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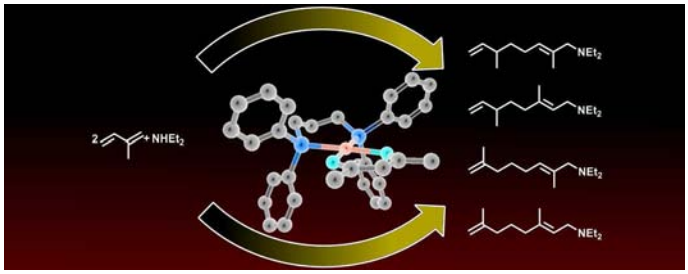

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- Models of the structure and IR wavenumbers assignments of the cations of 1-4 were obtained by DFT calculations.

- Synthesized complexes were tested as catalysts in the telomerization of isoprene and butadiene with diethylamine. In the case of telomerization of butadiene with diethylamine high catalyst activity was obtained.

Palladium(II)-Acetylacetonate Complexes Containing Phosphine and Diphosphine Ligands and Their Catalytic Activities in Telomerization of 1,3-Dienes with Diethylamine

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Keywords: palladium, acetylacetonate, telomerization, isoprene, butadiene, diethylamine, phosphines

Abstract:

A series of novel [Pd(acac-O,O′)(P^P)]BF_4 and known complexes [Pd(acac-O,O′)$(PR_3)_2$]BF_4 (P^P = dppm (1), dppp (2), dppb (3), dppf (4); R = Ph (5), *p*-Tol (6), *i*-Pr (7); acac = 2,4-pentanedionato) were prepared by the reaction of [Pd(acac-O,O′)$(MeCN)_2$]BF_4 (1) with appropriate ligands. Complex 2 was characterized by single-crystal X-ray analysis. Models of the structure and IR wavenumbers assignments of the cations of 1-4 were obtained by DFT calculations. Synthesized complexes were tested as catalysts in the telomerization of isoprene and butadiene with diethylamine. In the case of telomerization of butadiene with diethylamine high catalyst activity (e.g. TOF_{av} = 1940 h^{-1} and TON up to 17480 for complex 5) was obtained.

INTRODUCTION

Telomerization, linear dimerization of 1,3-dienes with simultaneous addition of a nucleophile in a catalytic reaction, is a very efficient “green” organic transformation with an overall atom economy of 100%. Since its discovery 45 years ago [1,2], telomerization has attracted significant interest due to its robustness and versatility in the production of a wide variety of valuable products. Easily available starting materials are converted in the presence of a catalyst in a 100% atom efficient manner to give functionalized octa-2,7-dienes. The resulting products have been used as intermediates in the total synthesis of several natural products, as well as precursors for plasticizer alcohols, industrial monomers, solvents, corrosion inhibitors, and non-volatile herbicides [3–12]. Complexes of palladium are known to effectively catalyze the reaction of dienes with a variety of nucleophiles. It is also known that the palladium catalyzed dimerization of butadiene-type substrates can take place, leading to linear or cyclic products, with chemoselectivity depending on nature of nucleophiles and ligands appended to the reactive palladium center [13–15].

The telomerization process has been intensively studied by many industrial and academic laboratories [1,2,16–27]. Studies of the mechanism by Jolly et al. have led to the generally accepted basic catalytic cycle (for methanol), which has been crucial for further development [28–31]. Very recently, a detailed DFT studies of Pd -catalyzed 1,3-butadiene (**BD**) telomerization of methanol was reported [13,15]

A series of palladium complexes with phosphines, diphospines and NHC (NHC = N-heterocyclic carbene) ligands were reported for the telomerization of dienes with amines, water and alcohols [7,12,14,32–34]. Beller and co-workers [35–43] reported the most selective, active, and productive catalyst, an $(NHC)Pd^0$ complex. In particular, the best-known Pd-catalyst for

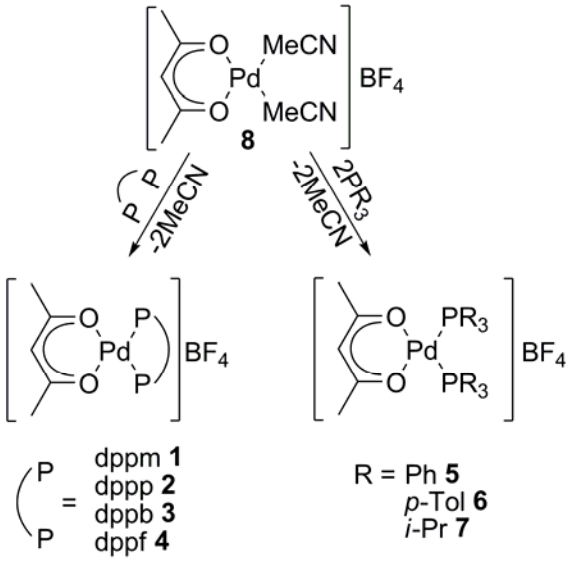
butadiene telomerization of diethylamine gives TON of 17800 mol_{BD}/mol_{Pd}, and TOF of 890 h^{-1} [36,37].

We reported that acetylacetonate-based cationic palladium complexes with triarylphosphine ligands, $[Pd(acac)(PAr_3)_2]BF_4$, can be used as very efficient precursors for the selective dimerization of styrene (to the best of our knowledge the highest catalyst turnover number ever reported for this reaction was achieved) [44]. Complexes of such type can be obtained in different manner: a) by acetylacetonate ligand abstraction from $Pd(acac)_2$ with $[CPh_3]BF_4$, $NaBPh_4$, $HBF_4 \cdot OEt_2$, CF_3SO_3H followed by further phosphine-ligand addition[45–48],b) by reaction of Pd(0) complexes with acetylacetone followed by addition of $[CPh_3]BF_4$ [49], c) by consecutive haloids displacement from starting palladium complex using Tl(acac) and $AgClO_4$ [50], or d) by acetonitrile displacement [51,52]. Only one example of use of $[Pd(acac)(PPh_3)_2]BF_4$ in the telomerization of isoprene with amines was reported [53b].

Here we report the results of synthesis of the novel palladium complexes $[Pd(acac)(P\hat{}P)]BF_4$ (P^P = dppm, dppp, dppb, dppf) as well as results of $[Pd(acac)(PR_3)_2]BF_4$ or $[(acac)Pd(P\hat{}P)]BF_4$-catalyzed telomerization of isoprene and butadiene with diethylamine.

RESULTS AND DISCUSSION

Scheme 1



Complex Synthesis. The synthetic procedures followed for the preparation of complexes **1-7** are summarized in Scheme 1. Methodology requires complex **8**, which can be prepared starting from $Pd(acac)_2$, MeCN and $HBF_4 \cdot OEt_2$ [47]. The cationic complexes were prepared in near quantitative yields. The structures of compounds **1-4** have been confirmed by the usual techniques (^1H, ^{13}C, ^{31}P, and ^{11}B NMR, FTIR, and elemental analysis). Due to the insolubility in available solvents complex **1** was characterized only by means of FTIR and elemental analysis. Structural details and Gibbs free energy for the cations of complexes **1-4** were obtained by our ZORA-BP86 calculations (Table 1, Figure 1). Comparison between observed and DFT-calculated IR wavenumbers for complexes **1-4** is presented in Table 2. In addition, the structure of compound **2** was also confirmed by single-crystal X-ray diffraction analysis.

Table 1. DFT-calculated (ZORA-BP86) structural parameters (bond lengths, Å; angles, °) and Gibbs free energy (kcal/mol) of reactions (see Scheme 1) for the cations of **1-4.**

	1	**2**	**3**	**4**
$[Pd\text{-}O]_{av}$	2,06	2,07	2,07	2,07
$[Pd\text{-}P]_{av}$	2,29	2,30	2,31	2,33
P-Pd-P	74,4	94,4	94,4	98,8
O-Pd-O	92,5	91,3	91,2	90,8
ΔG	-34,8	-44,7	-44,3	-40,7

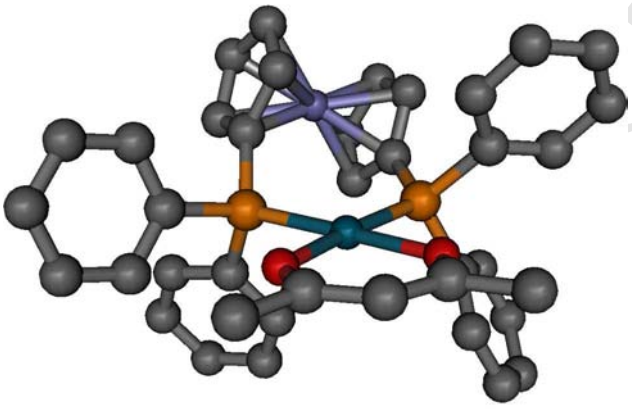


Figure 1. Optimized structure for cation of complex **4**, hydrogen atoms are ommited for clarity.

Complex $[Pd(acac)(dppp)]BF_4$ (**4)** crystallizes from CH_2Cl_2/Et_2O as light-yellow conglomerates of crystals. It possesses C2/c space group with a = 28.8084(6) Å, b = 14.2418(3) Å, c = 15.7720(3) Å, and β = 94.919(1) Å. In the crystal structure there are cations $[Pd(acac)(dppp)]^+$ with Pd(II) in a square planar coordination (Figure 2) and highly disordered BF_4^- anions. The DFT calculated structure (Table 1) agrees well with the experimental data (Figure 2). The Pd-O and Pd-P distances in the complexes described in literature are given in Table 3. As can be seen, all calculated and observed distances are in a good agreement with the corresponding values of known phosphine-acetylacetonate Pd complexes.

