Polymetalated Aromatic Compounds. 1. Synthesis of Mono-, Di-, and Tripalladated Mesitylene Derivatives

José Vicente*,[†] and Mykhaylo Lyakhovych

Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apartado 4021, Murcia 30071, Spain

Delia Bautista[‡]

SACE, Universidad de Murcia, Apartado 4021, Murcia 30071, Spain

Peter G. Jones[§]

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

Received June 22, 2001

The reaction of 1,3,5-triiodomesitylene ($C_6Me_3I_3$) with a mixture of [Pd(dba)$_2$] and PR$_3$ leads to the mononuclear complexes *trans*-[Pd($C_6Me_3I_2$)I(PR$_3$)$_2$] (R = Ph (**1**), R$_3$ = Me$_2$Ph (**2**)) or the dinuclear complex [{*trans*-PdI(PMe$_2$Ph)$_2$}$_2$(μ_2-C_6Me_3I)] (**3**), depending on the nature of the phosphine, the temperature, and the molar ratio of the reagents. All attempts to prepare trinuclear complexes, using this method of synthesis, were unsuccessful. However, addition of $C_6Me_3I_3$ to a mixture of [Pd(dba)$_2$] and L$_2$ gives at room temperature [(PdIL$_2$)$_3$-(μ_3-C_6Me_3)] (L$_2$ = 2,2'-bipyridine (bpy) (**4**), 4,4'-di-*tert*-butyl-2,2'-bipiridine (tbbpy) (**5**)), even if substoichiometric amounts of Pd were used. Complex **5** does not react with PPh$_3$ or PMe$_2$-Ph, but it does react with PMe$_3$ to give [*trans*-{PdI(PMe$_3$)$_2$}$_3$(μ_3-C_6Me_3)] (**6**). The crystal structures of **1**, **2**, and **5** have been determined by X-ray diffraction studies.

Introduction

The synthesis and applications of polymetalated derivatives of benzene ($C_6R_{6-n}M_n$, $n = 3-6$) are well-documented. However, most of these compounds involve only a few representative elements and many remain poorly characterized, especially from a structural viewpoint. The element best studied is Hg(II), of which compounds with three to six metal atoms have been reported.[1−17] Other members of this family of compounds include Sn(IV),[1,3,18−21] Li,[1,3,22−26] Mg,[3] Al,[27,28] and Ge derivatives.[29,30] Many Hg(II) derivatives were prepared by metalation, but in a few cases transmetalation reactions using the corresponding Sn(IV)[1] or Li[3] derivatives were used. Most Sn(IV) compounds were synthesized by reacting NaSnMe$_3$ with the corresponding halobenzene, but 1,3,5-C_6H_3(SnMe$_3$)$_3$ has also been prepared from the corresponding Li derivative.[3,21]

† Corresponding author regarding the synthesis of complexes. E-mail: jvs@scc.um.es. Web: http://www.scc.um.es/gi/gqo/.

‡ Corresponding author regarding the X-ray diffraction studies of complexes **1** and **2**. E-mail: dbc@um.es.

§ Corresponding author regarding the X-ray diffraction studies of complex **5**. E-mail: jones@xray36.anchem.nat.tu-bs.de.

(1) Rot, N.; De Kanter, F. J. J.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem* **2000**, *593−594*, 369.

(2) Layeghi, H.; Tyrra, W.; Naumann, D. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1601.

(3) Rot, N.; Bickelhaupt, F. *Organometallics* **1997**, *16*, 5027.

(4) Rothmaier, M.; Schaller, U.; Morfb, W. E.; Pretsch, E. *Anal. Chim. Acta* **1996**, *327*, 17.

(5) Popov, V. I.; Lib, M.; Haas, A. *Ukr. Khim. Zh.* **1990**, *56*, 1115. *Chem. Abstr.* **1991**, *114*, 185701.

(6) Khomutov, A. R.; Khurs, E. N.; Khomutov, R. M. *Bioorg. Khim.* **1988**, *14*, 385.

(7) Khomutov, R. M.; Khomutov, A. R. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, 2649; *Chem. Abstr.* **1986**, *105*, 209076.

(8) Deacon, G. B.; Farquharson, G. J. *Aust. J. Chem.* **1977**, *30*, 1701.

(9) Yagupol'skii, L. M.; Popov, V. I.; Kondratenko, N. V. *Zh. Org. Khim.* **1976**, *12*, 916. *Chem. Abstr.* **1976**, *85*, 46115.

(10) Deacon, G. B.; Farquharson, G. J. *Aust. J. Chem.* **1976**, *29*, 627.

(11) Deacon, G. B.; Farquharson, G. J. *J. Organomet. Chem.* **1974**, *67*, C1.

(12) Friedman, H. A.; Koelle, G. B. *Org. Prep. Proced. Int.* **1973**, *5*, 251.

(13) Formanek, H.; Formanek, S. *Eur. J. Biochem.* **1970**, *17*, 78.

(14) Alvey, F. B.; Jarboe, C. H. *J. Med. Chem.* **1968**, *11*, 1269.

(15) Malaiyandi, M.; Sawatzky, H.; Wright, G. F. *Can. J. Chem.* **1961**, *39*, 1827.

