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# Capturing a Ghost. Synthesis and Structural Characterization of Pd(dba)[P(*o*-Tol)$_3$]$_2$

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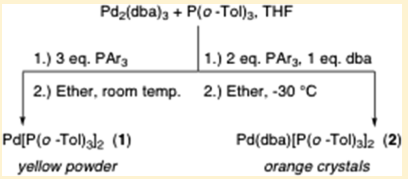
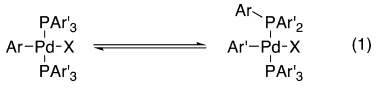
Supporting Information

**ABSTRACT:** In an effort to improve upon a literature synthesis of bis[tris(*o*-tolyl)-phosphine]palladium(0) (**1**) from tris(*o*-tolyl)phosphine and Pd$_2$(dba)$_3$, we instead isolated a new compound which proved to have the composition Pd(dba)[P(*o*-Tol)$_3$]$_2$ (**2**), upon analysis by X-ray crystallography. While this is not the first known palladium compound containing both dba and phosphine ligands, it is, to our knowledge, the first containing dba and tris(*o*-tolyl)phosphine. This is significant, because mixtures of Pd$_2$(dba)$_3$ and tris(*o*-tolyl)phosphine are routinely used in cross-coupling protocols, and palladium complexes containing dba and tris(*o*-tolyl)phosphine have been cited as intermediates in organometallic and polymerization reactions. The most interesting crystallographic parameter for **2** is an abnormally long Pd−P bond length of 2.388(1) Å, which we believe is the cause of this complex's metastability. We also present an alternative synthesis of **1** that does not require a large excess of phosphine.



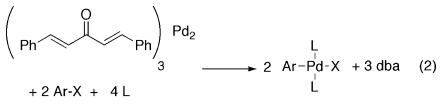

Since 1978, when Heck made the discovery that tris(*o*-tolyl)phosphine could be utilized to improve the yield of some palladium-catalyzed alkene coupling reactions,[1] this ligand has played a pivotal role in the development of numerous cross-coupling protocols. For example, Kosugi noted that PdCl$_2$[P(*o*-Tol)$_3$]$_2$ could be used in an early example of a C−N cross-coupling reaction,[2] an observation that led to tris(*o*-tolyl)-phosphine serving as a starting point in the development of more advanced catalyst systems for this and other cross-coupling reactions in the years that followed.[3,4]

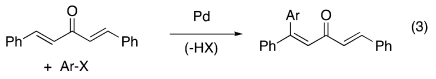
Along the same lines, others later showed that utilizing tris(*o*-tolyl)phosphine instead of the more common triphenylphosphine in Heck[5] and Suzuki[6] coupling reactions could markedly reduce the formation of byproducts caused by a concomitant aryl−aryl exchange reaction. In this process (eq 1),[7] a




palladium-bound aryl group swaps places with one from a phosphine, resulting in the latter being incorporated into the desired catalytic reaction. Novak then noted that the use of tris(*o*-tolyl)phoshpine in Suzuki polycondensation reactions could diminish the occurrence of this side reaction and produce polymers with molecular weights significantly higher than those obtained with more traditional catalyst systems.[8] The result of this observation is that tris(*o*-tolyl)phosphine is now, arguably, the ligand of choice to use in many Suzuki polycondensation reactions.[9,10]

Tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$) has had a similarly illustrious role in the development of cross-coupling reactions and polymerizations.[11−13] Its air stability and easy entry into the catalytic cycle (via a simple oxidative addition; eq 2) make it a convenient choice to use as a metal source for these palladium-catalyzed methodologies. However,




in extensive electrochemical studies, Amatore and Jutand have shown that the dibenzylideneacetone ligands thus released continue to affect the desired catalysis through additional ligation to the palladium, thereby reducing its activity toward oxidative addition.[14] In addition, others have noted that the dibenzylideneacetone ligands can actively participate in the catalysis through a Heck reaction at the double bonds (eq 3).[15] In support of these observations, several examples of Pd(dba)$_x$L$_y$ complexes, which incorporate both dibenzylideneacetone and phosphine ligands, have been isolated and characterized.[16−31] However, to our knowledge, a defined palladium complex with both dibenzylideneacetone and tris(*o*-tolyl)phosphine ligands is not known in the literature, despite its suspected intermediacy in organometallic[25] and polymerization[9] reactions, as well as the fact that mixtures of Pd$_2$(dba)$_3$ and tris(*o*-tolyl)phosphine are routinely used in cross-coupling[32] and other[33] palladium-catalyzed reactions.