Table 2. Comparison between observed and DFT-calculated (ZORA-BP86) IR spectra (wavenumbers ,cm^{-1}) for the cations of palladium complexes **1-4.**

	Assignment	IR	Calcd, unscaled
1	$\nu_{(C=O \text{ and } C=C)}$	1553, 1518	1559, 1529
	$\delta_{(C–H \text{ in } CH3)}$	1437, 1366	1426, 1343
	$\nu_{(C–CH3,\ C=O \text{ and } C=C)}$	1270	1260
	$\delta_{(C–H \text{ in } CH)}$	1190, 777	1184, 780
	$\delta_{(CH \text{ in Ph and } CH2)}$	762, 738, 716, 687	744, 721, 713, 686
2	$\nu_{(C=O \text{ and } C=C)}$	1559, 1516	1560, 1529
	$\delta_{(C–H \text{ in } CH3)}$	1435, 1343	1424, 1343
	$\nu_{(C–CH3,\ C=O \text{ and } C=C)}$	1269	1260
	$\delta_{(C–H \text{ in } CH)}$	1189	1185
	$\delta_{(C–H \text{ in } CH2)}$	1157, 835, 793	1144, 819, 768
	$\delta_{(CH \text{ from Ph})}$	1421, 745, 690	1400, 730, 686
3	$\nu_{(C=O \text{ and } C=C)}$	1571, 1517	1563, 1530
	$\delta_{(C–H \text{ in } CH3)}$	1438, 1368	1426, 1343
	$\nu_{(C–CH3,\ C=O \text{ and } C=C)}$	1276	1261
	$\delta_{(C–H \text{ in } CH)}$	1189	1184
	$\delta_{(C–H \text{ in } CH2)}$	1165, 906, 844, 797	1110, 896, 844, 775
	$\delta_{(CH \text{ in Ph})}$	1422, 742, 692	1403, 726, 682
4	$\nu_{(C=O \text{ and } C=C)}$	1555, 1514	1562, 1529
	$\delta_{(C–H \text{ in } CH3)}$	1434, 1366,	1426, 1343
	$\nu_{(C–CH3,\ C=O \text{ and } C=C)}$	1261	1261
	$\nu_{(C–C \text{ in Cp})}$	1171	1160
	$\delta_{(C–H \text{ from CH and Cp})}$	1197, 826	1180, 814
	$\delta_{(CH \text{ from Ph})}$	749, 690	730, 684

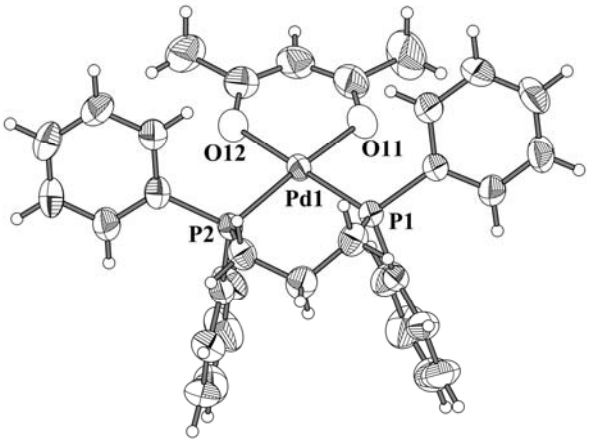


Figure 2. ORTEP plot (50% thermal ellipsoids) of the X-ray crystal structure of cation of compound **2**. BF_4 was omitted for clarity. Selected bond lengths [Å] and angles [°]: $[Pd\text{-}O]_{av}$, 2.052(3), $[Pd\text{-}P]_{av}$, 2.2466(12), P-Pd-P, 90.90(4),O-Pd-O, 90.54(13).

Table 3. Average Pd-O and Pd-P distances in the palladium(II)-acetylacetonate complexes containing phosphine ligands described in literature.

Complex	$[Pd\text{-}O]_{av}$	$[Pd\text{-}P]_{av}$	ref.
$(NBu_4)[(acac)Pd(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]\cdot(CH_3)CO$	2.082	2.246	[55]
$[(acac)Pd(\mu_3\text{-}PPh_2)_2Pt_2(C_6F_5)_2AgPh]\cdot CH_2Cl_2$	2.065	2.252	[55]
$[Pd(acac)(PPh_3)_2]BF_4\cdot H_2O$	2.034	2.265	[56]
$[Pd(CH_3COCHCOCH_2PhNO_2)(PPh_3)_2]BF_4$	2.046	2.268	[57]
$[Pd(CH_3COC(Ph(NO_2)_2)COCH_3)(PPh_3)_2]BF_4$	2.019	2.281	[57]
$[(hfa)Pd(\mu\text{-}PPh_2)_2Pd(hfa)]\cdot CHCl_3$	2.111	2.237	[58]
$[Pd(acac)((Ph_2P)_2binaphthyl)]BF_4$	2.031	2.251	[59]
$[Pd(acac)((Ph_2P)_2binaphthyl)]BF_4\cdot CH_2Cl_2$	2.026	2.259	[59]
$[Pd(acac)(PPh_3)_2]ClO_4$	2.022	2.259	[50]
$[Pd(acac)((MePhP)_2Fc)]BF_4$	2.053	2.266	[54]

Synthesis of the complex [Pd(acac)(dppe)]BPh_4 was reported by Basato et al [46,60]. In spite of DFT-calculated Gibbs free energy of acetonitrile exchange reaction by dppe was of the same value (-45.4 kcal/mol) as for other diphosphines, our attempts to prepare complex with the similar cation [Pd(acac)(dppe)]BF_4 failed. The reaction of **8** with dppe were performed ~~initially~~ in CH_2Cl_2, but the complex generated was unstable and decomposed upon workup. ^{31}P NMR spectrum of the reaction mixture showed signals at 25.8, 58.0, and 63.5 ppm which we assigned to the complex cations with following formal fragments: dppe-bridged $[Pd(\mu\text{-dppe})Pd]^{2+}$, dicationic $[Pd(dppe)]^{2+}$ and monocationic $[Pd(dppe)]^{+}$ respectively. For comparison ^{31}P NMR chemical shifts for $[Pd_2(\mu\text{-dppe})\{PPh(C_6H_4S)_2\}_2]$ is 20.9 ppm [61], for $[Pd(dppe)_2](OAc)_2$ is 58.7 ppm, and for $(OAc)_2Pd(dppe)$ is 63.4 ppm [62]. We assume that this is due to the transformation of [(acac)Pd(dppe)]BF_4 to ½$Pd(acac)_2$ and ½$[Pd(dppe)_2](BF_4)_2$ with formation of dppe-bridged by-product by analogy with data reported for $Pd(OAc)_2$ [62–64] and $Pd(dppe)Cl_2$ [65]. The nature of this phenomenon is the subject of special study.

Telomerization of 1,3-butadiene with diethylamine. In exploratory experiments using individual complex **5** as catalyst we discovered that addition of boron trifluoride etherate as co-catalyst is not required to obtain active catalyst, opposite to the results for dimerization of styrene [44]. Optimum temperature was found to be 70°C, at higher temperature catalyst decomposition occurs. Palladium complexes **1-8** were tested in the model reaction of diethylamine with 1,3-butadiene (Scheme 2, Table 4). Even at very low catalyst concentration conversions up to 91.0% and excellent selectivity (99.9%) were observed with complex **7**. To our delight whatever the ligand present on the palladium, only the linear telomerization product is formed. Telomerizations of butadiene with secondary amines show considerably higher selectivity compared to much more studied the telomerization in the presence of alcohol [12]. The ligand

structure is known to influence the product ratio in the telomerization reaction, but factors explaining the changes in chemo- and regioselectivity remained unraveled. Subtle changes in concentration of reagents, solvent, promoter, and reaction progress influence the selectivity of the telomerization reaction [33]. As it was shown by Drent [26], raising the temperature up to 135°C lead to formation of by-product octatriene up to 8% along with N,N-diethyl-2,7-octadienylamine. Similar temperature dependence of dimerization side-reaction in telomerization of butadiene with methanol was analyzed in details in recent review by van Leeuwen et al. [33]

We also performed catalyst activity studies in which conversion, product yield and selectivity were continuously measured. In Figure 3 selected runs using complex **5** formed *in situ* at 70°C are shown at different BD:Pd ratio. The conversion of ~50% of butadiene was observed after 0.5h with selectivity of >99% toward the linear telomerization product and reaction nearly complete after 3 h.

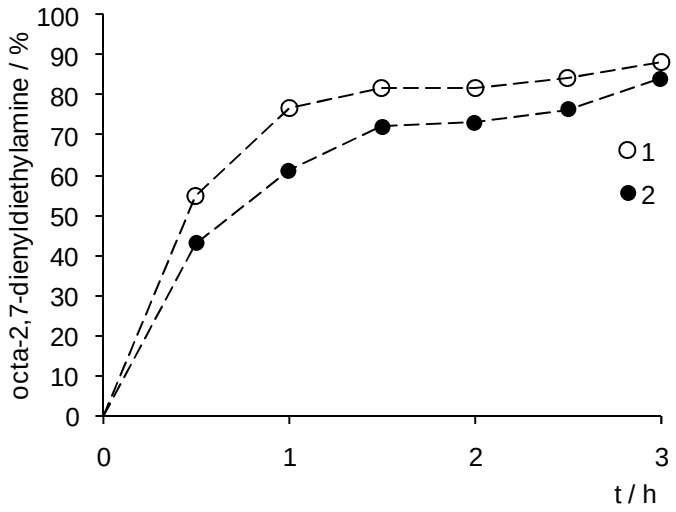


Figure 3. Activity, expressed as yields of octa-2,7-dienyldiethylamine as a function of reaction time. (Complex 5 was formed in situ by reaction of 8 with $2PPh_3$ in dichloromethane. Reaction conditions: (1) BD:Pd = 6000, Et_2NH:Pd = 3000, $1.3 \cdot 10^{-5}$ mol Pd, 70ºC, 3 h, 0.5 ml CH_2Cl_2 (2) BD:Pd = 3000, Et_2NH:Pd = 6000, $0.65 \cdot 10^{-5}$ mol Pd, 70ºC, 3 h, 0.5 ml CH_2Cl_2)

For complex **1** with dppm ligand, the methylene group in the diphosphine backbone led to dramatically reduced yield (Table 4). This could be simply explained by the poor solubilization of the complex **1**, since dppm based Pd catalyst showed comparable activity in telomerization with long-chained homologues [24]. Complex **8** showed almost no activity. Comparing results for telomerization of butadiene with diethylamine in terms of TOF and TON (up to 17480) with literature data shows that **2,3** and **5-7** should be regarded as highly efficient catalysts [12,36].

