EurJIC
European Journal of Inorganic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

Title: Synthesis, Structure, and Reductive Elimination of Cationic Palladium(IV) Monoaryl Complexes Supported by a Tripodal Oxygen Ligand

Authors: Yat-Ming So, Ka-Chun Au-Yeung, Herman H. Y. Sung, Ian D. Williams, and Wa-Hung Leung

To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.201700326

Link to VoR: http://dx.doi.org/10.1002/ejic.201700326

WILEY-VCH

10.1002/ejic.201700326

WILEY-VCH

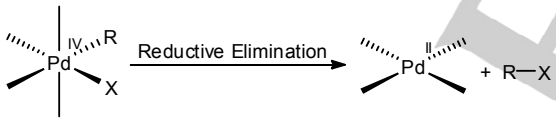
Synthesis, Structure, and Reductive Elimination of Cationic Palladium(IV) Monoaryl Complexes Supported by a Tripodal Oxygen Ligand

Yat-Ming So, Ka-Chun Au-Yeung, Herman H.-Y. Sung, Ian D. Williams, and Wa-Hung Leung*[a]

Abstract: Cationic Pd^{IV} mono-aryl complexes supported by the Kläui tripodal ligand $[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^-$ (L_{OEt}^-) have been synthesized and their reductive elimination has been studied. The treatment of *trans*-$[Pd(PPh_3)_2(Ar)(I)]$ and $[Pd(\eta^2\text{-}ppyBu^t)Cl]_2$ [ppyBu^{t}H = 2-(4-*tert*-butylphenyl)pyridine] with $[AgL_{OEt}]$ afforded $[Pd(Ar)(PPh_3)(\eta^2\text{-}L_{OEt})]$ (Ar = Ph (**1**), *p*-tolyl (**2**)) and $[Pd(\eta^2\text{-}ppyBu^t)(\eta^2\text{-}L_{OEt})]$ (**3**), respectively. The chlorination of **1**, **2** and **3** with $PhICl_2$ in the presence of NH_4PF_6 afforded the cationic Pd^{IV} aryl chloride complexes $[Pd(Ph)(PPh_3)(Cl)(L_{OEt})](PF_6)$ (**4**), $[Pd(p\text{-tolyl})(PPh_3)(Cl)(L_{OEt})](PF_6)$ (**5**) and $[Pd(\eta^2\text{-}ppyBu^t)(Cl)(L_{OEt})](PF_6)$ (**6**), respectively. Complexes **4** and **5** underwent $C(sp^2)$-Cl elimination at 40 °C in acetonitrile to give a Pd^{II}-L_{OEt} species and the corresponding chloroarene. On the other hand, the $C(sp^2)$-Cl elimination of **6** occurred at room temperature affording a Pd^{II} species, presumably $[Pd(ClppyBu^tH)(L_{OEt})](PF_6)$, which further reacted with $PhICl_2$ to yield $[Pd(\eta^2\text{-}ClppyBu^t)Cl(L_{OEt})](PF_6)$ (**7**) [ClppyBu^{t}H = 2-(4-*tert*-butyl-2-chlorophenyl)pyridine]. The structures of complexes **1**, **4**, **6** and **7** have been established by X-ray crystallography.

Introduction

High-valent organometallic complexes of Pd (especially Pd^{IV}) have attracted much attention because of their involvement as reactive intermediates in some Pd-catalyzed organic transformations.[1] As a consequence, there has been an increasing interest in the organometallic chemistry of Pd^{IV} in the past decade.[2] In particular, the reductive elimination of well-defined organo-Pd^{IV} complexes leading to the formation of carbon-carbon and carbon-heteroatom bonds has been investigated extensively (Scheme 1).[3] Also, recent studies have shown that in addition to reductive elimination, other fundamental organometallic reactions at the Pd^{IV} center, including ligand substitution, C−H activation, and migratory insertion, play key roles in the Pd^{II}/Pd^{IV} catalytic cycles.[4]

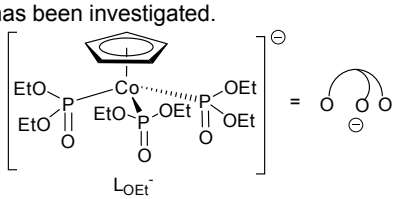


R = aryl, alkyl
X = carbene, nitrene, alkoxide, thiolate, alkyl, halide *etc.*

Scheme 1. Carbon-carbon and carbon-heteroatom elimination at the Pd^{IV} center.[3]

Despite the wealth of organometallic chemistry of Pd^0 and Pd^{II},[5] the coligand effect on the reactivity of Pd^{IV} complexes has not been well explored. Chelating coligands can increase the electron density of the Pd center, thus facilitating the Pd^{II}/Pd^{IV} oxidation and enhancing the chemo- and regio-selectivity of Pd-mediated C-H transformations. Of special interest are facially coordinating tridentate ligands that have proven to be excellent spectactor ligands for Pd^{IV}.[2]

Although Pd-based catalysts in oxygen-rich ligand environments (e.g. palladium(II) acetate and oxide) are well known,[1,6] not many well-defined organo-Pd^{IV} complexes with O-donor ligands have been synthesized;[7] reported Pd^{IV} complexes are mostly supported by N- and C-donor ligands.[2,8] We are particularly interested in the Kläui's tripodal ligand $[CoCp\{P(O)(OEt)_2\}_3]^-$ (Cp = η^5-C_5H_5; denoted as L_{OEt}^- hereafter) (Scheme 2) that is capable of stabilizing metal ions in high oxidation states.[9] Stable high-valent transition metal (e.g. Ru^{VI}),[9b,10a-d] and lanthanide (Ce^{IV})[10e] complexes with L_{OEt}^- have been synthesized, suggesting that the $\{PdL_{OEt}\}$ fragment can serve as a good platform for the study of Pd^{IV} organometallic chemistry. Previously, Kläui and coworkers synthesized Pd^{II} complexes with bidentate L_{OR}^- (R = Me, Et) ligands, e.g. $[(\eta^2\text{-}L_{OMe})Pd(allyl)]$ and $[(\eta^2\text{-}L_{OMe})Pd(PPh_3)Cl]$.[11] Nevertheless, the oxdiative addition of these Pd^{II}-L_{OMe} complexes has not been reported. The Pd^{IV} trialkyl complexes $[(L_{OMe})Pd(Me)_2R]$ were obtained by oxidative addtion of $[Pd(bpy)Me_2]$ (bpy = 2,2'-bipyridine) with RI in the presence of $[NaL_{Ome}]/[AgL_{Ome}]$;[12] however, like other Pd^{IV} trialkyl complexes, $[(L_{OMe})Pd(Me)_2R]$ do not undergo reductive elimination. To enhance the reactivity of the Pd^{IV} center, we sought to synthesize $L_{OEt}Pd^{IV}$ mono-aryl halide complexes. Herein, we describe the synthesis of cationic Pd^{IV}-L_{OEt} aryl complexes by oxidation of Pd^{II}-L_{OEt} complexes with $PhICl_2$. The $C(sp^2)$-Cl elimination of the Pd^{IV} aryl chloride complexes has been investigated.



L_{OEt}^-

Scheme 2. Structure of the Kläui tripodal ligand L_{OEt}^-.