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In an attempt to improve upon a literature[25] synthesis of bis[tris(*o*-tolyl)phosphine]palladium(0) (**1**) (the best catalyst for the Suzuki polycondensation reactions studied in our laboratory[9]), we instead isolated (dibenzylideneacetone)-palladium(0) bis[tris(*o*-tolyl)phosphine], or Pd(dba)[P(*o*-Tol)$_3$]$_2$ (**2**), as a red-orange crystalline solid. In this short paper, we present what we believe to be the first synthesis, isolation, and X-ray characterization of this ephemeral complex.

## RESULTS AND DISCUSSION

In a typical synthesis of **1**, $Pd_2(dba)_3$ (or $Pd(dba)_2$ as it is isolated in its powdered, noncrystallized form) is allowed to react in benzene with 7 equiv of tris(*o*-tolyl)phosphine to form a complicated mixture of palladium complexes with dba and phosphine, from which **1** ultimately precipitates upon the addition of diethyl ether (eq 4).[25] Successful isolation of **1** relies

$$\underset{+\ P(o\text{-Tol})_3}{Pd(dba)_2} \xrightarrow{\text{benzene}} Pd(dba)_x[P(o\text{-Tol})_3]_y \xrightarrow{\text{ether}} \underset{\mathbf{1}}{Pd[P(o\text{-Tol})_3]_2} \quad (4)$$

upon its relative insolubility in this solvent medium in comparison with the released dibenzylideneacetone and its intermediate complexes. In our laboratory, the large excess of phosphine complicated the isolation of the product. In addition, we wished to replace the carcinogenic benzene with a solvent that was more benign and easier to remove in a glovebox. (More recently, other syntheses of **1** have been developed. However, they either start from Pd(Cp)(allyl),[34] which is not presently commercially available, or involve less convenient solvents such as methanol[35] and DMF.[36]) Toward this end, we tried the reaction in THF and only 3 equiv of phosphine. Upon removal of the solvent and addition of ether (at which point the yellow crystals of **1** would normally precipitate), bright orange-red platelets (which proved to have the composition Pd(dba)[P(*o*-Tol)$_3$]$_2$ (**2**),; eq 5) crystallized out of the reaction. These were then analyzed by X-ray diffractometry.

$$\underset{+\ P(o\text{-Tol})_3}{Pd_2(dba)_3} \xrightarrow[2.)\ \text{ether}]{1.)\ \text{THF}} \underset{\mathbf{2}}{Pd(dba)[P(o\text{-Tol})_3]_2} \quad (5)$$

An ORTEP crystal structure for **2** is presented in Figure 1. The unit cell includes 1.5 molecules of diethyl ether solvent, a fact further confirmed with elemental analysis. Of the

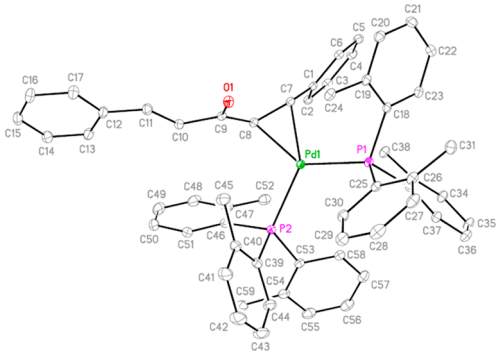


**Figure 1.** Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): Pd−C(7) = 2.163(2), Pd−C(8) = 2.189(2), Pd−P(1) = 2.372(1), Pd−P(2) = 2.388(1), C(7)−C(8) = 1.417(2), C(10)−C(11) = 1.334(2); C(7)−Pd−C(8) = 38.00(6), C(7)−Pd−P(1) = 101.33(5), P(1)−Pd−P(2) = 116.19(2), P(2)−Pd−C(8) = 105.15(5), P(2)−Pd−C(7) = 142.37(5), P(1)−Pd−C(8) = 138.37(5). The solvent of crystallization has been omitted for clarity.

