Inorg. Chem. **2009**, *48*, 2708−2710

Inorganic Chemistry
Communication

# Monomers and Polymers of Tripalladium(0) Ditropylium Halides

**Frank L. Mulligan,[†] Dominic C. Babbini,[†] Isaac R. Davis,[†] Stephanie K. Hurst,[*,†] and Gary S. Nichol[‡]**

*Department of Chemistry and Biochemistry, Northern Arizona University,
Flagstaff, Arizona 86011-5698, and Department of Chemistry, The University of Arizona,
Tucson, Arizona 85721-0041*

Received August 1, 2008

The synthesis and characterization of a series of polymeric complexes based upon a central tripalladium ditropylium (Tr) unit [$Pd_3Tr_2$] and containing different halide ligands are reported. The complexes were synthesized in good yield and characterized by multinuclei NMR spectroscopy, mass spectrometry, microanalysis, and X-ray crystallography. An unexpected product was an inorganic polymer consisting of linked individual tripalladium ditropylium units [$Pd_3Tr_2X_2$]$_\infty$ (X = Cl, Br, and I); this is the first reported, crystallographically characterized example of polymeric tripalladium complexes with halide ligands.

"Sandwich" complexes have found great utility since the discovery of ferrocene over 50 years ago, and the development of "sandwich" complexes with multiple metal centers represents a significant research objective.[1−3] The unique electronic and material properties of two-dimensional sheet structures such as graphene represent a new frontier for materials research.[4,5] There has been significant progress in the synthesis of zerovalent palladium complexes stabilized by coordination to polyene ligands, and the combination of this research with that of large polyaromatic hydrocarbons such as graphene may represent one potential way to develop polymeric two-dimensional sandwich materials.

In 2006, Murahashi et al. published the synthesis of a novel trimetallic palladium(0) sandwich complex [$Pd_3Tr_2Cl_3$][$PPh_4$] (**1**).[6] This complex incorporated a triangular arrangement of palladium(0) atoms "sandwiched" between two tropylium (Tr) rings ($C_7H_7^+$). Although both triangular and linear tripalladium(II) complexes have been reported previously, the stability and ease of substitution give rise to the possibility of new substitution patterns and molecular motifs.[7,8] Herein we report the development of a new series of monomeric and polymeric zerovalent tripalladium complexes.

The reported synthesis of **1** was repeated as part of an Advanced Inorganic Chemistry undergraduate course. While the synthesis of **1** was satisfactory, it was anticipated that replacement of the equatorial chloride ligands with other halogens might give enhanced yields. The reaction of $Pd_2(dba)_3$ with [$C_7H_7$][$BF_4$] and an excess of $PPh_4Br$ in $CH_2Cl_2$ for 1 h gave [$Pd_3Tr_2Br_3$][$PPh_4$] (**2**; Figure 1) as a dark-red solid. Recrystallization from hot MeCN gave an orange crystalline product in good yield. $^1$H NMR showed a sharp singlet at 4.72 ppm, characteristic of the tropylium protons, and a series of multiplets between 7.64 and 7.94 ppm, typical of the phenyl rings of the [$PPh_4$]$^+$ cation. $^{31}$P NMR showed a single peak at 24.4 ppm that also identified the [$PPh_4$]$^+$ cation. Electrospray mass spectrometry (ESMS) showed a molecular ion at 742.6 amu with a distinctive bromine isotope pattern, as anticipated for the [$Pd_3Tr_2Br_3$]$^-$ ion. Complex **2** was stable in a variety of organic solvents including MeCN, acetone, and chlorinated solvents.

A corresponding reaction substituted $PPh_4Br$ with $PPh_4I$ and gave the new complex [$Pd_3Tr_2I_3$][$PPh_4$] (**3**; Figure 1), which precipitated as a deep-purple crystalline solid after evaporation of a concentrated MeCN solution. ESMS indicated the parent ion at 881.6 amu, as expected for the [$Pd_3Tr_2I_3$]$^-$ anion. Complex **3** proved to be slightly less stable than **2**, with a greater propensity to precipitate out metallic palladium if left in solution for long periods of time. Thermogravimetric analysis experiments indicated that **2** and **3** were stable up to 180 and 200 °C in air, respectively, with significant decomposition above this temperature. Attempts to make [$Pd_3Tr_2F_3$][N(*n*-Bu)$_4$] were unsuccessful.