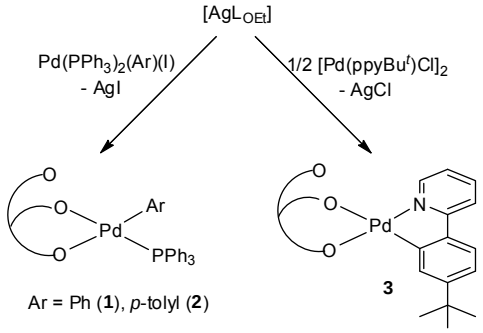
Results and Discussion

Synthesis of Pd^{II}-L_{OEt} Complexes

[a] Dr. Y.-M. So, Dr. K.-C. Au-Yeung, Dr. H. H.-Y. Sung, Prof. I. D. Williams, Prof. W.-H. Leung
Department of Chemistry
The Hong Kong University of Science and Technology
Clear Water Bay, Kowloon, Hong Kong (P. R. China)
Fax: (+852) 2356-1594
E-mail: chleung@ust.hk

Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate))

Metathesis of *trans*-[Pd(PPh$_3$)$_2$(Ar)(I)][13] with 1 equivalent of [AgL$_{OEt}$] in CH_2Cl_2 resulted in precipitation of AgI and a yellow solution, from which air-stable yellow crystals characterized as [Pd(Ar)(PPh$_3$)(η^2-L$_{OEt}$)] (Ar = Ph (**1**), *p*-tolyl (**2**)) were isolated (Scheme 3). Complexes **1** and **2** are soluble in common organic solvents including hexanes. Despite the η^2 binding mode of the L$_{OEt}^-$ ligand (see Figure 1), only one set of ethoxy signals was found in the ^{1}H NMR spectra of **1** and **2**. In addition, the ^{31}P NMR spectra displayed a single peak at *ca*. δ = 108 ppm attributable to the three equivalent phosphorus nuclei of L$_{OEt}^-$ along with the PPh$_3$ signal, indicating that the bidentate tripodal ligand is fluxional in solution at room temperature.



Scheme 3. Syntheses of [Pd(Ar)(PPh$_3$)(η^2-L$_{OEt}$)] (Ar = Ph (**1**), *p*-tolyl (**2**)) and [Pd(ppyBu^t)(η^2-L$_{OEt}$)] (**3**).

Recrystallization of **1** from CH_2Cl_2/hexanes afforded yellow single crystals that were suitable for X-ray diffraction. The solid-state structure of **1** is shown in Figure 1. The geometry around Pd is *pseudo* square planar and the L$_{OEt}^-$ binds to Pd in an η^2 mode. A weak Pd···O interaction was found between Pd and the uncoordinated P=O group [Pd(1)···O(7) 2.783(2) Å cf. 2.133(2) and 2.1259(19) Å for Pd(1)-O(8) and Pd(1)-O(9)]. Similar coordination geometry has been found for the reported Pd^{II}-L$_{OEt}$ complexes such as [Pd(Cl)(PPh$_3$)(η^2-L$_{OEt}$)][11a] and [Pd(C$_3$H$_5$)(η^2-L$_{OEt}$)][11b]. The Pd-C [1.968(3) Å] and Pd-P [2.203(7) Å] distances in **1** are comparable with those in *trans*-[Pd(PPh$_3$)$_2$(Ph)(I)] [2.029 (4) and av. 2.340 Å, respectively].[13]

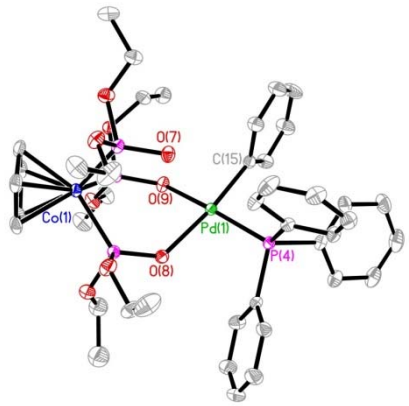
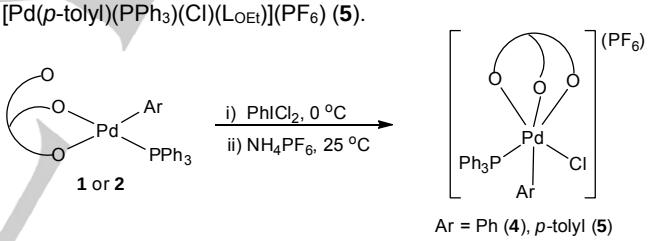


Figure 1. Molecular structure of **1**. The ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd-O(7) 2.783(2), Pd-O(8) 2.133(2), Pd-O(9) 2.1259(19), Pd-C(15) 1.968(3), Pd-P(4) 2.2025(7); O(8)-Pd-P(4) 97.74(6), O(9)-Pd-P(4) 167.07(6), O(9)-Pd-O(8) 84.48(8), C(15)-Pd-P(4) 88.64(8), C(15)-Pd-O(8) 173.35(10), C(15)-Pd-O(9) 89.71(10).

Recent studies have shown that cyclometalated ligands such as 2-phenylpyridine (ppy) are capable of stabilizing Pd^{IV} complexes.[14] This prompted us to synthesize cyclopalladated complexes supported by L$_{OEt}^-$. Treatment of [Pd(ppyBu^t)Cl]$_2$ [ppyBu^{t}H = 2-(4-*tert*-butylphenyl)pyridine] with 2 equivalents of [AgL$_{OEt}$] in CH_2Cl_2 afforded an air-stable yellow crystalline solid characterized as [Pd(ppyBu^t)(L$_{OEt}$)] (**3**) that presumably contains an η^2-L$_{OEt}$ ligand (Scheme 3). Complex **3** has been fully characterized by NMR spectroscopy and elemental analyses.

Synthesis of Pd^{IV}-L$_{OEt}$ Complexes

No oxidative addition was found when **1** or **2** was reacted with MeI. Since hypervalent iodine compounds have proven to be good 2-electron oxidants for Pd^{II},[14] the oxidation of **1** and **2** with $PhICl_2$ was studied. Treatment of **1** with 1 equivalent of $PhICl_2$ in MeCN at 0 °C afforded an orange species. Addition of NH_4PF_6 to the reaction mixture led to isolation of a cationic Pd^{IV}-L$_{OEt}$ complex, [Pd(Ph)(PPh$_3$)(Cl)(L$_{OEt}$)](PF$_6$) (**4**), in 79% yield (Scheme 4). Similarly, the treatment of **2** with $PhICl_2$, followed by the addition of NH_4PF_6 afforded the cationic Pd^{IV} *p*-tolyl complex [Pd(*p*-tolyl)(PPh$_3$)(Cl)(L$_{OEt}$)](PF$_6$) (**5**).



Scheme 4. Synthesis of [Pd^{IV}(Ar)(PPh$_3$)(Cl)(L$_{OEt}$)](PF$_6$) (Ar = Ph (**4**), *p*-tolyl (**5**))

Complexes **4** and **5** are reasonably stable in solution at room temperature, but they undergo reductive elimination readily at higher temperature (>40 °C) (see later section). Unlike that in **1**, the L$_{OEt}^-$ ligand in **4** is stereochemically rigid and three ^{31}P NMR signals (δ^P = 113.10, 118.55 and 127.98 ppm) were found for the three inequivalent phosphorus nuclei. In addition, a singlet at δ^P = 45.94 ppm due to the PPh$_3$ ligand, which is more downfield that that for **1** (δ^P = 30.77 ppm), was observed.

As the Pd atom in 6-coordinated **4** is stereogenic, **4** was isolated as a racemic mixture of two optical isomers. The crystal structure of one of the optical isomers of **4** is depicted in Figure 2. Selected bond lengths and angles are collected in Table 1. The geometry around Pd is *psuedo* octahedral and the L$_{OEt}^-$ ligand is in the more common η^3 binding mode. The Pd-O(7) bond [2.104(3) Å] is longer than that of Pd-O(8) bond [2.024(3) Å], but shorter than that of Pd-O(9) bond [2.155(3) Å]. The disparity of the Pd-O(L$_{OEt}$) distances is indicative of the order of the *trans* influence of the ligand Ph$^-$ > PPh$_3$ > Cl$^-$. It may be noted that reported organo-Pd^{IV} complexes usually contain two or three σ-donating hydrocarbyl ligands; not many Pd^{IV} mono-

organyl complexes have been isolated.[15] Although cationic Pd^{IV} compounds are well documented,[2] **4** is a rare example of a cationic Pd^{IV} mono-aryl complex characterized by X-ray crystalllography, demonstrating the ability of L_{OEt}^- to stabilize Pd^{IV}.