(16) Poethke, W.; Fuerst, W. *Arch. Pharm. (Weinheim, Ger.)* **1961**, *294*, 524; *Chem. Abstr.* **1962**, *56*, 1469f.

(17) Deacon, G. B.; O'Donoghue, M. F. *J. Organomet. Chem.* **1980**, *194*, C60.

(18) Corsico, E. F.; Rossi, R. A. *Synlett* **2000**, 230.

(19) Corsico, E. F.; Rossi, R. A. *Synlett* **2000**, 227.

(20) Schultz, G.; Hargittai, I.; Rot, N.; Bickelhaupt, F. *Struct. Chem.* **1998**, *9*, 209.

(21) Gibson, S. E.; Saladin, S. A.; Sur, S. *Chem. Commun.* **2000**, 2011.

(22) Theologitis, M.; Screttas, G. C.; Raptis, S. G.; Papadopoulos, M. G. *Int. J. Quantum Chem.* **1999**, *72*, 177.

(23) Adamson, G. A.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1535.

(24) Baran, J. R., Jr.; Hendrickson, C.; Laude, D. A., Jr.; Lagow, R. J. *J. Org. Chem.* **1992**, *57*, 3759.

(25) Howells, R. D.; Gilman, H. *Tetrahedron Lett.* **1974**, 1319.

(26) Buck, P.; Köbrich, G. *Chem. Ber.* **1970**, *103*, 1420.

(27) Troyanov, S. I.; Rybakov, V. B. *Metalloorg. Khim.* **1988**, *1*, 1061; *Chem. Abstr.* **1990**, *112*, 77414.

(28) Troyanov, S. I.; Tafeenko, V. A. *Zh. Obshch. Khim.* **1990**, *60*, 2416; *Chem. Abstr.* **1991**, *114*, 247441.

(29) Yamakawa, T.; Kagechika, H.; Kawachi, E.; Hashimoto, Y.; Shudo, K. *J. Med. Chem.* **1990**, *33*, 1430.

(30) Weissensteiner, W.; Schuster, I. I.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 6664.

Lithium derivatives were obtained by reacting organo-lithium compounds with halobenzenes.

Surprisingly, there are only two polymetalated derivatives of benzene with transition metals, namely those of formula 1,3,5-$C_6H_3[M]_3$, where [M] = $Mn(CO)_5$, $Fe(\eta^5$-Cp)(CO)$_2$. They were prepared in two steps involving the reaction of Na[M] with 1,3,5-$C_6H_3(COCl)_3$ and subsequent decarbonylation of the resulting triacyl complexes 1,3,5-$C_6H_3[C(O)M]_3$.[31]

The interest in these polymetallic compounds has manifested itself in the publication of one review on permetalated aromatic compounds,[32] some patents,[33−36] and many theoretical[22,37−44] or biological studies.[13,29,45−48] Some of them have been used as arene ligands, in [(η^6-1,3,5-$C_6H_3[M]_3$)Cr(CO)$_3$], [M] being $Fe(\eta^5$-Cp)(CO)$_2$[49] or $SnMe_3$,[21] or in [(η^6-C_6H_5)Ti(η^6-μ_4-1,3,5-$C_6H_3(AlI_2)_3$){Ti$_3$-(μ_2-I)$_6$}].[27,28] We believe that these polymetalated derivatives of benzene also have potential applications in the synthesis of metallodendrimers.

In this paper, we report some attempts to prepare the compounds 1,3,5-$C_6Me_3[M]_3$, where [M] = PdL$_2$I and L = PPh$_3$, PMe$_2$Ph, PMe$_3$ or L$_2$ = 2,2′-bipyridine (bpy), 4,4′-di-*tert*-butyl-2,2′-bipyridine (tbbpy). The successful synthesis of some of the desired compounds, using oxidative addition reactions, is not as direct and simple as we initially expected.

Experimental Section

Melting points were determined on a Reichert apparatus and are uncorrected. Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer 16FC FT-IR spectrometer with Nujol mulls between polyethylene sheets. ^{1}H, ^{31}P, and ^{13}C NMR spectra were carried out with a Varian Unity 300 or a Bruker 200 instrument. Chemical shifts are referenced to TMS (^{1}H and ^{13}C{^{1}H}) or to H$_3$PO$_4$ (^{31}P).

"Pd(dba)$_2$"[50,51] and 1,3,5-$C_6Me_3I_3$[52] were prepared as described previously.

(31) Hunter, A. D.; Szigety, A. B. *Organometallics* **1989**, *8*, 2670.

(32) Winteer, C. H.; Seneviratine Kapilan, N.; Bretschneider, H. *Comments Inorg. Chem.* **1996**, *19*, 1.

(33) Nakajima, K.; Sonoda, N.; Tanaka, K.; Yamabe, T. (Matsushita Electric Ind. Co. Ltd., Japan) Jpn. Patent JP 06122769; *Chem. Abstr.* **1994**, *121*, 301657.

(34) Chamberlain, L. R.; Defriend, P. A. (Shell International Research Maatschappij BV, The Netherlands) Eur. Patent EP 475495; *Chem. Abstr.* **1992**, *117*, 8752.