$Pd(dba)_xL_y$ complexes that have been characterized crystallographically, most incorporate a chelating ligand. Three notable exceptions are complexes **3**,[19] **4**,[19] and **5**,[24] which are the closest structurally determined analogues to **2** (Figure 2). Like

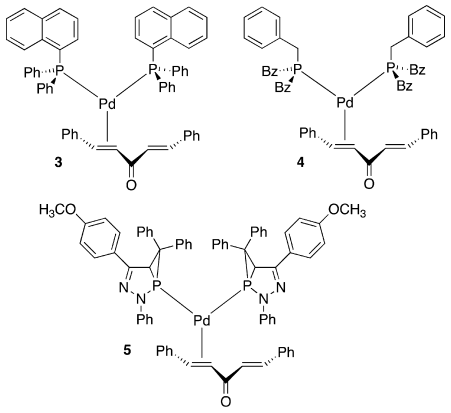


**Figure 2.** Closest structurally characterized analogues to **2**.

these compounds, **2** contains a dba ligand in a "W conformation"[37] with both double bonds *trans* and the palladium only bound to one of the olefins. This arrangement is typical for $Pd(dba)_xL_y$ derivatives, with one exception[31] that we found, in which the dba ligand is in the *s-cis/s-trans* conformation typically associated with the parent $Pd_2(dba)_3$.[27,38] Like the analogues, the palladium is in a trigonal geometry with respect to the three ligands, and the two phosphorus atoms and two olefin carbon atoms all lie in a plane with the palladium. The most remarkable parameters are the Pd−P bond lengths (2.372(1) and 2.387(1) Å), which are slightly longer than the corresponding values for **3** (2.338(6) and 2.357(6) Å)[19] and **4** (2.313(8) and 2.343(8) Å)[19] and significantly longer than the analogous parameters for **5** (2.257(2) and 2.255(2) Å).[24] Indeed, to our knowledge, these values for **2** are longer than any Pd−P bond measured for a $Pd(dba)_xL_y$ complex, which suggests a remarkably weak ligand/metal interaction that doubtlessly contributes to this compound's relative instability (vide infra) and generally spectral nature.

In solution, compound **2** could best be described as metastable. In our first synthesis of this compound, a few of the orange platelets were kept suspended in a small amount of solvent for subsequent crystallographic analysis. However, in the intervening time, the orange crystals transformed to the yellow powder characteristic of complex **1**. Furthermore, our attempts to recrystallize **2** by slow diffusion of ether into a concentrated THF solution (for better quality crystals) similarly resulted in the yellow powder. Fortunately, the dry crystals originally isolated proved to be of sufficient quality for successful X-ray analysis. When dry, the orange platelets appear to be stable when stored under argon at −30 °C.

The fickle nature of this compound further became apparent when we attempted to repeat its synthesis. The most common result of these trials was a heterogeneous mixture of orange platelets and yellow powder, which we attributed to a co-crystallization of both **1** and **2**. However, the balance can be reproducibly tipped toward the formation of **2** by utilizing only 2 equiv of phosphine and adding 1 equiv of dibenzylideneacetone. Correspondingly, we were able to achieve our alternative synthesis of **1** by pushing the reaction in the other direction and allowing the precipitation from ether to occur at


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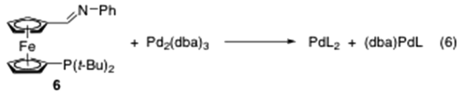
room temperature instead of −30 °C. It is worth noting that the reaction of $Pd_2(dba)_3$ and the hemilabile ligand **6** can similarly result in a mixture of $PdL_2$ and $Pd(dba)_xL_y$ complexes (eq 6) (the latter of which also exhibits an anomalously long




6

Pd−P bond length of 2.338(1) Å).[30] Along the same lines, the bulky tris(1-naphthyl)phosphine did not promote a reaction with $Pd_2(dba)_3$.[19] Thus, it appears that P(*o*-Tol)$_3$ is right at the tipping point for reactivity with $Pd_2(dba)_3$. Less sterically demanding (and/or more donating) ligands form stable $Pd(dba)_xL_y$ derivatives (with shorter Pd−P bonds), while larger (and/or less donating) phosphines fail to react.

