am. Chem. Soc., 109* (1987) 4111; R.H. Grubbs and W. Tumas, *Science*, (1989) 907; D.A. Straus, C. Zhang and T.D. Tilley, *J. Organomet. Chem., 369* (1989) C13; M.J. Burk, W. Tumas, M.D. Ward and D.R. Wheeler, *J. Am. Chem. Soc., 112* (1990) 6133; M.J. Burk, D.L. Staley and W. Tumas, *J. Chem. Soc., Chem. Commun.*, (1990) 809.

34 S.T. Carter, W. Clegg, V.C. Gibson, T.P. Kee and R.D. Sanner, *Organometallics, 8* (1989) 253; H.M. Anstice, H.H. Fielding, V.C. Gibson, C.E. Housecroft and T.P. Kee, *Organometallics, 10* (1991) 2183; M. Booji, A. Meetsma and J.H. Teuben, *Organometallics, 10* (1991) 3246; A.D. Horton, *Organometallics, 11* (1992) 3271 and references cited therein.

35 H.T. Jonkaman and J. Kommandeur, *Chem. Phys. Lett., 15* (1972) 496.

36 D.B. Chesnut and W.D. Phillips, *J. Chem. Phys., 35* (1961) 1002.

37 M.L. Luetkens, Jr., W.L. Elcesser, J.C. Huffman and A.P. Sattelberger, *Inorg. Chem., 23* (1984) 1718.

38 V.C. Gibson, J.E. Bercaw, W.J. Bruton, Jr. and R.D. Sanner, *Organometallics, 5* (1986) 976; V.C. Gibson, T.P. Kee and W. Clegg, *J. Chem. Soc., Dalton Trans.*, (1990) 3199.

39 H. Yasuda, T. Okamoto and A. Nakamura, *Organometallic Syntheses, 4* (1988) 22; R.D. Sanner, S.T. Carter and W.J. Bruton, Jr., *J. Organomet. Chem., 240* (1982) 157.

40 H.P. Koch, *J. Chem. Soc.*, (1948) 1111.

41 R.P. Lutz, S. Bernal, R.J. Boggio, R.O. Harris and M.W. McNicholas, *J. Am. Chem. Soc., 93* (1971) 3985.

42 C.J. Brown, *J. Chem. Soc.*, (1955) 2931.

43 I.C. Kogon, *J. Am. Chem. Soc., 78* (1956) 4911.

44 T.L. Davis and K. Blanchard, *J. Am. Chem. Soc., 51* (1929) 1790.

45 A.F. McKay, W.R.R. Park and S.J. Viron, *J. Am. Chem. Soc., 72* (1950) 3659.

46 A. Bühly and H.E. Fierz-David, *Helv. Chim. Acta, 26* (1943) 2123.

47 The solid samples of **10** were diamagnetic; Prof. W. Mori (Osaka Univ.), personal communication.