(35) Teranaka, O.; Kakutani, T.; Tabata, H.; Teraoka, T. (Japan Elastomer Co., Ltd., Japan) Eur. Patent EP 46668; *Chem. Abstr.* **1982**, *96*, 200828.

(36) Massachusetts Institute of Technology. Brit. Patent GB 1444174; *Chem. Abstr.* **1977**, *86*, 106764.

(37) Raptis, S. G.; Papadopoulos, M. G.; Sadlej, A. J. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3393.

(38) Belanzoni, P.; Sgamellotti, A.; Re, N.; Floriani, C. *Inorg. Chem.* **2000**, *39*, 1147.

(39) Papadopoulos, M. G.; Raptis, S. G.; Demetropoulos, I. N.; Nasiou, S. M. *Theor. Chem. Acta* **1998**, *99*, 124.

(40) Belanzoni, P.; Fantacci, S.; Re, N.; Rosi, M.; Sgamellotti, A.; Floriani, C. *Inorg. Chem.* **1997**, *36*, 2018.

(41) Smith, B. J. *Chem. Phys. Lett.* **1993**, *207*, 403.

(42) Glukhovtsev, M. N.; Simkin, B. Y.; Minkin, V. I. *Zh. Org. Khim.* **1991**, *27*, 432; *Chem. Abstr.* **1991**, *115*, 92329.

(43) Xie, Y.; Schaefer, H. F., III. *Chem. Phys. Lett.* **1991**, *179*, 563.

(44) Glukhovtsev, M. N.; Simkin, B. Y.; Minkin, V. I. *Metalloorg. Khim.* **1990**, *3*, 1289; *Chem. Abstr.* **1991**, *114*, 122460.

(45) Pepe, F. A. *J. Biophys. Biochem. Cytol.* **1961**, *11*, 515; *Chem. Abstr.* **1962**, *56*, 10763g.

(46) Pepe, F. A.; Finck, H. *J. Biophys. Biochem. Cytol.* **1961**, *11*, 521; *Chem. Abstr.* **1962**, *56*, 10763h.

(47) Pepe, F. A.; Finck, H.; Holtzer, H. *J. Biophys. Biochem. Cytol.* **1961**, *11*, 533; *Chem. Abstr.* **1962**, *56*, 10763i.

(48) Keil, R. *Pharmazie* **1959**, *14*, 76.

(49) Hunter, A. D. *Organometallics* **1989**, *8*, 1118.

(50) Takahashi, Y.; Ito, S.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065.

Synthesis of *trans*-[Pd($C_6Me_3I_2$)I(PPh$_3$)$_2$] (1). [Pd(dba)$_2$] (288 mg, 0.5 mmol), PPh$_3$ (262 mg, 1 mmol), and $C_6Me_3I_3$ (250 mg, 0.5 mmol) were mixed under nitrogen in degassed toluene (25 mL) and allowed to react at room temperature for 14 h. Workup was then continued in air. The solvent was evaporated to dryness and the residue extracted with CH$_2$Cl$_2$ (20 mL). The extract was filtered over Celite, the resulting solution concentrated to about 5 mL, and Et$_2$O (30 mL) added. The resulting solid was separated by filtration, washed with Et$_2$O, and recrystallized from CH$_2$Cl$_2$/Et$_2$O, to give **1** as a pale yellow solid. Yield: 460 mg (82%). Mp: 249 °C dec. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.56−7.14 (m, 30 H, PPh$_3$), 2.55 (s, 3 H, Me), 2.46 (s, 6 H, Me). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$): δ 159.91 (s, 2$C2$, Ar), 141.45 (t, C−Pd, $^2J_{PC}$ = 4 Hz), 138,22 (s, C4−Me, Ar), 134.71 ("t", ortho C's PPh$_3$, $^2J_{PC}$ + $^4J_{PC}$ = 6 Hz), 131.46 ("t", ipso C's PPh$_3$, $^1J_{PC}$ + $^3J_{PC}$ = 23 Hz), 130.13 (s, para C's PPh$_3$), 127.57 ("t", meta C's PPh$_3$, $^3J_{PC}$ + $^5J_{PC}$ = 5 Hz), 104.05 (s, C−I), 37.24 (s, Me), 34.88 (s, Me). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ 22.01 (s). Anal. Calcd for C$_{45}$H$_{39}$I$_3$P$_2$Pd: C, 47.88; H, 3.48. Found: C, 47.66; H, 3.44.

Synthesis of *trans*-[Pd($C_6Me_3I_2$)I(PMe$_2$Ph)$_2$] (2). [Pd(dba)$_2$] (288 mg, 0.5 mmol), PMe$_2$Ph (138 mg (142 μL), 1 mmol), and $C_6Me_3I_3$ (250 mg, 0.5 mmol) were mixed under nitrogen in degassed toluene (25 mL) and allowed to react at room temperature for 6 h. Workup was then continued in air. The solvent was evaporated to dryness and the residue extracted with CH$_2$Cl$_2$ (20 mL). The extract was filtered over Celite, the resulting solution concentrated to about 5 mL and an Et$_2$O/pentane mixture (15 mL/15 mL) added. The resulting solid was separated by filtration, washed with Et$_2$O, and recrystallized from CH$_2$Cl$_2$/pentane, to give **2** as a beige solid. Yield: 270 mg (61%). Mp: 162 °C dec. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.34−7.26 (m, 10 H, Ph), 2.75 (s, 3 H, Me), 2.47 (s, 6 H, Me), 1.67 ("t", 12H, $^2J_{PH}$ + $^4J_{PH}$ = 3 Hz, P*Me*$_2$Ph). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ −10.77 (s). Anal. Calcd for C$_{25}$H$_{31}$I$_3$P$_2$Pd: C, 34.10; H, 3.48. Found: C, 34.37; H 3.46.