The fluxionality of many $Pd(dba)_xL_y$ derivatives is well documented.[19,23,26] This, along with the metastability of **2** and its lack of symmetry, considerably complicated its analysis by NMR spectroscopy. When $d_6$-benzene was added to a sample of **2**, a small amount of yellow powder precipitated out. Analysis of the filtered solution by $^{31}$P NMR showed sharp signals at $\delta$ −30.2 (attributable to free phosphine) and 26.3, along with a broad signal centered at −7.7 ppm, which was the dominant peak in the spectrum. Much weaker broad signals were apparent at 24.6 and 20.3 ppm. Upon addition of 1 equiv of phosphine, the signal at −7.7 ppm broadened considerably and shifted slightly downfield, while the signals at 24.6 and 20.3 ppm broadened and shifted slightly upfield. The sharp peak at 26.3 ppm did not change in shape or chemical shift but weakened noticeably in comparison to the other signals. These results are consistent with a solution equilibrium between various complexes with the general formula $Pd([P(o\text{-Tol})_3]_x(dba)_y$, as has been suggested by others.[25] Complexes **1** and **2** happen to crystallize out of solution under certain, specific conditions. We tentatively assign the peak at −7.7 ppm to complex **1**, on the basis of its proximity to the literature[35] value (−7.3 ppm). In their synthesis of **1** from $Pd_2(dba)_3$ and 7 equiv of P(*o*-Tol)$_3$, Hartwig and co-workers observed a broad signal at 20 ppm in the $^{31}$P NMR spectrum of their reaction mixture, which they assigned to a complex mixture of $Pd([P(o\text{-Tol})_3]_x(dba)_y$ species.[25] From this, we believe it is reasonable to suggest that the signals at 26.3, 24.6, and 20.3 ppm correspond to different species of this general formula, one of which exhibits less fluxionality than the others. The fact that this signal consists of a single peak without multiplicity (configurationally stable $Pd(dba)(PR_3)_2$ derivatives typically exhibit two $^{31}$P signals with an AX splitting pattern, since the two phosphines are not equivalent[19]) indicates that this signal represents a species with a single phosphine, likely $Pd([P(o\text{-Tol})_3](dba)$. This suggests that, in solution, **2** can either lose a phosphine to form $Pd([P(o\text{-Tol})_3](dba)$ or lose a dba ligand to form **1**. The $^1$H NMR spectrum told a similar story. In addition to broad signals in the aromatic region, there were three dominant methyl signals—one broad resonance centered at 2.83 ppm (close to the literature[25] chemical shift of **1** at 2.92 ppm), a second at 2.41 ppm corresponding to free phosphine, and a weaker singlet at 2.72 ppm.

In conclusion, we have synthesized, isolated, and crystallographically characterized for the first time a palladium complex that contains both tris(*o*-tolyl)phosphine and dibenzylideneacetone. Although this complex has been implicated as an intermediate in other palladium-based chemistry, previous evidence for its existence had only been circumstantial. Indeed, the isolation of **2** is particularly interesting in light of electrochemical results that indicate $Pd([P(o\text{-Tol})_3]_x(dba)_y$ species do not exist in DMF solutions of $Pd(dba)_2$ and tris(*o*-tolyl)phosphine.[39] Finally, we were also successful in developing an alternate synthesis for the catalytically important bis[tris(*o*-tolylphoshpine)]palladium(0) (**1**).

## EXPERIMENTAL SECTION

**Materials and Methods.** All manipulations were performed in an argon-filled glovebox utilizing solvents that were used as received, dry and oxygen-free, from commercial suppliers. Tris(*o*-tolyl)phosphine and tris(dibenzylideneacetone)dipalladium(0) were obtained from a commercial supplier and not purified before use. NMR spectra were obtained using $d_6$-benzene as a solvent, which was degassed via three freeze−pump−thaw cycles (but not dried) prior to importation into the glovebox. $^1$H chemical shifts are reported relative to TMS and were calibrated by the signal due to residual protiated solvent. $^{31}$P chemical shifts are reported relative to 85% $H_3PO_4$ and were calibrated with an external standard of tris(*o*-tolyl)phosphine in toluene ($\delta$ −30.2 ppm[40]) with 10% (v/v) $d_6$-benzene added for locking and shimming purposes.