Recrystallization of **2** from MeCN gave orange crystalline needles that were suitable for single-crystal X-ray diffraction (Figure 1).[9−11] Analysis of the X-ray data showed that the central tripalladium motif in **2** is an almost equilateral triangle

---

[*] To whom correspondence should be addressed. E-mail: stephanie.hurst@nau.edu.

[†] Northern Arizona University.

[‡] The University of Arizona.

(1) Murahashi, T.; Kurosawa, H. *Coord. Chem. Rev.* **2002**, *231*, 207.

(2) Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 2125.

(3) Philpott, M. R.; Kawazoe, Y. *Chem. Phys.* **2007**, *337*, 55.

(4) Geim, A. K.; Novoselov, K. S. *Nat. Mater.* **2007**, *6*, 183.

(5) Wu, J.; Pisula, W.; Mullen, K. *Chem. Rev.* **2007**, *107*, 718.

(6) Murahashi, T.; Fujimoto, M.; Oka, M.-a.; Hashimoto, Y.; Uemura, T.; Tatsumi, Y.; Nakao, Y.; Ikeda, A.; Sakaki, S.; Kurosawa, H. *Science* **2006**, *313*, 1104.

(7) Balch, A. L.; Boehm, J. R.; Hope, H.; Olmstead, M. M. *J. Am. Chem. Soc.* **1976**, *98*, 7431.

(8) Lloyd, B. R.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1993**, *12*, 1231.

(9) *SMART, SAINT, and APEX*; Bruker AXS Inc.: Madison, WI, 2007.

(10) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

10.1021/ic8014578 CCC: $40.75

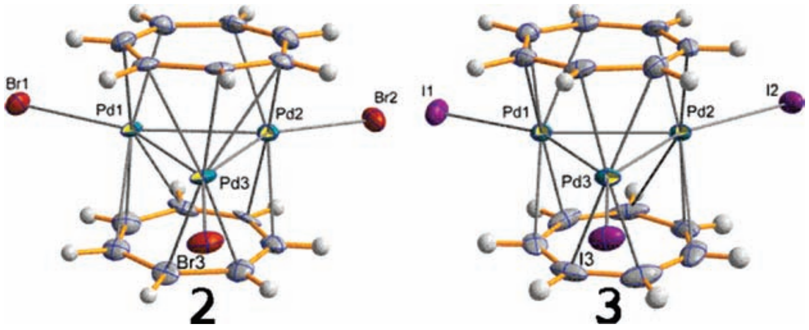


**Figure 1.** Structures of the discrete palladium complexes **2** and **3**. Displacement ellipsoids are at the 50% probability level.

**Table 1.** Selected Bond Lengths for Compounds **1**, **2**, **3**, **4** and **5**

| complex | Pd−Pd distances (Å) | Pd−X distances (Å) |
|---|---|---|
| **1** | Pd1−Pd2 2.7550(5), Pd1−Pd3 2.7889(5), Pd2−Pd3 2.7446(5) | Pd1−Cl1 2.471(1), Pd2−Cl2 2.471(1), Pd3−Cl3 2.441(1) |
| **2** | Pd1−Pd2 2.755(2), Pd1−Pd3 2.773(2), Pd2−Pd3 2.769(2) | Pd1−Br1 2.581(3), Pd2−Br2 2.581(3), Pd3−Br3 2.560(3) |
| **3** | Pd1−Pd2 2.7963(5), Pd1−Pd3 2.7757(5), Pd2−Pd3 2.7739(5) | Pd1−I1 2.7355(5), Pd2−I2 2.7543(5), Pd3−I3 2.7015(5) |
| **4** | Pd1−Pd2 2.7852(17), Pd1−Pd3 2.782(2), Pd2−Pd3 2.7755(17) | Pd1−Br1 2.649(2), Pd2−Br2 2.582(2), Pd3−Br3B 2.660(2) |
| **5** | Pd1−Pd2 2.7979(5), Pd1−Pd2B 2.7979(5), Pd2−Pd2B 2.8000(7) | Pd1−I1 2.7448(6), Pd2A−I2 2.8071(4), Pd2−I2 2.8071(4) |