Synthesis of [{*trans*-PdI(PMe$_2$Ph)$_2$}$_2$(μ_2-C_6Me_3I)] (3). [Pd(dba)$_2$] (432 mg, 0.75 mmol), PMe$_2$Ph (207 mg (214 μL), 1.5 mmol), and $C_6Me_3I_3$ (125 mg, 0.25 mmol) were mixed under nitrogen in degassed toluene (25 mL), and the reaction mixture was refluxed under a slow stream of nitrogen for 2 h. From this point the workup was carried out in air. The solvent was evaporated to dryness and the residue extracted with CH$_2$Cl$_2$ (20 mL). The extract was filtered over Celite, the resulting solution concentrated to about 5 mL, and an Et$_2$O/pentane mixture (15 mL/15 mL) added. The resulting solid was separated by filtration, washed with Et$_2$O, and recrystallized from CH$_2$Cl$_2$/pentane to give **3** as a beige solid. Yield: 210 mg (51%). Mp: 179 °C dec. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.74−7.65 (m, 8 H, PMe$_2$*Ph*), 7.33−7.26 (m, 12 H, PMe$_2$*Ph*), 2.74 (s, 6 H, Me), 2.36 (s, 3 H, Me), 1.54 ("t", 12H, $^2J_{PH}$ + $^4J_{PH}$ = 3 Hz, P*Me*$_2$Ph), 1.29 ("t", 12H, $^2J_{PH}$ + $^4J_{PH}$ = 3 Hz, P*Me*$_2$Ph). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ −12.28 (s). Anal. Calcd for C$_{41}$H$_{53}$I$_3$P$_4$Pd$_2$: C, 39.98; H, 4.23. Found: C, 39.90; H 4.62.

Synthesis of [{PdI(bpy)}$_3$(μ_3-C_6Me_3)] (4). Pd(dba)$_2$ (432 mg, 0.75 mmol), bpy (120 mg, 0.75 mmol), and $C_6Me_3I_3$ (125 mg 0.25 mmol) were mixed under nitrogen in degassed toluene (25 mL) and allowed to react at room temperature for 10 h. The precipitation of a dark yellow solid was observed. The solvent was evaporated to dryness and the residue extracted with DMF. The extract was filtered over Celite, the resulting solution concentrated to about 20 mL, and Et$_2$O (50 mL) added. The resulting solid was separated by filtration, washed with Et$_2$O, and recrystallized from DMF/Et$_2$O to give **4** as a brownish yellow solid. Yield: 140 mg (44%). Mp: 238 °C dec. IR (Nujol): ν(CN, bpy) 1596 cm^{-1}. Because of insufficient

(51) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

(52) Merkushev, E. B.; Simakhina, N. D.; Koveshnikova, G. M. *Synthesis* **1980**, 486.

Table 1. Crystal Data for Complexes 1, 2, and 5

	1	**2**·CDCl$_3$	**5**·3CH$_2$Cl$_2$·Et$_2$O
formula	C$_{25}$H$_{31}$I$_3$P$_2$Pd	C$_{46}$H$_{39}$DCl$_3$I$_3$P$_2$Pd	C$_{70}$H$_{97}$Cl$_6$I$_3$N$_6$OPd$_3$
M_r	880.54	1248.16	1951.14
cryst size (mm)	0.54 × 0.48 × 0.48	0.39 × 0.38 × 0.32	0.40 × 0.25 × 0.15
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$	$P2_1/n$
cell constants			
$\quad a$ (Å)	11.5674(5)	17.593(2)	18.9252(14)
$\quad b$ (Å)	12.4874(6)	11.9216(6)	22.7739(16)
$\quad c$ (Å)	19.2819(9)	21.5095(12)	18.9973(14)
$\quad \beta$ (deg)	90	100.457(5)	103.442(3)
V (Å^3), Z	2785.2(2), 4	4436.5(5), 4	7963.5(10), 4
λ (Å)	0.710 73	0.710 73	0.710 73
ρ(calcd) (Mg m^{-3})	2.100	1.867	1.627
F(000)	1664	2404	3864
T (K)	173	173	133
μ (mm^{-1})	4.118	2.791	2.077
transmissions	0.969−0.516	0.789−0.749	0.802−0.605
θ range (deg)	3.20−24.99	3.20−25.00	1.37−28.28
limiting indices	$-13 \le h \le 13$	$-20 \le h \le 0$	$-25 \le h \le 25$
	$-14 \le k \le 0$	$-14 \le k \le 1$	$-30 \le k \le 30$
	$-22 \le l \le 0$	$-25 \le l \le 25$	$-25 \le l \le 25$
no. of rflns			
$\quad$ measd	5262	8885	176 960
$\quad$ indep	4887	7795	19 781
R_{int}	0.0152	0.0222	0.0356
abs cor	ψ-scans	ψ-scans	multiscan
refinement method		full-matrix least squares on F^2	
no. of data/restraints/params	4886/24/287	7792/419/496	19 781/821/843
S (F^2)	1.126	1.011	1.096
R1^a	0.0221	0.0252	0.0350
wR2^b	0.0579	0.0629	0.1026
largest diff peak (e Å^{-3})	0.591	0.766	1.331