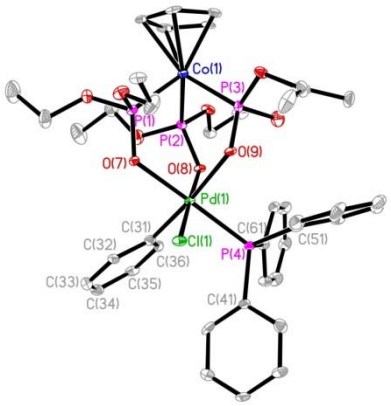
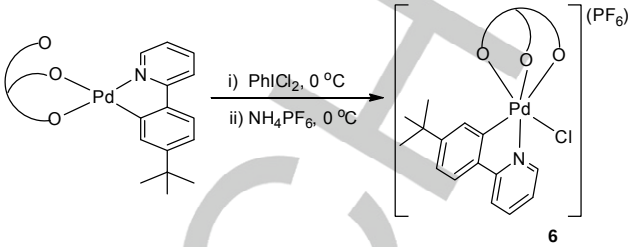


Figure 2. Molecular structure of one of the enantiomers of **4**. The ellipsoids are drawn at 30% probability level. Hydrogen atoms and PF_6^- are omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for **4**, **6** and **7**.

		4	
Pd-O(7)	2.104(3)	Pd-Cl(1)	2.2804(11)
Pd-O(8)	2.024(3)	Pd-P(4)	2.3097(11)
Pd-O(9)	2.155(3)	Pd-C(31)	2.026(5)
O(7)-Pd-P(4)	175.10(9)	O(8)-Pd-Cl(1)	178.46(9)
C(31)-Pd-O(9)	174.52(13)	Cl(1)-Pd-P(4)	85.84(4)
O(7)-Pd-Cl(1)	89.46(9)	O(7)-Pd-O(9)	86.70(12)
O(8)-Pd-P(4)	93.06(8)	O(8)-Pd-O(7)	91.61(11)
O(8)-Pd-O(9)	88.63(12)	O(8)-Pd-C(31)	88.15(16)
O(9)-Pd-Cl(1)	90.32(9)	O(9)-Pd-P(4)	91.93(8)
C(31)-Pd-Cl(1)	92.98(13)	C(31)-Pd-P(4)	92.68(12)
C(31)-Pd-O(7)	88.95(14)		
		6	
Pd-O(7)	2.021(3)	Pd-Cl(1)	2.2606(12)
Pd-O(8)	2.011(3)	Pd-N(1)	1.995(4)
Pd-O(9)	2.158(3)	Pd-C(41)	1.997(4)
O(7)-Pd-Cl(1)	176.44(9)	O(9)-Pd-Cl(1)	93.44(9)
O(7)-Pd-O(9)	89.14(12)	N(1)-Pd-Cl(1)	89.04(11)
O(8)-Pd-Cl(1)	89.60(9)	N(1)-Pd-O(7)	88.33(14)
O(8)-Pd-O(7)	92.77(12)	N(1)-Pd-O(8)	173.99(13)
O(8)-Pd-O(9)	91.79(12)	N(1)-Pd-O(9)	94.13(14)
N(1)-Pd-C(41)	81.80(18)	C(41)-Pd-O(8)	92.34(16)
C(41)-Pd-Cl(1)	89.48(13)	C(41)-Pd-O(9)	174.96(16)
C(41)-Pd-O(7)	87.77(15)		
		7	
Pd-O(7)	2.014(4)	Pd-Cl(1)	2.2622(17)
Pd-O(8)	2.021(4)	Pd-N(1)	1.995(5)
Pd-O(9)	2.167(5)	Pd-C(41)	1.984(7)
C(37)-Cl(2)	1.750(7)	C(41)-Pd-O(7)	88.5(2)
O(7)-Pd-Cl(1)	175.31(12)	O(9)-Pd-Cl(1)	95.56(13)
O(7)-Pd-O(9)	88.81(16)	N(1)-Pd-Cl(1)	90.15(15)
O(8)-Pd-Cl(1)	88.10(13)	N(1)-Pd-O(7)	87.92(19)
O(8)-Pd-O(7)	93.47(17)	N(1)-Pd-O(8)	175.0(2)
O(8)-Pd-O(9)	91.61(17)	N(1)-Pd-O(9)	93.2(2)
N(1)-Pd-C(41)	82.5(3)	C(41)-Pd-O(8)	92.8(2)
C(41)-Pd-Cl(1)	86.99(19)	C(41)-Pd-O(9)	175.0(2)

The treatment of **3** with $PhICl_2$ and NH_4PF_6 in MeCN at 0 °C afforded $[Pd^{IV}(\eta^2\text{-ppyBu}^t)(Cl)(L_{OEt})](PF_6)$ (**6**), isolated as reddish orange crystals in 80 % yield (Scheme 5).



Scheme 5. Synthesis of $[Pd^{IV}(\eta^2\text{-ppyBu}^t)(Cl)(L_{OEt})](PF_6)$ (**6**).

Contrary to **4** and **5**, **6** is unstable in solution at room temperature, as evidenced by NMR spectroscopy. When a solution of **6** in CD_3CN was left to stand at room temperature for ca. 1 h, the ^{31}P NMR signals due to **6** (δ^P = 112.0, 128.4 and 130.9 ppm) disapppeared and a new signal at δ^P = 116.6 ppm attributable to a Pd^{II} species (vide infra) appeared. The observation that **6** is less thermally stable than **4** or **5** is unexpected because one would expect the rigid metallacyclic structure would enhance the thermal stability of the Pd^{IV} center in **6**. It appears the rate of reductive elimination of the Pd^{IV} complexes is dependent on other factors (e.g. relative stability of the Pd^{IV} phosphine and pyridine complexes) that are not well understood. Additional experimental and computational studies are required in order to elucidate the factors affecting the reductive elimination of the Pd^{IV} complexes.

Recrystallization of **6** from CH_2Cl_2/hexanes at -20 °C afforded orange single crystals. X-ray crystallography indicated that the crystal was comprised of a racemic mixture of two optical isomers of **6** containing a stereogenic Pd center. The structure of one of the enantiomers of **6** featuring a chelating $ppyBu^t$ ligand is shown in Figure 3. Selected bond lengths and angles are listed in Table 1. The geometry around Pd^{IV} is *pseudo* octahedral. The Pd-C [1.997(4) Å] and Pd-N [1.995(4) Å] distances compare well with those in reported Pd^{IV} cyclometalated complexes.[14] The Pd-O bond trans to C [2.158(3 Å] is significantly longer than the other two Pd-O bonds [2.021(3) and 2.011(3) Å] bonds, owing to the *trans* influence of the phenyl ring.