Scheme 2

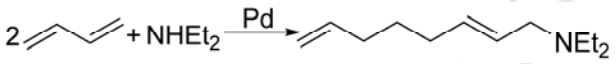


Table 4. Telomerization of 1,3-butadiene with diethylamine

Entry	Catalyst	Yield[a], %	Selectivity[b], %	TOF[c], $mol_{BD}/(mol_{Pd}\cdot h)$	TON[c], mol_{BD}/mol_{Pd}
1	**1**	10.6	99.9	210	640
2	**2**	79.4	99.9	1590	4760
3	**3**	76.6	99.9	1530	4600
4	**4**	49.0	99.9	980	2940
5	**5**	71.1	99.9	1420	4270
6[d]	**5**	87.4	99.9	1940	17480
7	**6**	73.8	99.9	1480	4430
8	**7**	91.0	99.9	1820	5460
9	**8**	0.3	-	~6	~20

Reaction conditions: 1,3-butadiene:Pd = 6000, Et_2NH:Pd = 3270, $1.3\cdot10^{-5}$ mol Pd (0.016 mol% with respect to 1,3-butadiene), 70ºC, 3 h.

[a]Yield of octa-2,7-dienyldiethylamine.

[b]Selectivity toward octa-2,7-dienyldiethylamine.

[c]Catalyst turnover frequency(number) with respect to 1,3-butadiene

[d]Reaction conditions: 1,3-butadiene:Pd = 20000, Et_2NH:Pd = 10000, $1.3 \cdot 10^{-5}$ mol Pd (0.005 mol% with respect to 1,3-butadiene), 70ºC, 9 h.

Telomerization of isoprene with diethylamine. The telomerization reaction of isoprene and diethylamine catalyzed by complexes **1-6** gives four isomers as major reaction products (Scheme 3). The telomerization reaction of isoprene and diethylamine catalyzed by a 2:1 mixture of PPh_3 and $PdCl_2$ has been reported to give isomer **IV** as the largest component (28%) of the product mixture (Scheme 3) [66]. In our case, when the complexes **1-6** used as catalyst isomer **I** becomes the major component of the product mixture (Table 5, entry 1-6). Detailed studies of the reaction (influence of the ligand, palladium precursor, reaction conditions, solvent, L/Pd ratio) using other types of palladium precursors was described by Finn et al. [67] and Keim et al. [53a,b]. The same selectivities to tail-to-head isomer were reported using $PdCl_2$- [67] and [(cod)Pd(η^3-allyl)]BF_4- based [53a,b, 67] systems with similar ligands, e.g. PPh_3, P(p-Tol)$_3$ and dppp (phosphine:Pd ratio of 1:1) [67]. Selectivity profile for complex **5** in MeCN (Table 5, entry 10) are comparable with the literature data [53b]. MeOH proved to be a better solvent than other organic solvents, especially with respect to selectivity towards telomers. Using MeCN, CH_2Cl_2, or CH_3NO_2 as solvents substantially decrease selectivity towards telomers (Table 5, entry 9-12). The reaction profile also changed dramatically with addition of Lewis acid, $20BF_3 \cdot OEt_2$, as co-catalyst. In this case, more products of amination (Table 6, entry 13-14) were obtained or, furthermore, polymeric products (Table 5, entry 15-16) were observed in the reaction mixture. The highest selectivity for tail-to-head coupling (giving a 59.4%) was observed with the dppm ligand, although the reaction was very slow. Complex **8** showed no activity in these conditions. Activity increase is observed on going to 1 equiv. of phosphine (entry 7), and the rate falls when

2 equiv is used (entry 8). These data are consistent with results by Finn et al. where a similar trend was observed. Authors speculated that "as more PPh_3 is added, $Pd(PPh_3)_2$ complexes are generated, which are relatively inactive compared with the monophosphine species, causing a drop in observed rate" [67].

Scheme 3

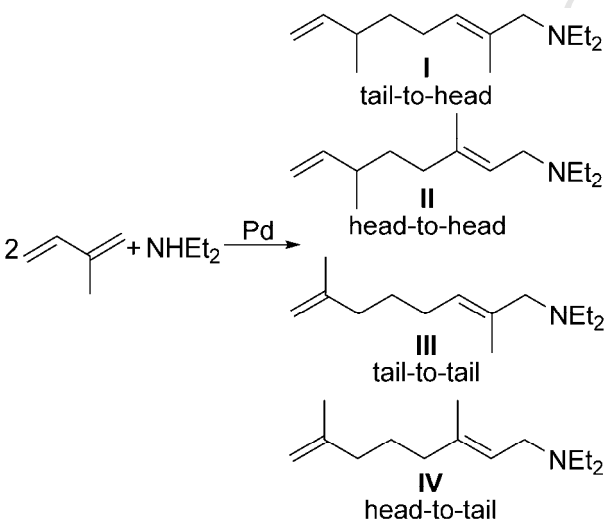


Table 6. Telomerization of isoprene with diethylamine

Entry	Solvent	Catalyst system	Conversion	Selectivity		Amt of telomers			
				Telomers	Products of aminations	I	II	III	IV
1	MeOH	**1**	8,00%	100%	0%	59,4%	28,6%	7,0%	5,0%
2	MeOH	**2**	44,00%	100%	0%	51,0%	23,0%	15,9%	10,0%
3	MeOH	**3**	83,00%	99%	1%	51,2%	24,0%	15,0%	9,8%
4	MeOH	**4**	96,00%	99%	1%	51,3%	21,2%	16,5%	10,9%
5	MeOH	**5**	75,00%	95%	5%	48,3%	23,7%	14,3%	13,6%
6	MeOH	**6**	100,00%	96%	4%	47,8%	26,0%	14,4%	11,8%
7	MeOH	**8**/1PPh_3	94,00%	99%	1%	52,6%	18,0%	16,8%	12,7%
8	MeOH	**8**/2PPh_3	82,40%	99%	1%	48,1%	21,9%	16,3%	13,7%
9	MeOH	**5**	78,00%	94%	6%	49,4%	26,4%	12,8%	11,3%
10	MeCN	**5**	79,00%	86%	14%	44,9%	32,5%	10,4%	12,2%
11	CH_2Cl_2	**5**	84,00%	83%	17%	41,3%	36,5%	9,8%	12,3%
12	CH_3NO_2	**5**	71,00%	49%	51%	38,0%	48,4%	6,5%	7,1%
13	MeOH	**5**/20$BF_3 \cdot OEt_2$	67,00%	69%	31%	58,0%	31,5%	6,6%	3,9%
14	MeCN	**5**/20$BF_3 \cdot OEt_2$	93,00%	44%	56%	38,2%	53,4%	4,1%	4,3%
15	CH_2Cl_2	**5**/20$BF_3 \cdot OEt_2$	polymeric product	–	–	–	–	–	–
16	CH_3NO_2	**5**/20$BF_3 \cdot OEt_2$	polymeric product	–	–	–	–	–	–

Reaction conditions: isoprene/Pd=200, $2.5 \cdot 10^{-5}$ mol Pd (0.5 mol%), 0.5 mL of isoprene, 0.5 mL of $NHEt_2$, 0.5 mL of solvent, 25°C, 20 h.

CONCLUSION

New cationic palladium complexes containing diphosphines were prepared in good yields. The tests of the [Pd(acac-O,O′)(P^P)]BF_4 and [Pd(acac-O,O′)$(PR_3)_2$]BF_4 complexes revealed the high potential of **2, 3, 5-7** for butadiene telomerization of diethylamine.

EXPERIMENTAL SECTION

General Information. All air- and/or moisture-sensitive compounds were manipulated by using standard high-vacuum line, Schlenk, or cannula techniques under an argon atmosphere. Diethyl ether and benzene were distilled from sodium−benzophenone. CH_2Cl_2, CH_3NO_2, CH_3CN, diethylamine and isoprene were distilled from CaH_2. Solvents were stored over molecular sieves. All glassware were dried for at least 3 h in a 180°C oven and cooled under an argon atmosphere. All NMR spectra were recorded at room temperature on a Varian 500S spectrometer. Chemical shifts refer to signals of tetramethylsilane in the case of ^{1}H and ^{13}C spectra, H_3PO_4 in the case of ^{31}P, and $BF_3{\cdot}OEt_2$ in the case of ^{11}B. Compound **8** was prepared according to literature procedures [47]. All other reagents were obtained commercially and used as received.

Preparation of [Pd(acac)(dppm)]BF_4 (1). To the mixture of dppm (0,577 g, 1.5 mmol) and 1 (0,562 g, 1.50 mmol) was added Et_2O (50 mL). Then, the reaction mixture was stirred for 2 h at ambient temperature. The resulting reaction mixture was filtered, and residue was dried under vacuum to yield an orange solid (0.926 g, 91%). The product was insoluble in acetone. chloroform, DMSO, methylene chloride, and nitromethane. IR, cm^{-1}: $\nu_{(C=O\ and\ C=C)}$, 1553, 1518; $\delta_{(C–H\ from\ CH3\ in\ acac)}$, 1437, 1366; $\nu_{(C–CH3\ in\ acac)}$, 1270; $\delta_{(C–H\ from\ CH\ in\ acac)}$, 1190, 777; $\delta_{(CH\ in\ Ph\ and\ CH2)}$, 762, 738, 716, 687; $\nu_{(B–F\ in\ BF4)}$, 1150-980. Anal. Calcd for $C_{30}H_{29}BF_4O_2P_2Pd$: C, 53.24; H, 4.32%. Found: C, 53.10; H, 4.24%. Since there were no evidences for η^2-coordination of dppm, one can suppose that complex 3a is oligomeric material with the following formula $[Pd(acac)_n(\mu\text{-}dppm)]_n[BF_4]_n$.

Preparation of [Pd(acac)(dppp)]BF_4(2). dppp (0,619 g, 1.50 mmol) was dissolved in dichloromethane (40 mL) and 1 (0,562 g, 1.50 mmol) was slowly added. Then, the reaction

mixture was stirred for 1 h at ambient temperature. The resulting yellow solution was filtered, and the solvent of the filtrate was removed under reduced pressure. The residue was washed with Et_2O (3 × 5 mL) and dried under vacuum to yield a yellow solid (0.850 g, 85%). ^{1}H NMR ($CDCl_3$): δ 7.7-7.2 (m, 20H, CH, Ph), 5.3 (s, 1H, CH), 2.9-2.7 (m, 6H, CH_2), 1.6 (6H, CH_3).^{13}C NMR ($CDCl_3$): δ 187.4 (s, C=O), 139.0 (d, *o*-CH, Ph), 132.6 (d, *p*-CH, Ph), 129.5 (d, *m*-CH, Ph), 128.5 (s, C, Ph), 100.1 (d, CH), 26.0 (q, CH_3), 26.0 (t, CH_2), 23.7 (t, CH_2). ^{31}P NMR ($CDCl_3$): δ 37.5. ^{11}B ($(CD_3)_2CO$): δ -0.54 (quintet, BF_4). Anal. Calcd for $C_{32}H_{33}BF_4O_2P_2Pd$: C, 54.53; H, 4.72%. Found: C, 54.60; H, 4.79%.