**Table 2.** Selected Crystal Data for Compounds **2**−**5**[a]

| | **2** | **3** | **4** | **5** |
|---|---|---|---|---|
| formula | $C_{40}H_{37}Br_3NPd_3$ | $C_{39}H_{36}Cl_2I_3PPd_3$ | $C_{18}H_{26}Br_2O_2Pd_3S_2$ | $C_{18}H_{26}I_2O_2Pd_3S_2$ |
| moiety formula | $C_{24}H_{20}P^+ \cdot C_{14}H_{14}Br_3Pd_3 \cdot C_2H_3N$ | $C_{24}H_{20}P^+ \cdot C_{14}H_{14}I_3Pd_3^- \cdot CH_2Cl_2$ | $C_{14}H_{14}Br_2Pd_2 \cdot 2C_2H_6OS$ | $C_{14}H_{14}I_2Pd_3 \cdot 2C_2H_6OS$ |
| fw | 1121.61 | 1306.45 | 817.53 | 911.51 |
| CCDC no. | 658437 | 693586 | 693587 | 693588 |
| radiation type | Mo Kα | synchrotron, $\lambda = 0.7749$ Å | Mo Kα | Mo Kα |
| space group | monoclinic, $P2_1/n$ | orthorhombic, $Pna2_1$ | orthorhombic, $Pca2_1$ | orthorhombic, $Cmc2_1$ |
| $a$, Å | 7.550(3) | 29.858(2) | 16.969(4) | 7.7483(9) |
| $b$, Å | 30.138(11) | 7.6601(6) | 7.4951(19) | 17.074(2) |
| $c$, Å | 16.293(6) | 17.4096(13) | 17.292(5) | 17.804(2) |
| $\beta$, deg | 90.838(6) | 90 | 90 | 90 |
| $V$, Å$^3$ | 3707(2) | 3981.8(5) | 2199.2(10) | 2355.3(5) |
| $Z$ | 4 | 4 | 4 | 4 |
| $\rho_{calcd}$, g cm$^{-3}$ | 2.010 | 2.179 | 2.469 | 2.571 |
| $\mu$, mm$^{-1}$ | 4.747 | 3.868 | 6.263 | 5.077 |
| $T$, K | 120(2) | 120(2) | 120(2) | 298(2) |
| no. of rflns collected | 19496 | 56538 | 11486 | 10000 |
| no. of indep rflns | 4794 [$R$(int) = 0.1032] | 9883 [$R$(int) = 0.0655] | 3576 [$R$(int) = 0.0350] | 2995 [$R$(int) = 0.0279] |
| final $R$ indices ($F^2 > 2\sigma$) | R1 = 0.0529, wR2 = 0.1042 | R1 = 0.0273, wR2 = 0.0574 | R1 = 0.0346, wR2 = 0.0901 | R1 = 0.0201, wR2 = 0.0.0438 |

[a] Programs used. Data collection and reduction: *SMART*, *SAINT*, and *APEX*.[9] Absorption correction: *SADABS*.[11] Structure solution and refinement: *SHELXTL*.[10]

with Pd−Pd bond lengths of 2.755(2), 2.769(2), and 2.773(2) Å (Table 1). The Pd−Pd bond lengths are significantly longer than those reported for other triangular tripalladium complexes synthesized by Puddephatt,[12] Francis,[13] and their co-workers. Overall, the structure of **2** is analogous to the structure of **1**, which possesses Pd−Pd bond distances of 2.7550(5), 2.7446(5), and 2.7889(5) Å. The reported Pd−Cl bond lengths in **1** of 2.471(1)−2.442(1) Å are shorter than the Pd−Br bond lengths in **2** [2.581(3) and 2.560(3) Å], as expected upon replacement of bromine with the lighter chlorine atom. Single crystals of **3** were also grown by slow vapor diffusion of Et$_2$O into a CH$_2$Cl$_2$ solution (**3**; Figure 1), although the side product [Pd$_2$I$_6$][PPh$_4$]$_2$ was also occasionally isolated.[14] In **3**, Pd−Pd bond lengths of 2.7739(5), 2.7757(5), and 2.7963(5) Å were observed with Pd−I bond lengths of 2.7015(5)−2.7963(5) Å. In general, although the change in halogen ligands does not significantly affect the internal angles of the Pd$_3$ unit, in contrast the bond lengths of the Pd$_3$ unit increase slightly but observably (greater than 3 standard deviations) with **1** < **2** < **3**. Selected crystal data for **2**−**5** are listed in Table 2.