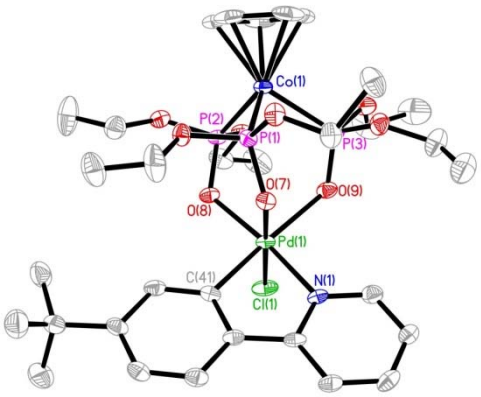
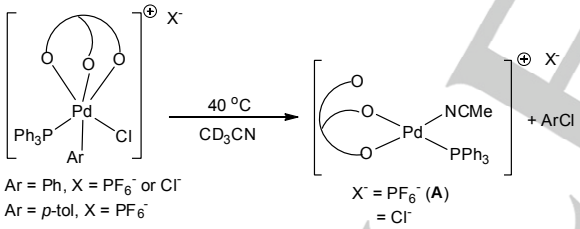


Figure 3. Molecular structure of one of the enantiomers of **6**. The ellipsoids are drawn at 30% probability level. Hydrogen atoms and PF_6^- are omitted for clarity.

Reductive Elimination of Pd^{IV}-L_{OEt} Complexes

Although complexes **4** and **5** are reasonably stable in solution at room temperature, they decomposed gradually in acetonitrile at higher temperature (> 40 °C), as evidenced by NMR spectroscopy. When a CD_3CN solution of **4** was warmed at 40 °C for 15 min, a new Pd-L_{OEt} species, presumably $[Pd^{II}(L_{OEt})(PPh_3)(CD_3CN)](PF_6)$ (**A**), with δ^P = 116.5 (L_{OEt}) and 26.16 (PPh_3) ppm, was formed. In addition, GLC analysis revealed that chlorobenzene was produced in 85% yield (with respect to **4**). This result suggests that **4** underwent C-Cl elimination to give a Pd^{II} species, **A** (Scheme 6). We have not been able to crystallize **A** for further identification. On the other hand, the reductive elimination of chloride anagloue of **4**, $[(L_{OEt})Pd^{IV}(Ph)(PPh_3)(Cl)]Cl$ that was generated *in-situ* from the reaction of **1** with $PhICl_2$ led to isolation of the previously reported compound $[Pd^{II}(L_{OEt})(PPh_3)(Cl)]$[11a] that was characterized by NMR spectroscopy, along with chlorobezene (Scheme 6). Similarly, **5** underwent reductive elimination in CD_3CN at 40 °C to give 4-chlorotoluene and **A**.

Addition of NH_4Cl did not accelerate the reductive elimination of **4**, thus indicating that the C-Cl bond elimination did not involve the nucleophilic attack of the phenyl ligand by dissociated chloride. Therefore, it is reasonable to assume that the the C-Cl elimination of **4** is an intramolecular process. A similar intramolecular C(sp^2)-Cl bond formation has been observed in the reductive elimination of a transient *O,N,N*-pincer ligated Pd^{IV} aryl chloride species previously.[3j]



Ar = Ph, X = PF_6^- or Cl^-
Ar = *p*-tol, X = PF_6^-

$X^- = PF_6^-$ (**A**)
$= Cl^-$

Scheme 6. Reductive elimination of Pd^{IV} aryl chloride complexes at 40 °C.

As mentioned earlier, **6** is not stable in solution at room temperature. NMR spectroscopy indicated that at room temperature in acetonitrile, **6** was gradually converted to a new Pd-L_{OEt} species (δ^P = 116.6 ppm), possibly the Pd^{II} complex $[Pd(Cl\text{-}ppyBu^t)(L_{OEt})(CD_3CN)](PF_6)$ (**B**) (Scheme 7). Unfortunately, we have not been able to crystallize **B** from the oily reaction mixture. However, the oxidation of as-prepared **B** with $PhICl_2$ afforded orange crystals that were identified as the Pd^{IV} cyclometalated complex $[Pd(Cl\text{-}ppyBu^t)Cl(L_{OEt})](PF_6)$ (**7**) [$ClppyBu^tH$ = 2-(4-*tert*-butyl-2-chlorophenyl)pyridine] containing a chlorinated $ppyBu^t$ ligand. Alternatively, **7** could be obtained in 75% yield from the reaction of **3** with excess $PhICl_2$ (> 2 equivalents) in MeCN in the presence of NH_4PF_6. It should be noted that the C(sp^2)-Cl elimination of $[Pd^{IV}(ppy)_2Cl_2]$ to give *ortho*-chlorinated phenylpyridine has been reported by Sanford and co-workers previously.[14a] Also, it was reported that a *N*-heterocyclic-carbene alkoxide supported Pd^{IV} complex, $[Pd^{IV}L(bzq)Cl_2]$ (L = $OCMe_2CH_2$(1-C{NCHCHNiPr}), bzq = benzo[*h*]quinoline), underwent facile C(sp^2)-Cl reductive elimination to give a Pd^{II} product.[8b]

Unlike **6**, complex **7** is stable in solution at room temperature. No reductive elimination was found for **7** in CD_3CN at room temperature for days, as evidenced by NMR spectroscopy. The higher stability of **7** compared with the unchlorinated analuge **6** is possibly owing to the stronger Pd-C bond. The MALDI mass spectrum of **7** exhibited a peak at *m/z* 922.0 that is assigned to $[M - PF_6]^+$. The structure of **7** (Figure 4) is very similar to that of **6**, except that the the meta hydrogen of the phenyl ring in the $ppyBu^t$ ligand is replaced by a chlorine. The Pd-C [1.984(7) Å] and Pd-N distances [1.995(5) Å] in **7** are similar those in **6**.

Scheme 7. Synthesis of $[Pd(\eta^2\text{-}Cl\text{-}ppyBu^t)Cl(L_{OEt})](PF_6)$ (**7**).

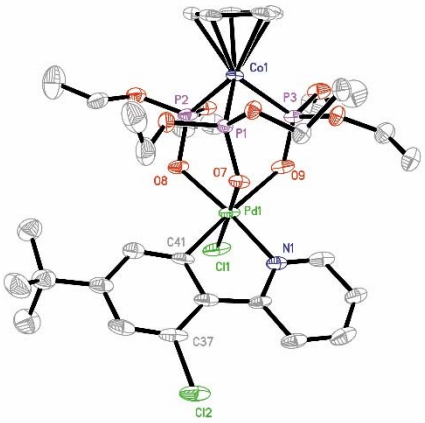


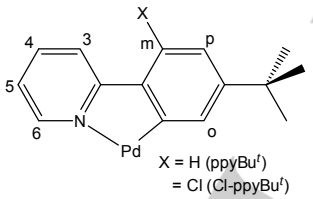
Figure 4. Molecular structure of one of the enantiomers of **7**. The ellipsoids are drawn at 30% probability level. Hydrogen atoms and PF_6^- are omitted for clarity.

Conclusions

In summary, we have synthesized the cationic Pd^{IV} aryl complexes $[Pd(Ar)(PPh_3)(Cl)(L_{OEt})](PF_6)$ (Ar = Ph (**4**), *p*-tolyl (**5**)) and $[(L_{OEt})Pd(ppyBu^t)Cl](PF_6)$ (**6**) by oxidation of the $L_{OEt}Pd^{II}$ precursors with $PhICl_2$. The $\{L_{OEt}Pd\}$ moiety proved to be a good platform for the study of reductive elimination of Pd^{IV} aryl complexes. **4** and **5** underwent C-Cl reductive elimination at 40 °C to give chloroarenes. On the other hand, the reductive elimination of **6** at room temperature gave a Pd^{II} species that further reacted with $PhICl_2$ to yield $[Pd(\eta^2\text{-Cl-ppyBu}^t)Cl(L_{OEt})](PF_6)$ (**7**). Complexes **4**, **6** and **7** are rare examples of structurally characterized cationic Pd^{IV} mono-aryl complexes, demonstrating the ability of L_{OEt}^- ligand to stabilize high oxidation state Pd complexes. The study of L_{OEt}-supported high-valent group 10 and 11 transition-metal (e.g. Ni, Cu) complexes that can find applications in C-H activation is underway.