Preparation of [Pd(acac)(dppb)]BF_4 (3). dppb (0,639 g, 1.50 mmol) was dissolved in Et_2O (20 mL), 1 (0,562 g, 1.50 mmol) was slowly added, and 20 mL of Et_2O were added. Then, the reaction mixture was stirred for 1 h at ambient temperature. The resulting reaction mixture was filtered, and residue was dried under vacuum to yield a lemon-yellow solid (1.029 g, 96%). ^{1}H NMR ($CDCl_3$): δ 7.8-7.2 (m, 20H, CH, Ph), 5.4 (1H, CH), 3.5(2H, CH_2), 2.8(2H, CH_2), 2.1(2H, CH_2), 1.7 (6H, CH_3), 1.3 (2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 187.7 (s, C=O), 134.0 (d, *o*-CH, Ph), 132.5 (d, *p*-CH, Ph), 129.5 (d, *m*-CH, Ph), 126.5 (s, C, Ph), 100.3 (d, CH), 26.0 (q, CH_3), 23.3 (t, CH_2), 18.9 (t, CH_2). ^{31}P NMR ($CDCl_3$): δ 40.3. ^{11}B ($(CD_3)_2CO$): δ -0.55 (quintet, BF_4). Anal. Calcd for $C_{33}H_{35}BF_4O_2P_2Pd$: C, 55.14; H, 4.91%. Found: C, 54.82; H, 5.01%.

Preparation of [Pd(acac)(dppf)]BF_4 (4). To the mixture of dppf (0,187 g, 0.337 mmol) and 1 (0.127 g, 0.337 mmol) was added Et_2O (20 mL). Then, the reaction mixture was stirred for 2 h at ambient temperature. The resulting reaction mixture was filtered, and residue was dried under vacuum to yield a red solid (0.262 g, 92%). ^{1}H NMR ($CDCl_3$): δ 8.0-7.2 (m, 20H, CH, Ph), 5.4 (1H, CH), 4.8 (4H, CH, Cp^*), 4.5 (4H, CH, Cp^*), 1.6 (6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 186.5 (s, C=O), 134.4 (d, *o*-CH, Ph), 132.6 (d, *p*-CH, Ph), 129.2 (s, C, Ph), 129.1 (d, *m*-CH, Ph), 101.7 (d,

CH), 78.2 (d, CH, Cp^*), 76.5 (d, CH, Cp^*), 25.7 (q, CH_3). ^{31}P NMR ($CDCl_3$): δ 43.5. Anal. Calcd for $C_{40}H_{38}BF_4FeO_2P_2Pd$: C, 55.75; H, 4.44%. Found: C, 55.49; H, 4.17%.

Preparation of [Pd(acac)(PPh_3)$_2$]BF_4 (5). PPh_3 (0,750 g, 2.78 mmol) was dissolved in dichloromethane (10 mL) and 1 (0,520 g, 1.39 mmol) was slowly added. Then, the reaction mixture was stirred for 0.5 h at ambient temperature. The resulting yellow solution was filtered, and the solvent of the filtrate was removed under reduced pressure. The residue was washed with Et_2O (3 × 5 mL) and dried under vacuum to yield an yellow solid (1.056 g, 93%). ^1H NMR ($CDCl_3$): δ 7.2–7.8 (m, 30H, Ph), 5.6 (s, 1H, CH), 1.5 (s, 6H, CH_3).^{13}C NMR ((CD_3)$_2$CO): δ 188.4 (s, C=O), 128-136 (m, Ph), 102.3 (d, CH), 27.5 (q, CH_3). Spectroscopic data were found to match literature data [45,48].

Preparation of [Pd(acac)(P(*p*-Tol)$_3$)$_2$]BF_4 (6). P(*p*-Tol)$_3$ (0,913 g, 3.00 mmol) was dissolved in dichloromethane (20 mL) and 1 (0,562 g, 1.50 mmol) was slowly added. Then, the reaction mixture was stirred for 1 h at ambient temperature. The resulting yellow solution was filtered, and the solvent of the filtrate was removed under reduced pressure yielding an yellow solid (1.283 g, 95%). ^1H NMR ($CDCl_3$): δ 7.2–7.6 (m, 24H, Ar), 5.5 (s, 1H, CH), 2.4 (s, 18H, Ar), 1.5 (s, 6H, CH_3).^{13}C NMR ((CD_3)$_2$CO): δ 186.2 (s, C=O), 141.5 (d, *p*-CH, Ar), 134.0 (d, *o*-CH, Ar), 129.3 (d, *m*-CH, Ar), 100.4 (d, CH), 26.0 (q, CH_3), 21.3 (q, CH_3, Ar). Spectroscopic data were found to match literature data [45,48].

Preparation of [Pd(acac)(P(*i*-Pr)$_3$)$_2$]BF_4 (7). P(*i*-Pr)$_3$ (0,490 g, 3.06 mmol) was dissolved in dichloromethane (20 mL) and 1 (0,573 g, 1.53 mmol) was slowly added. Then, the reaction mixture was stirred for 1 h at ambient temperature. The resulting yellow solution was filtered, and the solvent of the filtrate was removed under reduced pressure. The residue was washed with cold (~-15°C) Et_2O (3 × 5 mL) and dried under vacuum to yield a bright-yellow solid (0.871 g,

93%). ^{1}H NMR ($CDCl_3$): δ 5.5 (1H, CH), 2.5 (6H, CH_3), 2.0 (6H, CH), 1.4 (36H, CH_3).^{13}C NMR ($CDCl_3$): δ 185.7 (s, C=O), 100.7 (d, CH), 26.0 (q, CH_3), 24.3(d, CH), 19.9 (q, CH_3). Spectroscopic data were found to match literature data [68].

Calculations. All density functional theory (DFT) calculations were performed with the ORCA program [69]. All geometry optimizations were run with tight convergence criteria, using the BP86 functional [70,71], making use of the resolution of the identity (RI) technique [72]. The applicability of gradient-corrected functionals as BP86 for the structural prediction of transition metal compounds is well documented [73–76]. The basis sets that were used were the Weigend−Ahlrichs basis sets [77,78]. Triple-ξ-quality basis sets with one set of polarization functions (def2-TZVP) were used for the palladium, iron and the phosphorus atoms. The remaining atoms were described by slightly smaller def2-SVP basis sets. A scalar relativistic correction was applied using the zeroth-order regular approximation (ZORA) method [79–82]. Figure 1, and figures in Supporting Information were generated with Gabedit 2.3.0 [83].

X-ray Diffraction Studies

Crystallographic data and refinement details are given in Table 6. The diffraction data were collected on a Bruker X8Apex CCD diffractometer with MoKα radiation (λ = 0.71073 Å) by doing φ and ω scans of narrow (0.5°) frames at 296 K. Structure of **3b** was solved by direct method and refined by full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with SHELXTL programs set [84].Absorption corrections were applied empirically with SADABS program [85]. All non-hydrogen atoms of $[Pd(acac)(dppp)]^+$ were refined anisotropically. The hydrogen atoms were refined in their geometrically calculated positions; a riding model was used for this purpose. BF_4^- anion was found to be disordered over three close positions with 0.4/0.3/0.3 occupancy ratio. Since anion is highly disordered with

small occupancies, their atoms were refined in isotropic approximation. Further details may be obtained from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC 896672. This information may be obtained free of charge from http://www.ccdc.cam.ac.uk.

Table 7. Experimental details

Chemical formula	$C_{32}H_{33}BF_4O_2P_2Pd$
M_r	704.73
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	296
a, *b*, *c* (Å)	28.8084(6), 14.2418(3), 15.7720(3)
β (°)	94.919 (1)
V (Å^3)	6447.2 (2)
Z	8
F(000)	2864
Radiation type	Mo *K*α
μ (mm^{-1})	0.73
Crystal size (mm)	0.30 × 0.22 × 0.15
Diffractometer	Bruker Nonius X8Apex CCD diffractometer
Absorption correction	Multi-scan *SADABS* (Bruker-AXS, 2004)
T_{min}, T_{max}	0.812, 0.899
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	42878, 4973, 4022
R_{int}	0.069

Range of h, k, l	$-32 \leq h \leq 32$, $-16 \leq k \leq 16$, $l = -17 \leq l \leq 17$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.136, 1.13
No. of reflections, parameters, restraints	4973, 386, 0
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0866P)^2 + 2.9504P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.78, -0.94

Computer programs: *APEX2* (Bruker-AXS, 2004), *SAINT* (Bruker-AXS, 2004), *SHELXS97* (Sheldrick, 1998), *SHELXL97* (Sheldrick, 1998), *SHELXTL* (Bruker-AXS, 2004), CIFTAB-97 (Sheldrick, 1998).

General procedure for catalytic telomerizations of 1,3-butadiene. Palladium complex (0.013 mmol) was added in a dried and sealed vessel under argon. The stainless steel autoclave was cooled with liquid nitrogen and 4.2 g (78 mmol) of 1,3-butadiene was condensed (volume and mass control). Afterwards cold (-15°C) diethylamine (5.4 mL, 42.5 mmol) was added via syringe into the cooled (-10°C) autoclave and the vessel was heated to the desired reaction temperature. After 3 h the autoclave was cooled to room temperature and 1 mL of benzene as internal standard was added. In general, the yield of telomers was determined by GC. The main product was isolated from the reaction mixture via distillation and analyzed by GC-MS and ^{1}H,^{13}C NMR.

General procedure for catalytic telomerizations of isoprene. Palladium complex (0.025 mmol), MeOH (0.5 mL), isoprene (0.5 mL, 5 mmol), and diethylamine (0.5 mL) were stirred for 20 h at 25°C. The yield of telomers was determined by GC/GS-MS.