**X-ray Diffraction Studies.** X-ray diffraction data were collected on a CCD diffractometer with 0.71073 Å Mo K$\alpha$ radiation. Cell parameters were retrieved using APEX II software[41] and refined using SAINT+[42] on all observed reflections. The data set was treated with SADABS[43] absorption corrections based on redundant multiscan data; $T_{max}/T_{min}$ = 1.05. The structure was solved by direct methods and refined by least-squares methods on $F^2$ using the SHELXTL program package.[44] A single orange rhomb (0.08 × 0.08 × 0.20 mm) was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 110(2) K. Unit cell parameters were obtained from 60 data frames, 0.5° $\phi$, from three different sections of the Ewald sphere, yielding $a$ = 13.744(2) Å, $b$ = 13.865(2) Å, $c$ = 14.555(2) Å, $\alpha$ = 85.67(1)°, $\beta$ = 84.16(1)°, $\gamma$ = 83.84(1)°, and $V$ = 2737(1) Å$^3$. A total of 80432 reflections ($R_{int}$ = 0.0517) were collected (20641 unique) over $\theta$ = 1.50−33.18°. The data were consistent with the centrosymmetric, triclinic space group $P\bar{1}$. The asymmetric unit contains one $Pd(dba)[P(o\text{-Tol})_3]_2$ molecule and 1.5 molecules of diethyl ether solvent. One ether molecule was disordered about the inversion center, and GROW was used to find a whole molecule. A PART −1 command was used to ignore the symmetry at this position. The occupancy of this molecule was set at 0.5, and SADI and EADP commands were used to stabilize the refinement. All non-hydrogen atoms were refined with anisotropic displacement parameters. All other hydrogen atoms were treated as idealized contributions. The goodness of fit on $F^2$ was 1.016 with R1 (wR2) = 0.0421 (0.0806) for $I > 2\sigma(I)$ and with a largest difference peak and hole of 0.823 and −0.499 e/Å$^3$.

**Bis[tris(*o*-tolyl)phosphine]palladium(0) (1).** A 40 mL scintillation vial was charged with 79.8 mg (0.174 mmol of Pd) of tris(dibenzylideneacetone)dipalladium(0), 159.1 mg (0.523 mmol) of tris(*o*-tolyl)phosphine, 20 mL of THF, and a stir bar. The reaction mixture was stirred for 2 h at room temperature, after which it was filtered through a 3 cm pad of diatomaceous earth into a 100 mL round-bottomed flask. The solvent was then removed from the orange-yellow solution with a rotary evaporator. The resulting residue was treated with 3 mL of pentane to induce solid formation, after which the pentane was removed in vacuo. The crude product was then treated with 15 mL of ether, which resulted in the immediate precipitation of **1** as a yellow powder. This suspension was allowed to stand overnight at room temperature, after which the product was recovered via vacuum filtration. Repeated rinsing with ether resulted in the isolation of 88.8 mg (0.124 mmol, 71% yield) of **1** as a yellow powder: $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.04 (m, 18H), 6.82 (m, 6H), 2.97 (s, 18H) (lit.[25] (300 MHz, $C_6D_6$) $\delta$ 6.98 (m, 18H), 6.77 (m, 6H), 2.92 (s, 18H)). $^{31}$P NMR (161 MHz, $C_6D_6$): $\delta$ −8.14 (s) (lit.[35] (161 MHz, $C_6D_6$) $\delta$ −7.3 (s); commercial sample (161 MHz, $C_6D_6$) $\delta$ −8.13 (s)). A small amount of free phosphine was visible by $^{31}$P NMR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for both the synthesized and commercial samples. This has been attributed to dissociation of phosphine from **1** in solution.[35]

**(Dibenzylideneacetone)palladium(0) Bis[tris(*o*-tolyl)phosphine] (2).** A 40 mL scintillation vial was charged with 81.3 mg (0.178 mmol of Pd) of tris(dibenzylideneacetone)dipalladium(0), 110.6 mg (0.364 mmol) of tris(*o*-tolyl)phosphine, 42.8 mg (0.183 mmol) of dibenzylideneacetone, 20 mL of THF, and a stir bar. The reaction mixture was stirred for 2 h at room temperature, after which it was filtered through a 3 cm pad of diatomaceous earth into a 100 mL round-bottomed flask. The solvent was then removed with a rotary evaporator to yield a red-orange oil. To this was added 5 mL of ether, and the resulting solution was placed in a −30 °C freezer overnight. The resulting orange-red platelets were isolated via vacuum filtration and rinsed with ether at room temperature to redissolve any dibenzylideneacetone that cocrystallized. In this manner, 78.8 mg (0.0743 mmol, 42% yield) of **2** was isolated as the 1.5 diethyl ether solvate: IR (neat, $cm^{-1}$): $\nu$ 3054 (w), 2973 (w), 2847 (w), 1647 (m), 1590 (m), 1471 (m), 1440 (s), 1330 (m), 1269 (m), 1118 (m), 1091 (s), 1030 (m), 978 (m), 870 (m). Anal. Calcd for $C_{65}H_{71}O_{2.5}P_2Pd$: C, 73.61; H, 6.75; Found: C, 73.67; H, 6.62. Definitive NMR analysis was not possible due to the solution instability/fluxionality of this compound (see text).

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Tables and a CIF file giving crystallographic data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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