Experimental Section

General: All manipulations were carried out under dinitrogen by standard Schlenk techniques. Solvents were purified by standard procedures and distilled prior to use. NMR spectra were recorded on a Bruker ARX 400 spectrometer operating at 400, 376.5, and 162 MHz for ^1H and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H) and H_3PO_4 (^{31}P), respectively. Reductive elimination products were determined by a HP6850 Chromatograph equipped with a FID detector. Elemental analyses were performed by Medac Ltd., Surrey, UK. Mass spectrum was recorded on a Waters Mass Spectrometer, with MALDI Micro MX module. The compounds $PhICl_2$,[16] AgL_{OEt},[17] *trans*-$[Pd(PPh_3)_2(Ar)(I)]$ (Ar = Ph, *p*-tolyl)[13] and $[Pd(\eta^2\text{-ppyBu}^t)Cl]_2$[18] were prepared according to literature methods. All other reagents were purchased from standard commercial sources and used without further purifications. Atom labeling schemes for the $ppyBu^t$ and Cl-$ppyBu^t$ ligands are shown in Scheme 8.



Scheme 8. Atom labelling scheme for the $ppyBu^t$ and Cl-$ppyBu^t$ ligands.

$[Pd(Ph)(PPh_3)(\eta^2\text{-}L_{OEt})]$ (1): To a solution of trans-$[Pd(PPh_3)_2(Ph)(I)]$ (100 mg, 0.12 mmol) in CH_2Cl_2 (5 mL) was added $[AgL_{OEt}]$ (77 mg, 0.12 mmol). The reaction mixture was stirred at room temperature overnight. The grey solid (AgI) formed was filtered off and the solvent was pumped off. Recrystallization from hexanes at -18°C afforded yellow crystals. Yield: 98 mg (83%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.14 (t, *J* = 7.2 Hz, 18H, CH_3, L_{OEt}), 3.84-3.96 (m, 12H, OCH_2), 4.99 (s, 5H, Cp), 6.54 (m, 2H, H_m of Ph), 6.61 (m, 1H, H_p of Ph), 7.02 (m, 2H, H_o of Ph), 7.21 (m, 6H, PPh_3), 7.32 (m, 3H, PPh_3), 7.51 (m, 6H, PPh_3) ppm. ^{31}P $\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 108.23 (s, L_{OEt}), 30.77 (s, PPh_3) ppm. Elemental analysis calcd (%) for $C_{41}H_{55}CoO_9P_4Pd$ (980.12): C 50.19, H 5.65; found C 48.61, H 5.55.

$[Pd(p\text{-tolyl})(PPh_3)(\eta^2\text{-}L_{OEt})]$ (2): The compound was synthesized similarly as for **1** using trans-$[Pd(PPh_3)_2(p\text{-tolyl})(I)]$ in place of trans-$[Pd(PPh_3)_2(Ph)(I)]$. Yield: 78 %. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.15 (t, *J* = 7.2 Hz, 18H, CH_3, L_{OEt}), 2.06 (s, 3H, CH_3), 3.85-3.95 (m, 12H, OCH_2), 4.99 (s, 5H, Cp), 6.39 (m, 2H, H_o of tolyl), 6.85 (m, 2H, H_m of tolyl), 7.21 (m, 6H, PPh_3), 7.32 (m, 3H, PPh_3), 7.48 (m, 6H, PPh_3) ppm. ^{31}P $\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 108.26 (s, L_{OEt}), 30.99 (s, PPh_3) ppm. Elemental analysis calcd (%) for $C_{42}H_{57}CoO_9P_4Pd$ (994.13): C 50.69, H 5.77; found: C 51.72, H 5.60.

$[Pd(ppyBu^t)(\eta^2\text{-}L_{OEt})]$ (3): To a solution of $[Pd(ppyBu^t)Cl]_2$ (100 mg, 0.142 mmol) in CH_2Cl_2 (5 mL) was added $[AgL_{OEt}]$ (46 mg, 0.072 mmol). The reaction mixture was stirred at room temperature overnight. The AgCl formed was filtered off and the solvent was pumped off. Recrystallization from hexanes at -18 °C afforded yellow crystals. Yield: 44 mg (73%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.28 (t, *J* = 7.2 Hz, 18H, CH_3, L_{OEt}), 1.30 (s, 9H, $C(CH_3)_3$), 4.13-4.19 (m, 6H, OCH_2), 4.24-4.29 (m, 6H, OCH_2), 5.10 (s, 5H, Cp), 7.00 (dd, *J* = 6.2 Hz, 1H, H^4), 7.07 (d, *J* = 8.0 Hz, 1H, H_p), 7.23 (s, 1H, H_o), 7.38 (d, *J* = 8.0 Hz, 1H, H_m), 7.50 (d, *J* = 7.6 Hz, 1H, H^3), 7.71 (dd, *J* = 6.2 Hz, 1H, H^5), 8.54 (d, *J* = 4.8 Hz, 1H, H^6) ppm. ^{31}P $\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 110.8 (s) ppm. Elemental analysis calcd (%) for $C_{32}H_{51}CoNO_9P_3Pd$ (851.11): C 45.11, H 6.03, N 1.64; found: C 46.31, H 6.17, N 1.79.

$[Pd(Ph)(PPh_3)(Cl)(L_{OEt})](PF_6)$ (4): A solution of **1** (100 mg, 0.10 mmol) and $PhICl_2$ (28 mg, 0.10 mmol) in MeCN was stirred at 0°C for 5 min, the reaction mixture changed from yellow to orange immediately. NH_4PF_6 (16.3 mg, 0.10 mmol) was added and the mixture was stirred at room temperature for 10 min. The orange solution was vacuum dried, washed with hexanes and then extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2/hexanes at -20 °C afforded orange crystals which were suitable for X-ray diffraction study. Yield: 92 mg (79 %). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.89 (t, *J* = 7.2 Hz, 6H, CH_3, L_{OEt}), 0.97 (t, *J* = 7.2 Hz, 3H, CH_3, L_{OEt}), 1.33 (t, *J* = 7.2 Hz, 6H, CH_3, L_{OEt}), 1.38 (t, *J* = 7.2 Hz, 3H, CH_3, L_{OEt}), 3.04-3.10 (m, 1H, OCH_2), 3.29-3.62 (m, 4H, OCH_2), 3.69-3.75 (m, 1H, OCH_2), 3.93-4.08 (m, 2H, OCH_2), 4.14-4.26 (m, 4H, OCH_2), 5.07 (s, 5H, Cp), 6.91 (br, 3H, H_p and H_o of Ph), 7.13 (dd, *J* = 7.6 Hz, 2H, H_m of Ph), 7.39-7.41 (m, 12H, PPh_3), 7.66-7.69 (m, 3H, PPh_3). ^{31}P $\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 113.10 (m, L_{OEt}), 118.55 (m, L_{OEt}), 127.98 (m, L_{OEt}), 45.94 (s, PPh_3), -144.48 (sept, *J* = 712 Hz, PF_6) ppm. Elemental analysis calcd (%) for $C_{41}H_{55}ClCoF_6O_9P_5Pd$ (1160.05): C 42.40, H 4.77; found: C 42.17, H 4.40.