ASSOCIATED CONTENT

Supporting Information.

Optimized geometries, energies, Cartesian coordinates for all the calculated species, and crystallographic data for **3b** (in CIF format).

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- A series of novel $[Pd(acac\text{-}O,O')(P\text{^}P)]BF_4$ complexes $[Pd(acac\text{-}O,O')(PR_3)_2]BF_4$ (P^P = dppm (1), dppp (2), dppb (3), dppf (4)) were prepared

- Models of the structure and IR wavenumbers assignments of the cations of 1-4 were obtained by DFT calculations.

- Synthesized complexes were tested as catalysts in the telomerization of isoprene and butadiene with diethylamine. In the case of telomerization of butadiene with diethylamine high catalyst activity was obtained.

Supporting Information

Palladium(II)-Acetylacetonate Complexes Containing Phosphine and Diphosphine Ligands and Their Catalytic Activities in Telomerization of 1,3-Dienes with Diethylamine

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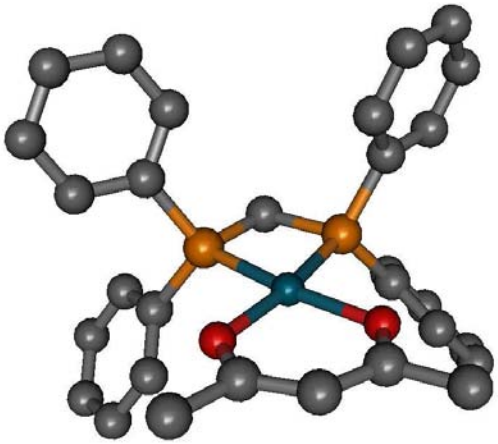
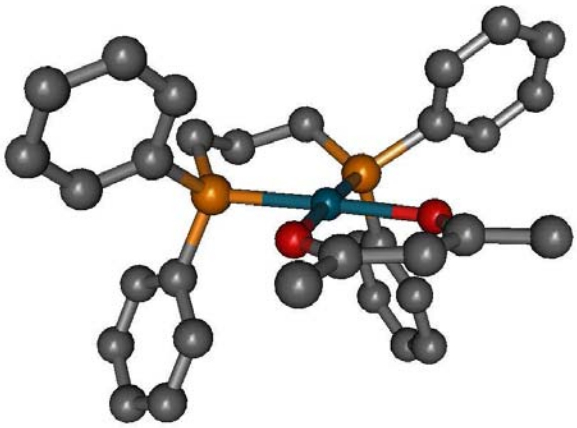
Contents:

1. Additional figures

Figure 1S. Calculated geometries of cations of **3a-c**. Solvation effects were neglected in the calculation. Hydrogen atoms are omitted for clarity.



Cation of **1**



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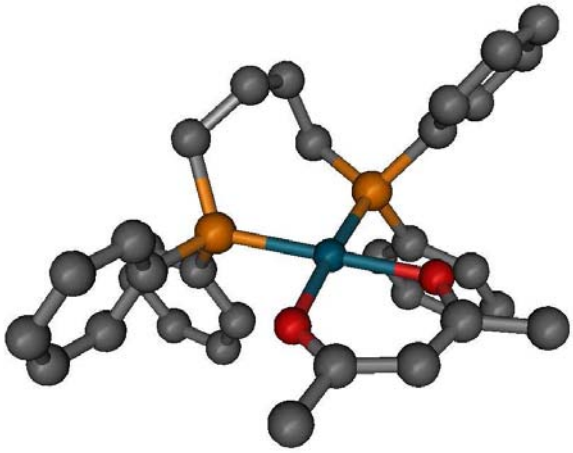

Cation of **3**

2. Cartesian coordinates and energies of all optimized structures

For each structure, energies are given as electronic energy and Gibbs free energy values at levels ZORA-BP86/def2-SVP/def2-TZVP.

a) Energies

Molecule	Ee, hartree	G, hartree
[(acac)Pd(dppm)], cation of **1**	-7100,994804	-7100,559472
dppm	-1651,305598	-1650,968616
[(acac)Pd(dppe)] cation	-7140,32755	-7139,862749
dppe	-1690,617773	-1690,255077
[(acac)Pd(dppp)], cation of **2**	-7179,637981	-7179,148613
dppp	-1729,930064	-1729,54202
[(acac)Pd(dppb)], cation of **3**	-7218,944451	-7218,429029
dppb	-1769,240217	-1768,823027
[(acac)Pd(dppf)], cation of **4**	-8725,670515	-8725,123398
dppf	-3275,968356	-3275,523116
[(acac)Pd($MeCN)_2$], cation of **8**	-5715,170374	-5715,011636
MeCN	-132,7592322	-132,7381383

b) Cartesian coordinates

[(acac)Pd(dppm)], cation of **1**

H	4.8634400000	-2.1684430000	0.0350190000
H	5.0668230000	-3.9727960000	-1.6911380000
C	3.9895160000	-2.4654850000	-0.5570230000
C	4.1015880000	-3.4800850000	-1.5236950000
H	4.5598850000	4.8367930000	-0.9758930000
H	4.7301970000	2.4436080000	-1.6956130000
H	-0.1721660000	-2.7364740000	5.5321450000
H	2.6521750000	-1.0663970000	0.4390840000
C	2.7515270000	-1.8403490000	-0.3342390000
C	2.9740240000	-3.8756260000	-2.2654980000
C	3.6809100000	4.1833840000	-0.9199370000
H	3.0581730000	-4.6780460000	-3.0086320000
C	3.7776650000	2.8398070000	-1.3238820000
H	-0.3810340000	1.8455660000	5.8718260000
H	-0.2925150000	-0.4283210000	5.5011370000
H	2.3785040000	5.7344450000	-0.1287110000
C	2.4577460000	4.6877410000	-0.4452180000
C	-0.2702400000	-2.8751450000	4.4442520000
H	0.5364240000	-3.5367080000	4.0822370000
C	2.6557880000	1.9988290000	-1.2553100000
H	2.7553910000	0.9499710000	-1.5619710000
C	1.6223620000	-2.2242230000	-1.0925390000
C	1.7329400000	-3.2535530000	-2.0536540000

C	-0.2621240000	-0.3468400000	4.4095360000
C	-0.3267330000	2.1480660000	4.8147730000
C	-0.2318590000	-1.5626380000	3.6891220000
H	-1.2280320000	-3.3889240000	4.2380340000
H	0.5709550000	2.7752200000	4.6633550000
C	-0.2753580000	0.9618700000	3.8750200000
H	-1.2020300000	2.7771510000	4.5715350000
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C	-0.0096970000	0.1373670000	-1.9860570000
P	-0.0459810000	1.4245320000	-0.6201890000
H	-1.5089020000	-3.1401220000	0.8148320000
H	-0.9423860000	0.1746000000	-2.5762120000
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H	-2.2560860000	2.1261820000	1.1677850000
C	-1.8897490000	-3.2484780000	-0.2090590000
C	-1.5319540000	2.4657420000	-0.8557300000
H	-1.4144740000	-1.9851150000	-3.3851970000
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C	-2.4500310000	2.6159130000	0.2056140000
H	-1.0463620000	3.0087480000	-2.9199020000
C	-1.7635840000	3.1083880000	-2.0943300000
C	-2.9286520000	-4.1487210000	-0.4945260000
H	-3.3613110000	-4.7519190000	0.3123650000
C	-2.8731800000	-3.4896600000	-2.8408300000
C	-3.5989150000	3.4054520000	0.0242600000
C	-3.4206000000	-4.2690940000	-1.8065730000
H	-4.3125990000	3.5244530000	0.8486940000
C	-2.9160690000	3.8898330000	-2.2660280000
H	-3.2582810000	-3.5817620000	-3.8634530000
C	-3.8336960000	4.0369690000	-1.2086110000
H	-4.2374140000	-4.9681550000	-2.0238110000
H	-3.0976530000	4.3872560000	-3.2262730000
H	-4.7337470000	4.6479710000	-1.3484320000

dppm

H	-2.9880130000	-5.6136160000	-1.0862620000
H	-1.6165890000	5.3898600000	2.7619130000
H	-2.5829370000	-5.1370850000	-3.5178190000
C	-2.4747210000	-4.6923740000	-1.3898050000
H	-2.2538690000	-3.9837770000	0.6466420000
C	-2.2473840000	-4.4260690000	-2.7527930000
C	-1.8167250000	4.4379410000	2.2542500000
C	-2.0558500000	-3.7756860000	-0.4138580000
H	-3.9796960000	4.6815140000	2.2926600000
H	0.2822250000	3.9279110000	2.1008990000
C	-3.1412320000	4.0420490000	1.9904610000
C	-0.7464140000	3.6136670000	1.8767060000
C	-1.5936410000	-3.2405960000	-3.1265270000
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C	2.1178220000	-2.5790640000	3.1818240000
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H	0.7013810000	-0.3221460000	-0.9251440000
H	3.2794070000	1.4156520000	-0.0245230000
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C	3.4814040000	2.8626400000	-1.6322350000
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H	4.5528070000	2.6678210000	-1.7704670000