^{a} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ for reflections with $I > 2\sigma(I)$. ^{b} wR2 = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.

solubility, NMR spectra of complex **4** could not be measured. Anal. Calcd for C$_{39}$H$_{33}$I$_3$N$_6$Pd$_3$: C, 36.44; H, 2.59, N, 6.54. Found: C, 36.43; H, 2.86; N, 7.05.

Synthesis of [{PdI(tbbpy)}$_3$(μ_3-C$_6$Me$_3$)] (5). Pd(dba)$_2$ (432 mg, 0.75 mmol), tbbpy (200 mg, 0.75 mmol), and C$_6$Me$_3$I$_3$ (125 mg 0.25 mmol) were mixed under nitrogen in degassed toluene (25 mL) and allowed to react at room temperature for 14 h. Workup was then continued in air. The solvent was evaporated to dryness and the residue extracted with CH$_2$Cl$_2$ (20 mL). The extract was filtered over Celite, the resulting solution concentrated to about 5 mL, and an Et$_2$O/pentane mixture (15 mL/ 15 mL) added. The resulting solid was separated by filtration, washed with Et$_2$O, and recrystallized from CH$_2$Cl$_2$/pentane to give **5** as a yellow solid. Yield: 335 mg (83%). Mp: 218 °C dec. ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.48 (d, 2H, $^3J_{HH}$ = 6 Hz, CH, tbbpy), 9.34 (d, 1H, $^3J_{HH}$ = 6 Hz, CH, tbbpy), 8.03 (d, 2H, $^3J_{HH}$ = 6 Hz, CH, tbbpy), 7.93−7.88 (m, 7H, tbbpy), 7.60 (dd, 1H, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1.8 Hz, tbbpy), 7.45−7.36 (m, 5H, tbbpy), 3.20 (s, 3 H, Ar*Me*), 3.17 (s, 6 H, Ar*Me*), 1.404, 1.401, 1.387 (54H, *t*-Bu). Anal. Calcd for C$_{63}$H$_{81}$I$_3$N$_6$Pd$_3$: C, 46.64; H, 5.03, N, 5.18. Found: C, 46.62; H, 5.06, N, 5.24.

Synthesis of [*trans*-{PdI(PMe$_3$)$_2$}$_3$(μ_3-C$_6$Me$_3$)] (6). Complex **5** (105 mg, 0.065 mmol) and PMe$_3$ (0.585 mL of a 1 M solution in toluene, 0.585 mmol) were mixed under nitrogen in degassed dichloromethane (20 mL) and allowed to react at room temperature for 12 h. The precipitation of a white solid was observed. The solvents and excess PMe$_3$ were evaporated under reduced pressure to give a slightly gray residue, which was transferred to the filter funnel and washed thoroughly with acetone to give analytically pure **6** as a slightly gray solid. Yield: 75 mg (90%). Mp: 235 °C dec. ^{1}H NMR (200 MHz, CDCl$_3$): 2.66 (s, 9H, Me), 1.41 ("t", 54H, $^2J_{PH}$ + $^4J_{PH}$ = 3 Hz, P*Me*$_3$). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ −21.57 (s). Anal. Calcd for C$_{27}$H$_{63}$I$_3$P$_6$Pd$_3$: C, 25.46; H, 4.99. Found: C, 25.78; H, 4.96.

X-ray Structure Determinations. The crystals were mounted in inert oil on a glass fiber and transferred to the

diffractometer (**1** and **2**, Siemens P4 with LT2 low-temperature attachment; **5**, Bruker SMART 1000 CCD with LT3 low-temperature attachment), as summarized in Table 1. The structures were solved by the heavy-atom method and refined anisotropically on F^2 (program SHELX-93 or SHELX-97, G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included using a riding model or rigid methyl groups.

Special features of the refinement are as follows. For compound **2**, the absolute structure parameter[53] is −0.05(2). Compound **5** crystallizes with three molecules of dichloromethane and one of diethyl ether, which display slightly high U values but are otherwise well ordered. The *tert*-butyl groups at C17 and C27 are disordered over two positions.