In the process of purifying **2** via recrystallization in MeCN, a small amount of dark insoluble material (**4**) remained undissolved in refluxing MeCN. This material was filtered off and was found to be insoluble in all solvents except for dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF). $^1$H NMR of this solid in DMSO-$d^6$ revealed the peak characteristic of the tropylium protons at 4.72 ppm, but no signals were observed in the phenyl region between 6 and 8 ppm. The absence of any signal in the $^{31}$P NMR indicated the absence of the [PPh$_4$]$^+$ cation; however, the UV−vis spectrum of **4** in DMSO was similar to that of the parent complex **2**. Slow recrystallization of **4** from a concentrated DMSO solution gave large dark-purple blade-like crystals suitable for X-ray diffraction. X-ray diffraction analysis showed that displacement of a single bromine ligand from **2** had occurred and the formation of **4** as a polymer chain of neutral [Pd$_3$Tr$_2$Br$_2$] units had occurred as a result of the vacant coordination site on one of the palladium atoms (**4**; Figure 2). Crystallization from DMSO of insoluble residue from the synthesis of **3** gave X-ray diffraction quality crystals of the analogous complex [Pd$_3$Tr$_2$I$_2$] (**5**; Figure

---

(11) Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 1996.

(12) Manojlovi-Muir, L.; Muir, K. W.; Lloyd, B. R.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1336.

(13) Francis, C. G.; Khan, S. I.; Morton, P. R. *Inorg. Chem.* **1984**, *23*, 3680.

(14) Mulligan, F.; Nichol, G. S.; Hurst, S. K. *Acta Crystallogr., Sect. E* **2007**, *63*, m2558.

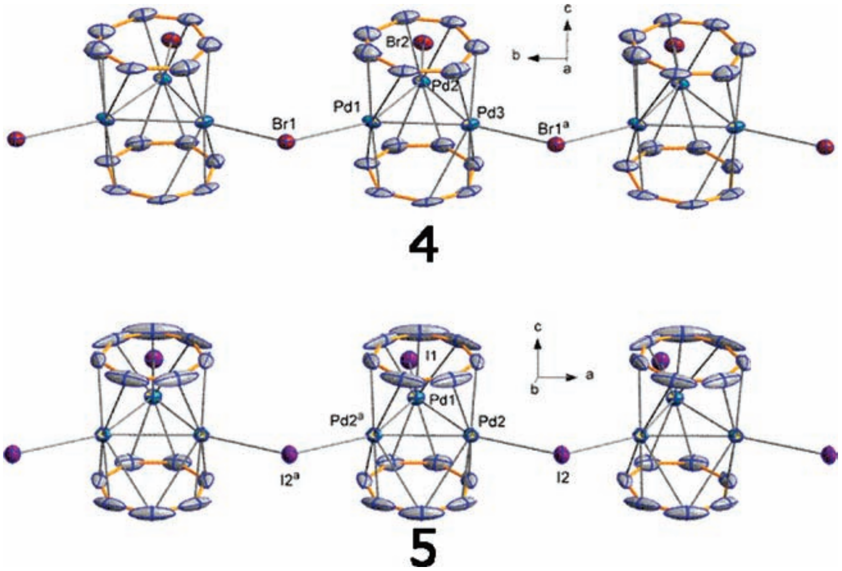
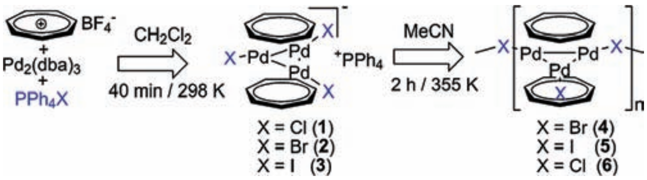


**Figure 2.** Structures of the polymeric palladium complexes **4** and **5**. Displacement ellipsoids are at the 50% probability level, and hydrogen atoms are omitted.