[(acac)Pd(dppe)] cation

H	-4.3652750000	-4.7870810000	-1.7523950000
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C	-2.9439490000	-3.9663750000	-0.3261300000
H	-4.9712820000	2.4947570000	0.1356770000
H	-4.8586210000	4.9053650000	-0.5339920000
H	-3.2761530000	-3.7048730000	-3.7300570000
C	-2.8664520000	-3.5530680000	-2.7242870000
C	-4.0227860000	2.9268990000	-0.2052120000
C	-3.9576300000	4.2814800000	-0.5790900000
C	-1.8111220000	-3.1584260000	-0.1441570000
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H	-1.2633160000	-2.2908410000	-3.4348260000
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C	0.1698550000	-2.6990260000	4.2353920000
C	-1.6466520000	2.6835320000	-0.6909370000
C	0.0269700000	-1.4217670000	3.4337380000
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H	-0.2501570000	-0.2546240000	5.2036640000
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C	-0.1962650000	-0.2013080000	4.1112930000
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H	1.6755580000	-0.2074730000	-2.4256140000
H	2.7669690000	-5.8254220000	-1.4765780000
H	0.2725410000	2.9667790000	4.3592620000
C	2.8081480000	-4.7903060000	-1.1177150000
C	1.7548140000	3.2041660000	0.3644230000
C	1.3031800000	2.6674660000	-0.8648960000
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C	2.9089970000	-2.1357330000	-0.1837760000
H	2.9413360000	-1.1085040000	0.2014060000
C	3.9927280000	-4.2841130000	-0.5548710000
H	3.2208840000	4.4623270000	1.3449910000
C	2.8769570000	4.0458750000	0.3907880000
C	1.9928740000	2.9772860000	-2.0579850000
H	1.6610550000	2.5790900000	-3.0239760000
C	4.0419820000	-2.9581260000	-0.0872980000
H	4.8781670000	-4.9262600000	-0.4727140000
C	3.5620710000	4.3512350000	-0.7993200000
C	3.1196550000	3.8166960000	-2.0207670000
H	4.9623710000	-2.5667630000	0.3624670000
H	4.4423440000	5.0049700000	-0.7742670000
H	3.6495830000	4.0539590000	-2.9509010000

dppe

H	1.0740150000	4.9815680000	3.4130580000
H	3.1765460000	4.0774980000	2.3875030000
C	1.0252730000	4.3751490000	2.4999940000
C	2.2032980000	3.8660400000	1.9268160000
H	-4.3913280000	-2.4474060000	2.2253980000
C	-3.4637310000	-2.5204160000	1.6436400000
H	-1.1383660000	4.5072610000	2.3333800000
C	-0.2152290000	4.1079720000	1.8943330000
H	-2.2179650000	-1.6927580000	3.2221790000
H	-4.4333800000	-3.3843850000	-0.1004600000
C	2.1387350000	3.0958880000	0.7533920000
H	3.0641640000	2.7187230000	0.2968900000
C	-2.2440720000	-2.0994530000	2.2035780000
C	-3.4877550000	-3.0431630000	0.3393580000
C	-0.2810970000	3.3286850000	0.7266400000
C	0.8954050000	2.8076910000	0.1447950000
C	-1.0542010000	-2.1925700000	1.4614410000
C	-2.2956460000	-3.1466110000	-0.3988440000
H	1.4519790000	-0.0643940000	0.1364220000
H	-0.1085140000	-1.8664210000	1.9109090000
H	-2.3141180000	-3.5757960000	-1.4096180000
C	-1.0642120000	-2.7152860000	0.1466610000
H	-1.2541130000	3.1281880000	0.2608560000
C	0.6167170000	0.0605680000	-0.5790000000
P	0.9293890000	1.7411640000	-1.3859710000
H	-0.3089230000	0.0846960000	0.0257770000
P	0.4278130000	-2.8626120000	-0.9603170000
H	-0.2467450000	-0.9735890000	-2.3027350000
C	0.5964840000	-1.0859680000	-1.5934870000
H	0.2075940000	3.7694580000	-3.2825870000
H	0.8069520000	-4.4783990000	1.4930360000
C	-0.7115400000	2.1452690000	-2.1658650000
H	-1.9454760000	0.5987830000	-1.2389640000
C	-0.7258380000	3.2279450000	-3.0768490000
H	1.5076410000	-1.0773010000	-2.2237110000
C	-1.9178550000	1.4459910000	-1.9360320000
C	1.8333140000	-3.0191250000	0.2401170000
C	1.7492880000	-3.9475080000	1.3063520000
C	-1.9121130000	3.6162410000	-3.7194540000
C	-3.1040600000	1.8250020000	-2.5907360000

H	-1.9025100000	4.4647540000	-4.4156760000
H	3.1857490000	-1.6638050000	-0.8131270000
C	3.0721640000	-2.3720320000	0.0179890000
C	2.8556840000	-4.1995690000	2.1333330000
H	2.7624900000	-4.9193360000	2.9570820000
C	-3.1062270000	2.9128810000	-3.4795250000
H	-4.0302130000	1.2679090000	-2.3998550000
H	-4.0327180000	3.2085840000	-3.9871780000
C	4.1801810000	-2.6278620000	0.8445400000
C	4.0769650000	-3.5398160000	1.9078710000
H	5.1283820000	-2.1094170000	0.6534940000
H	4.9417100000	-3.7389090000	2.5531480000

[(acac)Pd(dppp)], cation of **2**

H	3.3247010000	6.2771270000	0.7539780000
H	4.2864370000	3.9633200000	0.7895620000
C	2.7002090000	5.4191140000	0.4779110000
C	3.2415560000	4.1205510000	0.4962630000
H	4.0319160000	-5.8892190000	-0.2949830000
H	0.9322560000	6.6264330000	0.1015830000
C	1.3580380000	5.6155580000	0.1123770000
C	3.3067000000	-5.0763050000	-0.4217660000
C	2.4418540000	3.0206560000	0.1501740000
H	2.8620000000	2.0066960000	0.1876050000
H	4.6998750000	-3.5250060000	0.1985220000
H	1.7025540000	-6.3951090000	-1.0642970000
C	3.6833000000	-3.7489840000	-0.1465930000
C	1.9999930000	-5.3609630000	-0.8522180000
H	1.8734220000	-0.9239980000	-2.7145950000
C	0.5517150000	4.5193240000	-0.2395550000
C	1.0947710000	3.2173120000	-0.2272380000
H	0.5641270000	-1.8649780000	-3.4342040000
C	2.7555590000	-2.7081140000	-0.3029380000
C	1.0656700000	-4.3234890000	-1.0136510000
H	3.0458430000	-1.6764590000	-0.0654240000
H	0.0458230000	-4.5537480000	-1.3444640000
C	1.4443680000	-2.9913100000	-0.7455190000
C	0.7714790000	-1.0252090000	-2.7457000000
H	0.3532650000	0.3790900000	-4.3211390000
H	-0.4960750000	4.6798240000	-0.5197560000
C	0.1212910000	0.2773300000	-3.2434430000
C	0.6336640000	1.5412580000	-2.5320950000
H	-1.8112070000	2.6620640000	-2.9449340000
P	0.1044710000	1.7635450000	-0.7654800000
P	0.2890370000	-1.5915880000	-1.0437850000
H	-1.5509740000	-2.2965610000	-3.3559980000
H	0.3334210000	2.4563580000	-3.0763060000
H	-0.9822230000	0.2128070000	-3.1772710000
Pd	0.3882250000	-0.0318390000	0.6408930000
C	-2.3238480000	2.6781130000	-1.9764290000
C	-1.6547780000	2.2977280000	-0.7917750000
C	-2.0400070000	-2.5467470000	-2.4078180000
O	0.4248280000	1.3320590000	2.2020690000
O	0.5964770000	-1.6190680000	1.9592880000
H	-4.1763790000	3.3898630000	-2.8489840000
C	-1.3979840000	-2.3105860000	-1.1718190000
H	1.4137870000	2.9432230000	4.0187820000
C	-3.6653490000	3.0949510000	-1.9247490000
C	0.6381240000	1.0227940000	3.4359170000
H	1.1195860000	-2.6641810000	5.0443950000
C	0.7870810000	-1.4922240000	3.2286670000
H	-0.3120490000	2.7155090000	4.3643110000
C	0.8296460000	-0.2789090000	3.9518640000
H	1.8572000000	-3.3294760000	3.5451190000
H	-3.8147020000	-3.2989940000	-3.4004790000
C	0.6703840000	2.2088870000	4.3765720000
C	-3.3241900000	-3.1181830000	-2.4365630000
C	0.9788940000	-2.8033000000	3.9615030000
C	-2.3455860000	2.3400640000	0.4423270000

H	1.0131440000	-0.3566870000	5.0281030000
C	-2.0578100000	-2.6524200000	0.0324700000
H	-1.8264580000	2.0522210000	1.3650170000
H	-1.5591970000	-2.4743150000	0.9932950000
C	-4.3457040000	3.1385840000	-0.6962940000
H	0.9097670000	1.9197430000	5.4112570000
C	-3.6826130000	2.7636850000	0.4861750000
H	0.1049760000	-3.4572120000	3.7889260000
C	-3.9731900000	-3.4597120000	-1.2384660000
H	-5.3912670000	3.4661610000	-0.6598620000
C	-3.3366230000	-3.2286120000	-0.0054710000
H	-4.2097050000	2.7987480000	1.4474230000
H	-4.9742730000	-3.9055070000	-1.2649480000
H	-3.8392050000	-3.4961200000	0.9316120000
H	1.7399910000	1.5544170000	-2.5069840000

dppp

H	-3.2675650000	-7.0244650000	0.8976740000
H	-4.4671350000	-5.7372410000	-0.8895970000
C	-2.7811340000	-6.1678020000	0.4147540000
C	-3.4538430000	-5.4457830000	-0.5864640000
H	-3.2603330000	4.0985240000	3.9118510000
H	-0.9451590000	-6.3567490000	1.5643020000
C	-1.4776580000	-5.7938750000	0.7867410000
C	-2.8224910000	-4.3579280000	-1.2135900000
H	-3.3430020000	-3.8110740000	-2.0119010000
H	-2.5156660000	6.4929300000	3.9374970000
C	-2.6213110000	4.4857680000	3.1073930000
H	-2.5581550000	2.5851940000	2.0825490000
C	-2.2036980000	5.8260250000	3.1240380000
C	-0.8499400000	-4.7001670000	0.1663310000
C	-2.2210500000	3.6283890000	2.0656760000
C	-1.5171740000	-3.9655360000	-0.8392510000
H	-2.2808960000	-1.2512470000	-0.2776720000
H	0.1694640000	-4.4194790000	0.4592000000
H	-2.3782930000	1.2669860000	0.2736020000
C	-1.3845730000	6.3077030000	2.0855620000
C	-1.1885050000	-1.1593400000	-0.4354310000
H	-0.7166130000	-1.3999730000	0.5388400000
C	-1.3990490000	4.0984890000	1.0167810000
P	-0.7866390000	-2.4864350000	-1.7136380000
H	-1.0514330000	7.3532870000	2.0867040000
C	-1.2828400000	1.3324390000	0.1235620000
C	-0.9957680000	5.4563250000	1.0406900000
H	0.2475130000	0.3546070000	-1.0750700000
C	-0.8418220000	0.2678750000	-0.8960620000
H	-0.8017690000	1.1601710000	1.1065480000
P	-0.9291520000	3.0876880000	-0.4704380000
H	1.0341220000	-4.2061400000	-3.1235500000
C	1.0335340000	-2.7844690000	-1.4747460000
H	-0.3645870000	5.8481170000	0.2311920000
H	-1.3262980000	0.4636510000	-1.8731680000
H	1.4100050000	-1.4078110000	0.1772300000
C	1.6446390000	-3.7058770000	-2.3591630000
C	1.8457820000	-2.1347380000	-0.5192970000
C	0.9327370000	3.1085050000	-0.3437960000
H	1.1379060000	3.0836660000	-2.5077430000
H	1.0775310000	3.1694270000	1.8285150000
C	3.0158400000	-3.9900070000	-2.2719670000
C	3.2245440000	-2.4066600000	-0.4417650000
C	1.6717660000	3.0822390000	-1.5474510000
C	1.6347450000	3.1296270000	0.8830970000
H	3.4672140000	-4.7157440000	-2.9608790000
C	3.8125790000	-3.3385470000	-1.3124030000
H	3.8375500000	-1.8868030000	0.3055410000
H	4.8866150000	-3.5544240000	-1.2477330000
C	3.0779340000	3.0634010000	-1.5283160000
C	3.0389400000	3.1180810000	0.9027760000