Results and Discussion

The reaction of 1,3,5-triiodomesitylene (C$_6$Me$_3$I$_3$) with a mixture of [Pd(dba)$_2$] ([Pd$_2$(dba)$_3$]·dba) and PPh$_3$ (1: 1:2 molar ratio) in toluene at room temperature gave *trans*-[Pd(C$_6$Me$_3$I$_2$)I(PPh$_3$)$_2$] (**1**) in high yield (Scheme 1). The same compound was obtained when the reagents were reacted in the molar ratio 1:2:4 or even 1:3:6. When the reaction of C$_6$Me$_3$I$_3$ with a mixture of [Pd(dba)$_2$] and PPh$_3$ (1:3:6 molar ratio) was carried out in boiling toluene for 3 h, complex **1** was obtained in low yield (41%) and decomposition also occurred. Refluxing a mixture of C$_6$Me$_3$I$_3$, [Pd(dba)$_2$], and PPh$_3$ (1:3:6 molar ratio) in toluene for 6 h led to decomposition to Pd metal and an unresolved mixture of compounds. The use of the more basic and less sterically demanding phosphine PMe$_2$Ph allowed the preparation of mono- and dinuclear complexes. Thus, *trans*-[Pd(C$_6$Me$_3$I$_2$)I(PMe$_2$Ph)$_2$] (**2**) was obtained by reacting at room temperature, in a 1:1:2

(53) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876.
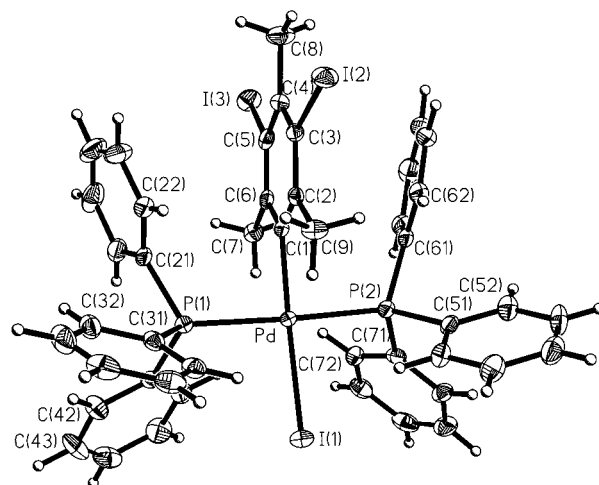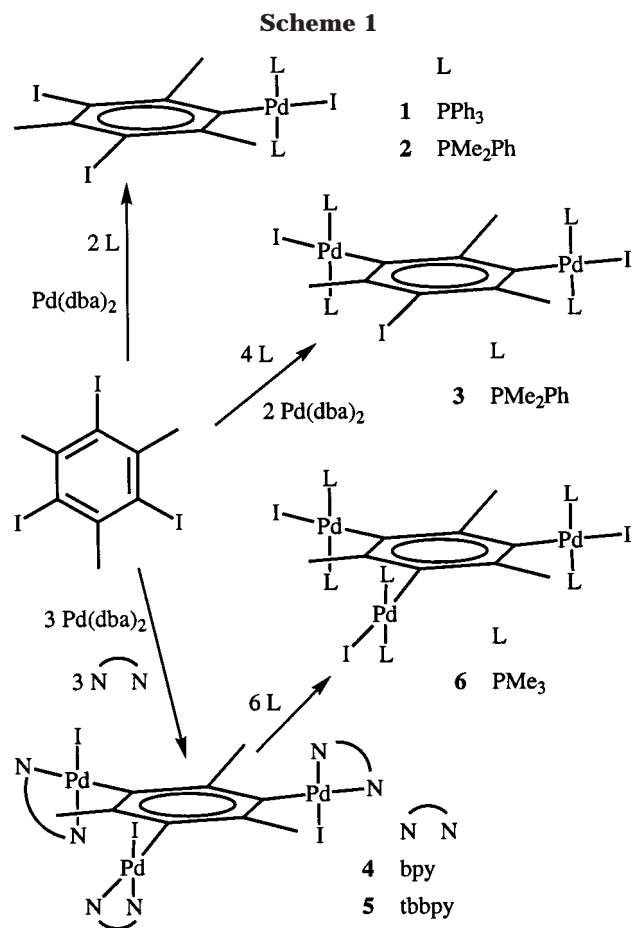
Scheme 1

Figure 1. Thermal ellipsoid plot (50% probability level) of **1**. Selected bond lengths (Å) and angles (deg): Pd−C(1) = 2.044(3), Pd−P(1) = 2.3409(9), Pd−P(2) = 2.3429(9), Pd−I(1) = 2.7000(4); C(1)−Pd−P(1) = 88.82(9), C(1)−Pd−P(2) = 88.58(9), P(1)−Pd−I(1) = 92.20(2), P(2)−Pd−I(1) = 91.24(2).

The access to the trinuclear complexes **4** and **5**, containing nitrogen donor ligands, encouraged us to synthesize trinuclear complexes containing phosphine donor ligands by employing ligand exchange reactions. Although attempts to replace tbbpy in **5** by PPh_3 or PMe_2Ph resulted in decomposition to Pd metal, the use of PMe_3 was successful; the desired trinuclear complex [*trans*-{PdI(PMe_3)_2}_3(μ_3-C_6Me_3)] (**6**) was obtained when **5** was stirred at room temperature for 12 h with an excess of PMe_3 in dichloromethane.

Structure of Complexes. The NMR data agree with the structures proposed in Scheme 1 for complexes **1**−**6**. Of particular interest are those of complex **5** (its homologue **4** is insufficiently soluble in organic solvents). Two 2:1 singlets in the ^{1}H NMR spectrum, corresponding to mesitylene methyls, indicate that the structure found in the solid state (see Scheme 1 and Figure 3) is maintained in solution and that the PdI-(tbbpy) moieties do not rotate around the Pd−C bond. The expected four singlets from the tbbpy methyls appear as three very close signals.