$[Pd(p\text{-tolyl})(PPh_3)(Cl)(L_{OEt})](PF_6)$ (5): A solution of **2** (100 mg, 0.10 mmol) and $PhICl_2$ (28 mg, 0.10 mmol) in MeCN was stirred at 0 °C for 5 min, during which the color of the mixture changed from yellow to orange. NH_4PF_6 (16.3 mg, 0.10 mmol) was added and the mixture was stirred at room temperature for 10 min. The solvent was pumped off, and the residue was washed with hexanes and then extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2/hexanes at -20 °C afforded orange crystals Yield: 87 mg (72 %). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.83 (t, *J* = 7.2 Hz, 3H, CH_3, L_{OEt}), 0.86 (t, *J* = 7.2 Hz, 3H, CH_3, L_{OEt}), 0.92 (t, *J* = 7.2 Hz, 3H, CH_3, L_{OEt}), 1.23 (t, *J* = 7.2 Hz, 6H, CH_3, L_{OEt}), 1.28 (t, *J* = 7.2 Hz, 3H, CH_3, L_{OEt}), 2.62 (s, 3H, CH_3), 3.01-3.08 (m, 1H, OCH_2), 3.20-3.52 (m, 4H, OCH_2), 3.60-3.66 (m, 1H, OCH_2), 3.84-4.01 (m, 2H, OCH_2), 4.10-4.21 (m, 4H, OCH_2), 5.01 (s, 5H, Cp), 6.89-6.91 (m, 4H, H_m and H_o of tolyl), 7.35-7.38 (m, 12H, PPh_3), 7.60-7.62 (m, 3H, PPh_3) ppm. ^{31}P $\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 112.60 (m, L_{OEt}), 118.05 (m, L_{OEt}), 126.95 (m, L_{OEt}), 45.64 (s, PPh_3), -144.5 (sept, *J* = 712 Hz, PF_6) ppm. Elemental analysis calcd (%) for $C_{42}H_{57}ClCoF_6O_9P_5Pd$ (1174.07): C 42.91, H 4.89; found: C 42.47, H 4.92.

$[Pd(\eta^2\text{-}ppyBu^t)(Cl)(L_{OEt})](PF_6)$ (6): A solution of **3** (100 mg, 0.12 mmol) and $PhICl_2$ (33 mg, 0.12 mmol) in MeCN was stirred at 0 °C for 5 min. NH_4PF_6 (19.5 mg, 0.12 mmol) was added and the orange mixture was stirred for 10 min. The solvent was removed *in vacuo*, and the residue was washed with hexanes and then extracted with CH_2Cl_2.

Recrystallization from CH_2Cl_2/hexanes at -20 °C afforded orange crystals. Yield: 99 mg (80 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.99 (t, *J* = 7.2 Hz, 3H, CH_3, L_{OEt}), 1.03 (t, *J* = 7.2 Hz, 3H, CH_3, L_{OEt}), 1.37 (t, *J* = 7.2 Hz, 6H, CH_3, L_{OEt}), 1.40 (s, 9H, $C(CH_3)_3$), 1.44 (t, *J* = 7.2 Hz, 6H, CH_3, L_{OEt}), 3.35-3.44 (m, 1H, OCH_2), 3.64-3.79 (m, 3H, OCH_2), 4.11-4.19 (m, 1H, OCH_2), 4.28-4.46 (m, 7H, OCH_2), 5.15 (s, 5H, Cp), 7.47 (d, *J* = 8.0 Hz, 1H, H_p), 7.53 (dd, *J* = 6.0 Hz, 1H, H^4), 7.56 (s, 1H, H_o), 7.71 (d, *J* = 8.0 Hz, 1H, H_m), 8.00 (d, *J* = 8.0 Hz, 1H, H^3), 8.21 (dd, *J* = 6.0 Hz, 1H, H^5), 8.89 (d, *J* = 4.0 Hz, 1H, H^6) ppm. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 112.0 (m, L_{OEt}), 128.4 (m, L_{OEt}), 130.9 (m, L_{OEt}), -144.6 (sept, *J* = 712 Hz, PF_6) ppm. Elemental analysis calcd (%) for $C_{32}H_{51}ClCoF_6NO_9P_4Pd$ (1031.05): C 37.23, H 4.98, N 1.36; found: C 37.01, H 4.89, N 1.49.

[Pd(η^2-Cl-ppyBu^t)(Cl)(L_{OEt})](PF$_6$) (7): **6** (100 mg, 0.098 mmol) was dissolved in MeCN (10 mL) and solution was left to stand at room temperature (25 °C) for 1 h, during which color of the solution changed from orange to yellow. ^{31}P NMR spectroscopy indicated that the yellow solution contained a new Pd^{II} species (δ^P = 116.6 ppm), tentatively assigned as "[Pd(Cl-ppyBu^t)(L_{OEt})(CD_3CN)](PF_6)" (**B**). To the yellow solution was added $PhICl_2$ (27 mg, 0.098 mmol) and the mixture was stirred at 0 °C for 10 min. The solvent was removed in vacuo, and the residue was washed with hexanes and then extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2/hexanes at -20 °C afforded orange single crystals that were characterized as [Pd(η^2-Cl-ppyBu^t)(Cl)(L_{OEt})](PF_6) (**7**). Yield: 76 mg (73 %). Alternatively, **7** could be obtained in 75 % yield from the reaction of **3** with excess $PhICl_2$ (> 2 equiv.) in MeCN in the presence of NH_4PF_6 at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.01 (t, *J* = 7.2 Hz, 3H, CH_3, L_{OEt}), 1.04 (t, *J* = 7.2 Hz, 3H, CH_3, L_{OEt}), 1.38 (t, *J* = 7.2 Hz, 6H, CH_3, L_{OEt}), 1.41 (s, 9H, $C(CH_3)_3$), 1.43 (t, *J* = 7.2 Hz, 6H, CH_3, L_{OEt}), 3.38-3.48 (m, 1H, OCH_2), 3.67-3.75 (m, 3H, OCH_2), 4.10-4.21 (m, 1H, OCH_2), 4.28-4.48 (m, 7H, OCH_2), 5.17 (s, 5H, Cp), 7.46 (s, 1H, H_p), 7.65 (s, 1H, H_o), 7.73 (dd, *J* = 6.0 Hz, 1H, H^4), 8.25 (dd, *J* = 6.0 Hz, 1H, H^5), 8.89 (d, *J* = 7.2 Hz, 1H, H^3), 9.11 (d, *J* = 4.8 Hz, 1H, H^6). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 111.7 (m, L_{OEt}), 128.3 (m, L_{OEt}), 131.0 (m, L_{OEt}), -144.5 (sept, *J* = 712 Hz, PF_6) ppm. MALDI-MS: *m/z*: 922.0 [*M* - PF_6]$^+$. Elemental analysis calcd (%) for $C_{32}H_{50}Cl_2CoF_6NO_9P_4Pd$ (1065.01): C 36.02, H 4.72, N 1.31; found: C 36.76, H 4.71, N 1.28.

Reductive elimination of 4 and 5 in CD_3CN: The reductive eliminations of **4** (0.01 mmol) and **5** (0.01 mmol) in CD_3CN (0.5 mL) at 40 °C were monitored by ^{1}H and ^{31}P {^{1}H} NMR spectroscopy. During the course of the reaction, the signals due to **4** and **5** dropped while a new signal attributable to a Pd^{II} species, **A** (δ^P = 116.5 (L_{OEt}), 26.16 (PPh_3) ppm), appeared. The signals of **4** and **5** disappeared in ca. 15 min. The yields of chlorobenzene (85 %) and 4-chlorotoluene (83 %) were determined by GLC analysis using bromobenzene as the internal standard. Characterization data for **A**: ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ = 1.26 (t, *J* = 7.2 Hz, 18H, CH_3, L_{OEt}), 4.04 (m, 12H, OCH_2), 5.24 (s, 5H, Cp), 7.52 (m, 6H, PPh_3), 7.62 (m, 3H, PPh_3), 7.74 (m, 6H, PPh_3) ppm. ^{31}P {^{1}H} NMR (162 MHz, CD_3CN, 25 °C): δ = 116.55 (s, L_{OEt}), 26.16 (s, PPh_3) ppm.