H	3.6363220000	3.0410230000	-2.4728010000
H	3.5706050000	3.1401700000	1.8630760000
C	3.7640470000	3.0825080000	-0.3027030000
H	4.8616110000	3.0754860000	-0.2851400000

[(acac)Pd(dppb)], cation of **3**

H	0.6762830000	-5.0306470000	3.7070860000
H	5.1332550000	-2.3776770000	2.0046090000
H	0.1942500000	3.7761460000	4.2786940000
H	5.2545610000	2.2207560000	1.5453840000
H	1.1175010000	-6.8694510000	2.0618080000
H	5.0435880000	-0.0853210000	1.6221510000
C	0.4971100000	-4.8668630000	2.6371820000
H	-0.8081820000	5.9704310000	3.6026290000
C	4.1491620000	-2.6005480000	1.5648940000
C	-0.2071600000	3.9093390000	3.2669510000
C	4.2629390000	2.4145680000	1.1089270000
H	4.3011790000	-3.1606470000	0.6235510000
C	0.7472380000	-5.8979270000	1.7129540000
H	3.5754460000	-3.2578560000	2.2407400000
H	-0.1509270000	-2.8242610000	2.9260550000
C	3.9891660000	-0.0876810000	1.3310980000
H	4.4002520000	2.8265480000	0.0922430000
H	0.3020390000	1.8913400000	2.6397420000
H	3.7425050000	3.1839510000	1.7056850000
C	-0.7674560000	5.1406280000	2.8863570000
C	3.3500650000	-1.3476850000	1.2729110000
C	0.0199750000	-3.6242130000	2.1939750000
C	3.4103490000	1.1641610000	1.0327070000
C	-0.1532720000	2.8459700000	2.3497500000
O	2.1170830000	-1.5666270000	0.9730180000
O	2.1890540000	1.3771680000	0.6747360000
C	0.5241080000	-5.6790760000	0.3436850000
C	-1.2710760000	5.3119610000	1.5840900000
H	0.7199750000	-6.4785060000	-0.3811350000
C	-0.2253430000	-3.4066020000	0.8188730000
C	-0.6631910000	3.0113580000	1.0444430000
Pd	0.7456550000	-0.1016280000	0.4818180000
H	-1.7028590000	6.2738030000	1.2824960000
C	0.0433030000	-4.4371550000	-0.1061730000
C	-1.2193640000	4.2540350000	0.6625650000
P	-0.8533410000	-1.7627120000	0.2730220000
P	-0.6866130000	1.6016320000	-0.1401300000
H	-1.6834570000	0.2425270000	2.3546430000
H	-0.1316310000	-4.2799510000	-1.1767030000
H	0.4133780000	-1.0494020000	-2.2510690000
H	-1.6018110000	4.4021270000	-0.3550780000
C	-1.3742110000	-2.0178020000	-1.4772740000
H	-1.7853350000	1.4065590000	-2.9418020000
H	-3.2330920000	-3.0852320000	-1.0306870000
C	-0.5136990000	-1.5792420000	-2.5084270000
C	-0.1765920000	2.3068250000	-1.7597820000
C	-2.5626630000	-2.7077260000	-1.8123200000
C	-0.8879010000	2.0355420000	-2.9506070000
H	1.5446270000	3.3170820000	-0.8904640000
C	-2.6328170000	-0.1298350000	1.9225120000
C	0.9826620000	3.1167320000	-1.8095470000
C	-0.8391270000	-1.8201250000	-3.8542180000
C	-2.4004440000	-1.5246270000	1.3162050000
C	-2.8876970000	-2.9382140000	-3.1588940000
H	-0.1622860000	-1.4776630000	-4.6456930000
C	-3.2377850000	0.9292720000	0.9867220000
C	-2.4914620000	1.1901760000	-0.3338870000
C	-0.4505420000	2.5791760000	-4.1704940000
H	-2.3010500000	-2.2675980000	2.1266280000
C	-2.0276360000	-2.4955090000	-4.1805270000
H	-3.8121890000	-3.4716860000	-3.4106710000
H	-1.0144500000	2.3726160000	-5.0881310000

H	-2.9603470000	2.0383950000	-0.8668770000
C	1.4119360000	3.6543200000	-3.0321120000
H	-3.3195920000	-0.2508400000	2.7815920000
C	0.6968010000	3.3886410000	-4.2139370000
H	-2.2833640000	-2.6830090000	-5.2305430000
H	2.3078390000	4.2863700000	-3.0622030000
H	-3.2671890000	-1.8462040000	0.7088420000
H	-2.5504660000	0.3161690000	-1.0100760000
H	1.0322880000	3.8146230000	-5.1669260000
H	-3.3238560000	1.8791210000	1.5467700000
H	-4.2741180000	0.6377080000	0.7256330000

dppb

H	5.2190480000	-5.3304870000	-0.6782400000
H	3.0782190000	-6.3416550000	-1.5012810000
C	4.2557960000	-4.8887080000	-0.3946850000
C	3.0551510000	-5.4538020000	-0.8561370000
H	5.1460510000	-3.3152970000	0.8154050000
C	4.2146630000	-3.7584190000	0.4410470000
C	1.8187360000	-4.8887110000	-0.4967630000
H	0.8892640000	-5.3371460000	-0.8673240000
H	3.9223190000	4.8526630000	-1.3429730000
H	4.3011800000	6.3588490000	0.6255450000
C	3.2568600000	4.7984590000	-0.4711920000
C	3.4684940000	5.6438770000	0.6296210000
H	0.9687240000	1.2052390000	-0.9367140000
H	1.0856270000	-0.9122860000	-0.0403970000
C	2.9800240000	-3.2036680000	0.8139020000
C	1.7648180000	-3.7512130000	0.3380580000
H	-0.0904070000	2.4342260000	-1.6755530000
H	-1.1190960000	0.2733010000	-2.0763310000
C	2.1898470000	3.8808460000	-0.4685460000
H	2.0423320000	3.2392840000	-1.3453620000
C	2.6089540000	5.5625650000	1.7409480000
H	2.7687520000	6.2138070000	2.6101040000
H	2.9581310000	-2.3376750000	1.4910240000
C	-0.0259240000	1.6858600000	-0.8622170000
H	0.2507090000	-1.8060950000	-1.3206020000
C	0.1563460000	-1.4682730000	-0.2690200000
C	1.3191450000	3.7885960000	0.6403670000
C	1.5540650000	4.6382510000	1.7489220000
H	-1.3219290000	-5.0501550000	2.1406090000
C	-1.1425370000	0.6375780000	-1.0287030000
P	0.1892520000	-2.9365950000	0.9144600000
H	0.9008390000	4.5690820000	2.6299530000
C	-1.0794240000	-0.5739490000	-0.0747280000
P	-0.0710440000	2.5660880000	0.8080840000
H	-2.1263490000	1.1342810000	-0.9100670000
H	-1.9953810000	-1.1779900000	-0.2247560000
C	-1.6777340000	-5.0119360000	1.1020590000
H	-0.5990440000	5.1516580000	-0.7237910000
C	-1.1184770000	-4.0625860000	0.2154910000
H	-1.1118230000	-0.2248690000	0.9765740000
H	-3.1028130000	-6.6254270000	1.3794980000
C	-2.6835080000	-5.8951060000	0.6756910000
C	-1.5360250000	4.8336310000	-0.2487830000
C	-1.5566940000	3.6642540000	0.5446320000
C	-1.6074670000	-4.0132520000	-1.1096320000
H	-2.6679330000	6.5083100000	-1.0377280000
H	-1.1944960000	-3.2895500000	-1.8237760000
C	-2.7008470000	5.5988630000	-0.4239440000
C	-3.1630010000	-5.8310670000	-0.6442740000
C	-2.7691900000	3.2864250000	1.1644530000
H	-2.7929760000	2.3928850000	1.8030810000
C	-2.6236630000	-4.8867260000	-1.5348910000
H	-3.9588940000	-6.5100690000	-0.9760940000
C	-3.9058250000	5.2048150000	0.1863280000
C	-3.9383460000	4.0464120000	0.9803780000

H	-2.9953400000	-4.8286030000	-2.5659190000
H	-4.8147480000	5.8039480000	0.0480090000
H	-4.8723980000	3.7372670000	1.4661790000