In the solid state, complexes **1** and **2** each show a palladium atom in a square-planar coordination environment consisting of two trans phosphine ligands, an iodo ligand, and the aryl ligand $C_6Me_3I_2$ (Figures 1 and 2). The mean deviation of the atoms Pd, P(1), P(2), I(1), and C(1) from the best plane is 0.1146 Å in complex **1** and 0.0722 Å in complex **2**. As expected, Pd−C bond distances (2.044(3) (**1**), 2.048(5) (**2**) Å) are not significantly different. However, the Pd−I bond distance in **1** (2.7000(4) Å) is significantly longer than that in **2** (2.6882(5) Å), probably because of the greater steric requirement of PPh_3 as compared to that of PMe_2Ph. The Pd−P distances in **1** (2.3409(9), 2.3429(9) Å) are longer than those in complex **2** (2.316(2), 2.328(2) Å). Both are in the ranges found in other *trans*-[PdX_2L_2] (L = PPh_3 (2.340−2.326 Å),[54−57] PMe_2Ph (2.333−2.317 Å)[58−60]) complexes.

molar ratio, a mixture of $C_6Me_3I_3$, [Pd(dba)_2], and PMe_2-Ph, whereas using a 1:2:4 molar ratio of these reagents in refluxing toluene, the dinuclear complex [{*trans*-PdI-(PMe_2Ph)_2}_2(μ_2-C_6Me_3I)] (**3**) was obtained. Complex **3** was also isolated instead of the desired trinuclear species using 1:3:6 and 1:4:8 molar ratios. More severe conditions were examined. Thus, the reaction of C_6-Me_3I_3, [Pd(dba)_2], and PMe_2Ph in a 1:3:6 molar ratio and long reaction time at room temperature (72 h) led to a drastic decrease of the yield of **3** (<10%), and when the reaction was carried out in refluxing toluene more than 3 h or in a Carius tube at 150 °C, decomposition to Pd occurred and an intractable mixture was obtained. We attempted to prepare the trinuclear complex using the less bulky phosphine PMe_3, but the reaction of 1,3,5-triiodomesitylene with a mixture of [Pd(dba)_2] and PMe_3 (1:3:6 molar ratio) in toluene at room temperature resulted only in the formation of Pd metal and an unresolved mixture of compounds.

In contrast to the above results, addition of $C_6Me_3I_3$ to a mixture of [Pd(dba)_2] and 2,2′-bipyridine (bpy) or 4,4′-di-*tert*-butyl-2,2′-bipyridine (tbbpy) in toluene gave at room temperature [(PdIL_2)_3(μ_3-C_6Me_3)] (L_2 = bpy (**4**), tbbpy (**5**)), even if substoichiometric amounts of Pd were used. Thus, with 1:2:2 or 1:3:3 molar ratios and L_2 = tbbpy, only the formation of **5** was observed, and with 1:1:1 molar ratios and L_2 = tbbpy, a mixture of complexes was obtained containing mainly **5**. Therefore, it seems that the substituent [M] = [PdIL_2], when L_2 = bpy, tbbpy, activates the $C_6Me_3I_2$[M] or C_6Me_3I[M]_2 rings for the next oxidative addition reactions, whereas the contrary occurs when L = PR_3.

(54) Vicente, J.; Abad, J. A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem. Eur. J.* **1999**, *5*, 3066.
(55) Flemming, J. P.; Pilon, M. C.; Borbulevitch, O. Y.; Antipin, M. Y.; Grushin, V. V. *Inorg. Chim. Acta* **1998**, *280*, 87.
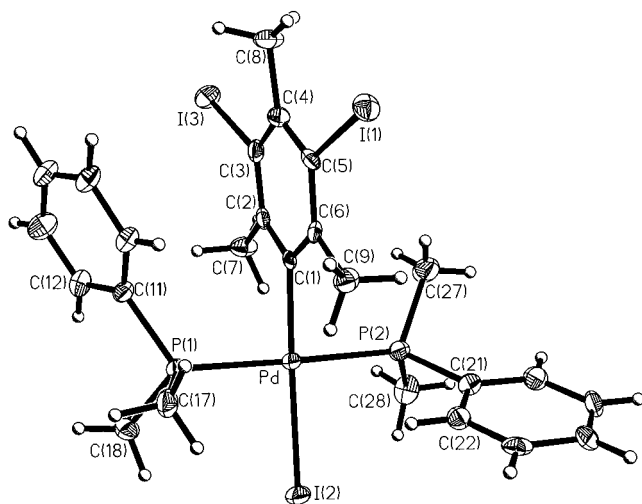
Figure 2. Thermal ellipsoid plot (50% probability level) of **2**. Selected bond lengths (Å) and angles (deg): Pd−P(2) = 2.316(2), Pd−P(1) = 2.328(2), Pd−I(2) = 2.6882(5); C(1)−Pd−P(2) = 90.03(14), C(1)−Pd−P(1) = 88.99(14), P(2)−Pd−I(2) = 90.34(4), P(1)−Pd−I(2) = 90.88(4).