2). These are the first characterized examples of polymeric tripalladium compounds with terminal and bridging halide ligands. Upon refluxing of **1** in MeCN for 2 h, the analogous complex [$Pd_3Tr_2Cl_2$] (**6**) precipitated. $^1H$ NMR showed a single peak for the tropylium protons at ~4.75 ppm, indicative of a single common environment. $^{13}C$ NMR analysis of **1** (X = Cl), **2** (X = Br), and **3** (X = I) showed a small but consistent shift in the position of the tropylium carbon resonance between **1** (75.6 ppm), **2** (75.2 ppm), and **3** (72.8 ppm). The position of the tropylium peak for the polymeric complexes also exhibited effects dependent upon the substituent for **6** (X = Cl; 76.2 ppm), **4** (X = Br; 75.8 ppm), and **5** (X = I; 73.4 ppm), with these effects being correlated to the relative electronegativity of the halide. The UV−vis spectra of complexes **1**−**6** are very similar, with two absorptions near 474 and 414 nm that display negligible solvatochromic shift. The lack of significant change in the UV−vis spectra upon substitution can be attributed to localization of the highest occupied and lowest unoccupied molecular orbitals on the [$Pd_3Tr_2$] core, which is supported by the density functional theory calculations of Murahashi et al.[6] Weakening and therefore lengthening of the Pd−halogen−Pd bond is expected and is also observed in **5**, with Pd−I and Pd−I−Pd bond lengths being 2.7448(6) and 2.8071(4) Å, respectively. The closest Pd−Pd distances between separate [$Pd_3Tr_2$] units are approximately 4.714 Å in **4** and 4.948 Å in **5**; however, Murahashi and co-workers have recently shown that separate [$Pd_3Tr_2$] units may form direct Pd−Pd bonds, and thus polymers of directly linked [$Pd_3Tr_2$] units may be possible.[15] Recent theoretical investigations have suggested that the excited states of large two-dimensional palladium sandwich materials may have magnetic properties that are not typically observed in the ground state, and such investigations are underway.[16] The straightforward synthetic route and the air and moisture stability of these complexes have allowed the introduction of these syntheses into our undergraduate Advanced Inorganic Chemistry laboratory, with significant interest and positive feedback from our students. In addition, this demonstrates that the reaction pathway (Scheme 1) is general, and we are currently investigating the reaction with [$PPh_4$][X] (X = $CN^-$, $SCN^-$, and $N_3^-$). Careful selection of the equatorial ligands may be one way to manipulate the overall electronic and structural characteristics of the system, and investigations into the reactivity of these and other related tripalladium complexes are underway.

**Scheme 1.** Synthesis of Monomeric and Polymeric Complexes



**Acknowledgment.** We thank Northern Arizona University and the College of Engineering, Forestry and Natural Sciences for start-up funding. The X-ray diffractometer for **2**, **4**, and **5** was purchased with funds from NSF Grant CHE-9610374. We thank Dr. Jeanette A. Krause and Dr. Allen G. Oliver for data collection of **3** through the Service Crystallography at Advanced Light Source program. Crystallographic data were collected at Beamline 11.3.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The ALS is supported by the U.S. Department of Energy, Office of Energy Sciences, under Contract DE-AC02-05CH11231.

**Supporting Information Available:** Experimental details for the synthesis and characterization of **2**−**6** and details of the single-crystal X-ray diffraction analysis in CIF format for **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org. The Cambridge Crystallographic Data Centre files 658437 and 693586−693588 also contain the supporting crystallographic data for this paper. These can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

IC8014578

---

(15) Murahashi, T.; Hashimoto, Y.; Chiyoda, K.; Fujimoto, M.; Uemura, T.; Inoue, R.; Ogoshi, S.; Kurosawa, H. *J. Am. Chem. Soc.* **2008**, *130*, 8586.

(16) Philpott, M. R.; Kawazoe, Y. *Chem. Phys.* **2007**, *342*, 223.