[(acac)Pd(dppf)], cation of **4**

H	-0.8458750000	-6.9358910000	-2.1424770000
H	-3.5268620000	-3.6171500000	-2.2272070000
H	0.6878670000	-5.4240320000	-3.4244120000
C	-0.5820310000	-5.9506660000	-1.7399950000
H	-4.4260030000	-3.5029800000	-0.6990340000
C	0.2779470000	-5.1034210000	-2.4595100000
C	-4.2127660000	-2.9757710000	-1.6473750000
H	-5.1576420000	-2.8450130000	-2.1966750000
H	-1.7678790000	-6.1964840000	0.0665410000
C	-1.0996360000	-5.5357490000	-0.4994950000
H	-5.2679240000	-0.5392530000	-1.9341510000
C	0.6255750000	-3.8448260000	-1.9406210000
C	-3.5375790000	-1.6545910000	-1.3416410000
H	1.3092580000	-3.1977370000	-2.5034820000
C	-0.7617950000	-4.2776160000	0.0219830000
C	-4.2523860000	-0.4503730000	-1.5379570000
H	-4.2201680000	2.7080730000	-2.2519800000
C	0.1131490000	-3.4287370000	-0.6925920000
O	-2.3325920000	-1.7675160000	-0.9019640000
H	-1.1702840000	-3.9623790000	0.9888990000
H	-0.5228370000	3.1384520000	-4.6158880000
C	-3.7901190000	0.8521980000	-1.2562110000
C	-4.6943650000	2.0403420000	-1.5095670000
H	-5.6889800000	1.7421590000	-1.8740260000
H	2.4259100000	-4.3005530000	3.8829360000
H	2.0317930000	-3.8937260000	1.4587650000
H	-0.2905490000	1.4709380000	-2.7695770000
C	1.8223590000	-3.4403460000	3.5679380000
C	1.6097750000	-3.2043190000	2.2002640000
H	1.4170260000	-2.7798180000	5.5985900000
C	1.2527560000	-2.5875320000	4.5311420000
C	-0.4284690000	3.4826670000	-3.5785900000
C	0.8327370000	-2.0970560000	1.7854630000
P	0.5471520000	-1.7751880000	-0.0071070000
C	0.4606720000	-1.5003880000	4.1251620000
C	0.2474010000	-1.2567670000	2.7567600000
H	-0.0019750000	-0.8437750000	4.8711840000
H	-4.8078530000	2.6266260000	-0.5799970000
Pd	-1.0992390000	-0.1846780000	-0.4024500000
C	-0.2859660000	2.5451160000	-2.5428860000
H	-0.3882390000	-0.4188420000	2.4415430000
O	-2.6290990000	1.1645440000	-0.7876940000
H	-0.5806220000	5.5891200000	-4.0931060000
H	1.5393520000	-0.2913690000	-2.6401590000
C	-0.4636540000	4.8575390000	-3.2843550000
C	2.1670690000	-1.3869470000	-0.7499030000
C	2.3423510000	-0.6692620000	-2.0014170000
C	-0.1653690000	2.9794780000	-1.2051160000
H	-2.4631820000	1.6683550000	1.5351550000
P	0.1218210000	1.7316150000	0.1256920000
C	-0.3590260000	5.2921060000	-1.9513010000
H	3.7105760000	-2.1872840000	0.7136500000
C	3.4893140000	-1.6841210000	-0.2303400000
C	3.7527220000	-0.5295900000	-2.2379410000
C	-0.2097470000	4.3587770000	-0.9118050000
H	2.6099050000	2.8428210000	-1.5751950000
H	4.2104630000	-0.0091260000	-3.0835510000
C	-1.7879290000	2.2883670000	2.1358970000
H	-0.3971300000	6.3630220000	-1.7161330000
C	-0.4584270000	2.4973040000	1.7040850000
Fe	3.1874390000	0.3180160000	-0.4451190000
C	4.4553320000	-1.1521010000	-1.1502560000
C	1.9448050000	1.7323310000	0.2886430000

C	2.8795660000	2.3241060000	-0.6521320000
H	-3.2786620000	2.7184950000	3.6488890000
H	-0.1352680000	4.7078060000	0.1251490000
C	-2.2458590000	2.8870270000	3.3207240000
H	5.5410280000	-1.1813070000	-1.0212600000
C	0.4031220000	3.3120810000	2.4744180000
C	2.7248340000	1.1294270000	1.3564580000
C	4.2097650000	2.0860040000	-0.1660050000
H	1.4388640000	3.4797070000	2.1569030000
H	5.1340890000	2.3834580000	-0.6679600000
C	-1.3862130000	3.6969470000	4.0836530000
H	2.3256320000	0.5954210000	2.2230240000
C	4.1145710000	1.3578550000	1.0693360000
C	-0.0640200000	3.9098460000	3.6572980000
H	-1.7457550000	4.1601500000	5.0102300000
H	4.9548190000	1.0047570000	1.6732510000
H	0.6111600000	4.5412440000	4.2480270000

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H	4.5339600000	-0.5835190000	4.2115250000
H	4.2120550000	-2.8293880000	5.2816770000
H	-1.3204130000	3.0413220000	-5.6795930000
H	-2.5682120000	0.9441200000	-5.0988500000
C	4.0633840000	-1.4002440000	3.6495150000
C	3.8846040000	-2.6588560000	4.2487120000
C	-1.6353440000	2.8557890000	-4.6450170000
C	-2.3316670000	1.6792990000	-4.3191620000
H	-2.4066560000	-2.1495310000	1.3709960000
H	0.1970400000	-2.5524700000	2.0769450000
H	0.2258870000	2.0633290000	-0.8770050000
H	3.8151390000	-0.2112950000	1.8499870000
H	1.9097260000	1.2120480000	1.0830740000
C	3.6502730000	-1.1888840000	2.3224800000
H	-0.8188270000	4.7253290000	-3.8920340000
C	-1.3528650000	3.7998550000	-3.6410660000
C	-2.7390240000	1.4483490000	-2.9933160000
C	3.2961040000	-3.7035270000	3.5128720000
H	-3.3036940000	0.5392520000	-2.7473870000
C	-1.5335660000	-1.9790390000	0.7353160000
C	-0.1600470000	-2.1909610000	1.1094740000
C	-0.0685810000	1.7067290000	0.1131780000
C	0.8192840000	1.2593900000	1.1525650000
H	3.1639620000	-4.6921800000	3.9716190000
C	-1.7558260000	3.5653860000	-2.3156230000
C	3.0409020000	-2.2242910000	1.5796760000
C	-2.4458300000	2.3804080000	-1.9732640000
C	2.8792070000	-3.4891410000	2.1883070000
Fe	-0.4737980000	-0.2342730000	0.6143560000
H	-1.5414370000	4.3125190000	-1.5407440000
C	-1.5548730000	-1.4673070000	-0.6096350000
C	0.6832900000	-1.8109830000	-0.0059870000
C	-1.4306760000	1.5796060000	0.5906770000
C	0.0231390000	0.8447050000	2.2792240000
H	-2.4486070000	-1.1822340000	-1.1703960000
H	0.4035160000	0.4319880000	3.2172970000
P	2.5194460000	-1.8487310000	-0.1746450000
H	2.4341040000	-4.3135970000	1.6169090000
P	-3.0252040000	1.9879190000	-0.2418340000
C	-0.1949240000	-1.3469070000	-1.0651940000
C	-1.3617360000	1.0315420000	1.9334280000
H	0.7130470000	-4.1968880000	-0.9566970000
H	-1.4919340000	3.9774390000	1.5142940000
H	0.1273510000	-0.9676420000	-2.0386190000
H	-2.2216490000	0.7973530000	2.5677640000
C	2.7786220000	-3.5135800000	-0.9758430000
C	-3.3502080000	3.7028110000	0.4163470000
C	1.7429210000	-4.4329310000	-1.2517740000
C	-2.4603860000	4.4178190000	1.2475350000

H	-5.3113380000	3.7346440000	-0.5304300000
H	4.9102060000	-3.1211300000	-1.1903890000
C	-4.5984110000	4.2870340000	0.0974280000
C	4.0960560000	-3.8348710000	-1.3788000000
C	2.0212330000	-5.6482470000	-1.9039450000
H	1.2047500000	-6.3515660000	-2.1128410000
C	-2.8068430000	5.6900520000	1.7374950000
H	-2.1034750000	6.2329240000	2.3824530000
C	-4.9379910000	5.5619850000	0.5763230000
C	4.3747480000	-5.0530060000	-2.0185070000
C	-4.0427130000	6.2676140000	1.4009810000
C	3.3362390000	-5.9638650000	-2.2849800000
H	-5.9084800000	6.0015520000	0.3135400000
H	5.4035020000	-5.2871020000	-2.3206660000
H	-4.3102450000	7.2604560000	1.7826970000
H	3.5517970000	-6.9124090000	-2.7924480000

[(acac)Pd(MeCN)$_2$], cation of **8**

H	-3.1819230000	-3.1743040000	-0.7156070000
H	-4.0030530000	1.8574020000	-1.1438330000
H	4.8245350000	-2.5623070000	-0.3146180000
H	3.6255360000	-3.8619120000	0.0000600000
H	-1.8034250000	-3.7225170000	0.2996770000
C	-2.5865260000	-2.9579120000	0.1900050000
C	-1.9679690000	-1.5806410000	0.0891340000
O	-0.6757000000	-1.5778080000	0.1134360000
H	-3.8818980000	-0.6251240000	-0.0270010000
C	-2.8006930000	-0.4496240000	-0.0203930000
C	2.8963760000	-1.9029080000	0.2184130000
C	3.9776320000	-2.8668050000	0.3249850000
N	2.0278980000	-1.1294470000	0.1343090000
C	-2.3661700000	0.8866630000	-0.1236380000
Pd	0.4264400000	0.0729790000	0.0023510000
C	-3.3854930000	1.9989500000	-0.2384440000
O	-1.1387140000	1.2909520000	-0.1322110000
H	-2.8829630000	2.9759870000	-0.2924630000
N	1.5694110000	1.7185500000	-0.1038580000
C	2.1616470000	2.7202790000	-0.1780240000
C	2.9011400000	3.9673180000	-0.2683110000
H	-3.2704440000	-3.0074820000	1.0562800000
H	-4.0654550000	1.9853740000	0.6324930000
H	4.3233460000	-2.9352370000	1.3714710000
H	2.2730820000	4.8025990000	0.0890560000
H	3.1909660000	4.1617520000	-1.3158560000
H	3.8124230000	3.9152240000	0.3525800000

MeCN

H	1.0627910000	0.3512160000	0.7644210000
H	0.9565510000	-0.1990060000	-0.9383190000
C	0.3939350000	0.2677110000	-0.1106010000
H	0.0955580000	1.2843510000	-0.4204730000
C	-0.7828840000	-0.5314180000	0.2202850000
N	-1.7259530000	-1.1728530000	0.4846890000