Reductive elimination of [(L_{OEt})Pd(Ph)(PPh_3)(Cl)]Cl in CD_3CN: The reductive elimination of [(L_{OEt})Pd(Ph)(PPh_3)(Cl)]Cl, which was generated *in-situ* from the reaction of **1** (15 mg, 0.015 mmol) with $PhICl_2$ (4.2 mg, 0.015 mmol), in CD_3CN (1 mL) at 40 °C was monitored by ^{1}H and ^{31}P NMR spectroscopy. During the course of the reaction, the signals due to [(L_{OEt})Pd(Ph)(PPh_3)(Cl)]Cl dropped while new signals attributable to the known Pd^{II} complex [Pd(L_{OEt})(PPh_3)(Cl)] appeared. The reaction completed in ca. 15 min, and then volatiles were removed *in vacuo* and the residue was extracted with CH_2Cl_2/hexanes (1:1, v/v). Slow evaporation of the solvent afforded yellow crystals that were identified as the known compound [Pd(L_{OEt})(PPh_3)(Cl)][11a] by NMR spectroscopy. Yield: 12 mg (85 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.20 (t, *J* = 7.2 Hz, 18H, CH_3, L_{OEt}), 3.85-3.93 (m, 6H, OCH_2), 3.95-4.02 (m, 6H, OCH_2), 4.99 (s, 5H, Cp), 7.36 (m, 6H, PPh_3), 7.44 (m, 3H, PPh_3), 7.78 (m, 6H, PPh_3) ppm. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 111.22 (s, L_{OEt}), 24.76 (s, PPh_3) ppm.

X-ray Crystallography: Crystallographic data and refinement details for **1**, **4**, **6** and **7** are listed in Table 2. The diffraction intensity data of **1** was collected with a Rigaku Gemini™ S X-ray Diffractometer with monochromatized Cu-Kα radiation (λ = 1.54178 Å) at 173 K. The diffraction intensity data of **4** and **7** were collected with a Rigaku SuperNova Atlas X-ray Diffractometer with monochromatized Mo-Kα radiation (λ = 0.71073 Å) at 100 K. The diffraction intensity data of **6** was collected with a Rigaku SuperNova Atlas X-ray Diffractometer with monochromatized Mo-Kα radiation (λ = 0.71073 Å) at 173 K. Diffraction data of **1**, **4**, **6** and **7** were collected and processed using the CrysAlisPro software (Rigaku, 2012). Empirical absorption corrections were performed using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm in the CrysAlisPro software suite. Structure solution and refinement for all complexes were performed using the Olex2 software package[19] (which embedded SHELXTL[20]). All the structures were solved by direct methods, expanded by difference Fourier syntheses and refined by full matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically with a riding model for the hydrogen atoms except noted separately. All the pictures of molecules were made using XP implemented in SHELXTL.[20] CCDC 1484763, 1484764, 1484765 and 1528378 contain the supplementary crystallography data for complexes **1**, **4**, **6** and **7**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table 2. Crystallographic data and experimental details for **1**, **4**, **6** and **7**.

	1	**4**	**6**	**7**
Formula	$C_{41}H_{55}CoO_9P_4Pd$	$C_{41}H_{55}ClCoF_6O_9P_5Pd$	$C_{32}H_{51}ClCoF_6NO_9P_4Pd$	$C_{32}H_{50}Cl_2CoF_6NO_9P_4Pd$
F_w	981.06	1161.48	1032.40	1066.84

Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P-1	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	11.8720(6)	12.7928(4)	19.5875(10)	19.4486(12)
b [Å]	11.9815(5)	16.4736(5)	11.4890(5)	11.4144(5)
c ([Å]	18.0435(9)	22.3511(6)	20.9892(10)	21.4261(14)
α [°]	100.759(4)	90.00	90	90
β [°]	96.812(4)	94.034(3)	114.452(6)	113.872(8)
γ [°]	116.176(4)	90.00	90	90
V [Å^3]	2203.31(18)	4698.7(2)	4299.8(4)	4349.6(5)
Z	2	4	4	4
ρ_{calcd} [g cm^{-1}]	1.479	1.642	1.595	1.629
T [K]	173	100	173	100
F(000)	1012	2368	2104	2168
μ [mm^{-1}]	8.040	1.039	1.089	1.139
No. of reflns	12963	26931	24810	24571
No. of indep reflns	7712	8536	8332	8275
R_{int}	0.0347	0.0754	0.0582	0.0655
GoF[a]	1.003	1.000	1.003	1.001
R_1[b], wR_2[c]($I > 2\sigma(I)$)	0.0340, 0.0816	0.0492, 0.0805	0.0559, 0.1195	0.0686, 0.1645
R_1, wR_2 (all data)	0.0380, 0.0847	0.0825, 0.0888	0.0818, 0.1305	0.1139, 0.1891

[a]GoF = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$. [b]$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [c]$wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

Acknowledgements

The support from the Hong Kong Research Grants Council (project nos. 602913 and 16307216) and the Hong Kong University of Science and Technology is gratefully acknowledged.

Keywords: tripodal oxygen ligand • palladium(IV) • aryl • reductive elimination

[1] Reviews on Pd–catalyzed organic transformations that involve Pd^{IV} intermediates, see for example: a) P. Sehnal, R. J. K. Taylor, I. J. S. Fairlamb, *Chem. Rev.* **2010**, *110,* 824-889; b) D. A. Petrone, J. Ye, M. Lautens, *Chem. Rev.* **2016**, *116*, 8003-8104.

[2] Reviews on organometallic chemistry of Pd^{IV} complexes, see for example: a) L.-M. Xu, B.-J. Li, Z. Yang, Z.-J. Shi, *Chem. Soc. Rev.* **2010**, *39*, 712-733; b) A. J. Hickman, M. S. Sanford, *Nature* **2012**, *484*, 177-185; c) K. Muñiz, *Angew. Chem. Int. Ed.* **2009**, *48*, 9412-9423.

[3] Reductive elimination of Pd^{IV} complexes, see for example: a) J. M. Racowski, M. S. Sanford, *Top Organomet. Chem.* **2011**, *35*, 61-84; b) A. Vigalok, *Acc. Chem. Res*. **2015**, 48, 238-247; c) I. M. Pendleton, M. H. Pérez-Temprano, M. S. Sanford, P. M. Zimmerman, *J. Am. Chem. Soc.* **2016**, *138*, 6049-6060; d) M. H. Pérez-Temprano, J. M. Racowski, J. W. Kampf, M. S. Sanford, *J. Am. Chem. Soc.* **2014**, *136*, 4097-4100; e) N. M. Camasso, M. H. Pérez-Temprano, M. S. Sanford, *J. Am. Chem. Soc.* **2014**, *136*, 12771-12775; f) M. D. Lotz, M. S. Remy, D. B. Lao, A. Ariafard, B. F. Yates, A. J. Canty, J. M. Meyer, M. S. Sanford, *J. Am. Chem. Soc.* **2014**, *136*, 8237-8242; g) X. Zhao, V. M. Dong, *Angew. Chem. Int. Ed.* **2011**, *50*, 932-934; h) J. Hývl, J. Roithová, *Org. Lett.* **2014**, *16*, 200-203. i) J. R. Brandt, E. Lee, G. B. Boursalian, T. Ritter, *Chem. Sci.* **2014**, *5*, 169-179; j) L. A. Wright, E. G. Hope, G. A. Solan, W. B. Cross, K. Singh, *Dalton Trans.* **2015**, *44*, 6040-6051.