In complex **5** (Figure 3), three palladium atoms are bonded to the mesitylene ring. Each shows a square-planar coordination, but the extent of distortion is very different. Pd(1) and its four immediate neighbors are coplanar with a mean deviation of only 0.016 Å. At Pd-(3) the distortion is greater (mean deviation 0.09 Å), with N(51) lying 0.33 Å out of the plane of the other four atoms (mean deviation 0.001 Å). The greatest distortion is observed at Pd(2), with a mean deviation of 0.17 Å; N(41) lies 0.74 Å out of the plane of the other four atoms (mean deviation 0.05 Å). The nine carbon atoms of the mesityl ring are coplanar, with a mean deviation of only 0.025 Å, but the palladium substituents lie out of this plane by 0.24, −0.83, and −0.26 Å for Pd(1), Pd(2), and Pd(3), respectively. They are arranged with the Pd−I vectors all approximately perpendicular to the mesityl plane, whereby I(1) lies on one side of the plane I(2) and I(3) are on the other side. Scheme 1 shows a simple representation of this arrangement. The Pd−C bond distances (2.001(4), 1.989-(4), 2.009(4) Å) are shorter than those in **1** (2.044(3) Å) or **2** (2.048(5) Å) because of the order of trans influence I > tbbpy. Similarly, the order of trans influence aryl
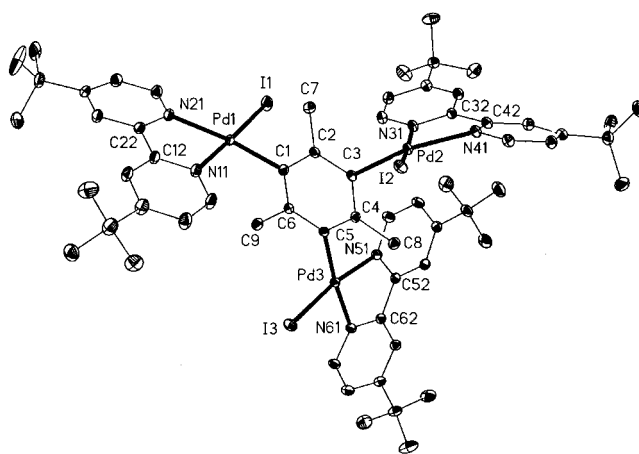

Figure 3. Thermal ellipsoid plot (30% probability level) of **5**. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd-(1)−C(1) = 2.001(4), Pd(1)−N(11) = 2.072(3), Pd(1)−N(21) = 2.146(3), Pd(1)−I(1) = 2.5886(4), Pd(2)−C(3) = 1.989-(4), Pd(2)−N(31) = 2.111(3), Pd(2)−N(41) = 2.163(3), Pd-(2)−I(2) = 2.5846(4), Pd(3)−C(5) = 2.009(4), Pd(3)−N(51) = 2.081(3), Pd(3)−N(61) = 2.148(3), Pd(3)−I(3) = 2.5791-(4); C(1)−Pd(1)−N(11) = 93.31(14), N(11)−Pd(1)−N(21) = 78.47(13), C(1)−Pd(1)−I(1) = 88.77(10), N(21)−Pd(1)−I(1) = 99.45(9), C(3)−Pd(2)−N(31) = 91.93(13), N(31)−Pd(2)−N(41) = 77.74(12), C(3)−Pd(2)−I(2) = 92.17(10), N(41)−Pd(2)−I(2) = 100.29(8), C(5)−Pd(3)−N(51) = 94.13(13), N(51)−Pd(3)−N(61) = 77.54(12), C(5)−Pd(3)−I(3) = 89.02-(10), N(61)−Pd(3)−I(3) = 99.46(8).

> tbbpy is manifested in the much shorter Pd−I bond lengths in **5** (2.5886(4), 2.5846(4), 2.5791(4) Å) as compared to those in complex **1** (2.7000(4) Å) or **2** (2.6882(5) Å). Finally, the order of trans influence aryl > I is shown in the longer Pd−N(21) (2.146(3) Å), Pd−N(41) (2.163(3) Å), and Pd−N(61) (2.148(3) Å) bonds compared to Pd−N(11) (2.072(3) Å), Pd−N(31) (2.111-(3) Å), and Pd−N(51) (2.081(3) Å).

Supporting Information Available: Listings of both refined and calculated atomic coordinates, all anisotropic thermal parameters, and all bond lengths and angles for compounds **1**, **2**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0105472

(56) Veya, P.; Floriani, C.; Chiesivilla, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 4899.
(57) Vicente, J.; Abad, J. A.; Rink, B.; Hernández, F.-S.; Ramírez de Arellano, M. C. *Organometallics* **1997**, *16*, 5269.
(58) Crociani, B.; Sala, M.; Polo, A.; Bombieri, G. *Organometallics* **1986**, *5*, 1369.
(59) Ozawa, F.; Sugawara, M.; Hasebe, K.; Hayashi, T. *Inorg. Chim. Acta* **1999**, *296*, 19.
(60) Benetollo, F.; Bombieri, G.; Dibianca, F.; Crociani, B. *Inorg. Chim. Acta* **1991**, *188*, 51.