[4] a) J. S. Topczewski, M. S. Sanford, *Chem. Sci.* **2015**, *6*, 70-76; b) Y. Ye, N. D. Ball, J. W. Kampf, M. S. Sanford, *J. Am. Chen. Soc.* **2010**, *132*, 14682-14687; c) C. F. Rosewall, P. A. Sibbald, D. V. Liskin, F. E. Michael, *J. Am. Chem. Soc.* **2009**, *131*, 9488-9489; d) A. J. Hickman, M. S. Sanford, *ACS Catal.* **2011**, *1*, 170-174; e) J. M. Racowski, N. D. Ball, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 18022-18025; f) L. T. Pilarski, N. Selander, D. Bose, K. J. Szabo, *Org. Lett.* **2009**, *11*, 5518-5521; g) N. Selander, B. Willy, K. J. Szabo, *Angew. Chem. Int. Ed.* **2010**, *49*, 4051-4053; h) R. Alam, L. T. Pilarski, E. Pershagen, K. J. Szabo, *J. Am. Chem. Soc.* **2012**, *134*, 8778-8781.

[5] a) A. R. Muci, S. L. Buchwald, *Top. Curr. Chem.* **2002**, 219, 131-209; b) D. A. Culkin, J. F. Hartwig, *Acc. Chem. Res.* **2003**, *36*, 234-245; c) *Palladium Reagents and Catalysts: New Perspectives for the 21st Century* (Ed: J. Tsuji), Wiley and Sons, New York, **2003**; d) A. F. Littke, G. C. Fu, *Angew. Chem. Int. Ed.* **2002**, *41*, 4176-4211; e) D. S. Surry, S L. Buchwald, *Angew. Chem. Int. Ed.* **2008**, *47*, 6338-6361; f) J. F. Hartwig, *Inorg. Chem.* **2007**, *46*, 1936-1947.

[6] D. Ciuparu, M. R. Lyubovsky, E. Altman, L. D. Pfefferle, A. Datye, *Catal. Rev. Sci. Eng.* **2002**, *44*, 593-649.

[7] a) J. Bruns, D. van Gerven, T. Klüner, M. S. Wickleder, *Angew. Chem. Int. Ed.* **2016**, *55*, 8121-8124; b) P. L. Arnold, M. S. Sanford, S. M. Pearson, *J. Am. Chem. Soc.* **2009**, *131*, 13912-13913; E. Abada, P. Y. Zavalij, A. N. Vedernikov, *J. Am. Chem. Soc.* **2017**, *139*, 643-646.

[8] a) A. Maleckis, M. S. Sanford, *Organometallics* **2011**, *30*, 6617-6627; b) A. J. Canty, H. Jin, J. D. Penny, *J. Organomet. Chem.* **1999**, *573*, 30-35 c) J. Cámpora, P. Palma, D. del Rio, E. Carmona, C. Graiff, A. Tiripicchio, *Organometallics* **2003**, *22*, 3345-3347; d) J. Cámpora, P. Palma, D. del Rio, J. A. Lopez, E. Alvarez, N. G. Connelly, *Organometallics* **2005**, *24*, 3624-3628; e) A. J. Canty, H. Jin, A. S. Roberts, B. W. Skelton, A. H. White, *Organometallics* **1996**, *15*, 5713-5722; f) A. Milet, A. Dedieu, A. J. Canty, *Organometallics* **1997**, *16*, 5331-5341.

[9] a) W. Kläui, *Angew. Chem. Int. Ed.* **1990**, *29*, 627-637. (b) W.-H. Leung, b) Q.-F. Zhang, X.-Y. Yi, *Coord. Chem. Rev.* **2007**, *251*, 2266-2279.

[10] a) Y.-M. So, W.-H. Chiu, W.-M. Cheung, H.-Y. Ng, H. K. Lee, H. H.-Y. Sung, I. D. Williams, W.-H Leung, *Dalton Trans.* **2015**, *44*, 5479-5487; b) W.-H. Leung, E. Y.-Y. Chan, T. C.-Y. Lai, W.-T. Wong, *Dalton Trans.* **2000**, 51-56; c) X.-Y. Yi, Y.-K. Sau, T. C.-H. Lam, I. D. Williams, W.-H. Leung, *Inorg. Chem.* **2007**, *46*, 7193-7198; d) H.-F. Ip, Y.-M. So, H. K. Lee, I. D. Williams, W.-H. Leung, *Eur. J. Inorg. Chem.* **2012**, 3289-3295 e) Y.-M. So, W.-H. Leung, *Coord. Chem. Rev.* **2016**, http://dx.doi.org/10.1016/j.ccr.2016.12.009.

[11] a) W. Kläui, M. Glaum, E. Hahn, T. Lügger, *Eur. J. Inorg. Chem.* **2000**, 21-28; b) B. Domhiiver, H. Hamers, W. Kläui, M. Pfeffer, *J. Organomet. Chem.* **1996**, *522*, 197-206.

[12] W. Klaui, M. Glaum, T. Wagner, M. A. Bennett, *J. Organomet. Chem.* **1994**, *472*, 355-358.

[13] J. P. Flemming, M. C. Pilon, V. V. Grushin, *Inorg. Chim. Acta* **1998**, *280*, 87-98.

[14] a) S. R. Whitfield, M. S. Sanford, *J. Am. Chem. Soc.* **2007**, *129*, 15142-15143; b) N. R. Deprez, M. S. Sanford, *Inorg. Chem.* **2007**, *46*, 1924-1935; c) J. M. Racowski, N. D. Ball, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 18022-18025.

[15] a) W. N. Oloo, P. Y. Zavalij, A. N. Vedernikov, *Organometallics* **2013**, *32*, 5601-5614; b) W. N. Oloo, P. Y. Zavalij, J. Zhang, E. Khaskin, A. N. Vedernikov, *J. Am. Chem. Soc.* **2010**, *132*, 14400-14402; c) N. D. Ball,

M. S. Sanford, *J. Am. Chem. Soc.* **2009**, *131*, 3796-3797; d) T. Furuya, T. Ritter, *J. Am. Chem. Soc.* **2008**, *130*, 10060-10061; e) J. Vicente, A. Arcas, F. Julia-Hernandez, D. Bautista, *Chem. Commun.* **2010**, *46*, 7253-7255; f) J. Vicente, A. Arcas, F. Julia-Hernandez, D. Bautista, *Inorg. Chem.* **2011**, *50*, 5339-5341.

[16] X. F. Zhao, Z. Zhang, *Synthesis* **2007**, *4*, 551-557.

[17] W. Kläui, *Naturforsch.* **1979**, *34 B*, 1403.

[18] E. C. Constable, T. A. Leese, D. A. Tocher, *Inorg. Chim. Acta.* **1991**, *182*, 93-100.

[19] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341. OLEX2: A complete structure solution, refinement and analysis program.

[20] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.

10.1002/ejic.201700326

WILEY-VCH

Entry for the Table of Contents (Please choose one layout)

Layout 2:

FULL PAPER

Cationic Pd^{IV} monoaryl complexes supported by the Kläui tripodal ligand $[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^-$ (L_{OEt}^-) have been synthesized and their reductive elimination has been studied.

Organopalladium(IV) complexes*

*Yat-Ming So, Ka-Chun Au-Yeung, Herman H.-Y. Sung, Ian D. Williams, and Wa-Hung Leung**

Page No. – Page No.

Synthesis, Structure, and Reductive Elimination of Cationic Palladium(IV) Monoaryl Complexes Supported by a Tripodal Oxygen Ligand

*one or two words that highlight the emphasis of the paper or the field of the study