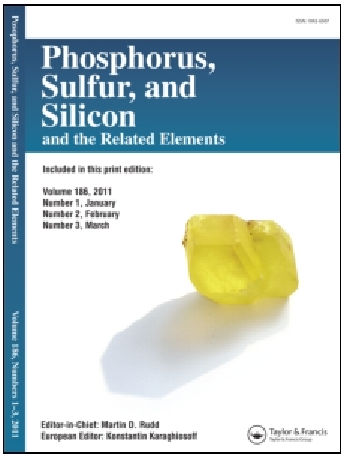

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Coordination Chemistry of ADPO

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COORDINATION CHEMISTRY OF ADPO

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J. C. CALABRESE

Contribution No. 6744 from DuPont Central Research and Development, Experimental Station, Wilmington, Delaware 19880-0328, U.S.A.

The hypervalent phosphorus compound, 3,7-di-*t*-butyl-5-aza-2,8-dioxa-1-phosphabicyclo-[3.3.0]octa-2,4,6-triene (ADPO) forms adducts with chromium, tungsten, nickel and palladium metal centers. All four new adducts contain tetrahedral phosphorus atoms as a result of folding of the ADPO unit. This folding of the planar 10-P-3 ADPO molecule to provide an 8-P-3 center for coordination to the transition metal center is the result of the close energy balance between 10-P-3 ADPO and 8-P-3 ADPO and the strength of the phosphorus-metal interaction. In the case of a homoleptic palladium(II) complex, dimerization of the coordinated ADPO unit was observed.

Key words: ADPO, Nickel(0), Palladium(II), 8-P-3, 10-P-3, 8-P-4.

INTRODUCTION

We have reported the syntheses and structures of a number of transition metal adducts of 5-aza-2,8-dioxa-1-pnictabicyclo[3.3.0]octa-2,4,6-triene (ADPnO[1]). These metal complexes have demonstrated the chemical or stereochemical activity of equatorial lone pairs at antimony and arsenic centers.[2-5] All of the complexes which contain an intact ADAsO or ADSbO unit retain the planar ring geometry. The phosphorus derived ADPO ring system has afforded complexes which appear to be derived from either the planar 10-P-3[6] ADPO[7, 8] or, more commonly, the folded 8-P-3 ADPO[3-5, 9, 10]. The special behavior of the ADPO molecule for producing transition metal adducts with a folded ADPO ring system can be traced to the delicate energy balance between the 8-P-3 and 10-P-3 forms.[7, 8, 11] This folding behavior of ADPO on complexation stems from a configuration mixing which transfers σ-electron density to the π-systems at phosphorus in the parent ADPO system.[11] This mixing stabilizes planar 10-P-3 ADPO by ~14 kcal/mole over its folded 8-P-3 form.[11] Most complexes of ADPO have employed metals (Mn[4], Fe[10], Ru[3], Pt[9]) with suffiently high P→M bond strengths to disturb the 8-P-3 *vs* 10-P-3 ADPO balance. Only the weakly coordinating silver(I) center has given complexes containing the planar ADPO unit.[7, 8] The low activation energies for dissociation of P→Ag bonds (less than 11 kcal/mole)[12] is believed to be the origin of this unique behavior toward silver. We now report four new transition metal adducts of ADPO in which the folding of the ADPO units is observed. In one case, palladium, a dimerization of the ADPO subunits is observed and this dimerized unit can be displaced from the metal center without immediate reversion to planar 10-P-3 ADPO.

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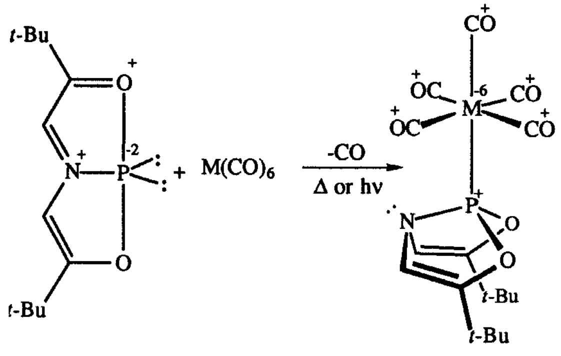
RESULTS AND DISCUSSION

Both tungsten and chromium pentacarbonyl units form complexes with ADPO in which the ADPO unit folds and adopts a tetrahedral geometry as observed in the above mentioned ruthenium, iron, platinum, and manganese complexes (eq. 1).



(1)

ADPO **ADPO•M(CO)$_5$**

M = Cr, W

Each of these metal pentacarbonyl adducts shows the characteristic upfield shift of the ring proton of the ADPO unit to δ 5.7-5.8 and an increase in $^3J_{PH}$ to ~25 Hz (Table I). These data strongly support the assignment of the expected folded geometry for the ADPO unit.[5] Although these types of metals have been employed in the synthesis of pnictinidene complexes,[13-26] this result underscores the importance of the P→M bond strength in preserving the planar ADPO geometry (*vide supra*).

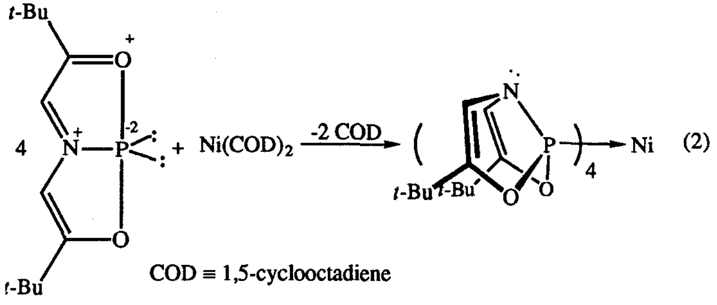
TABLE I

Selected NMR Chemical Shifts (ppm δ) in ADPO and its metal complexes.

Compound	^{1}H NMR $H_{4(6)}$ ($^3J_{PH}$)[a]	^{13}C NMR $C_{3(7)}$	^{13}C NMR $C_{4(6)}$	^{31}P NMR P_1	reference
ADPO	7.50 (9.6)	169.9	111.2	187.0	5
$(ADPO)_2$•PtI_2	5.95 (29.0)	156.0	113.9	126.5	9
ADPO•$Fe(CO)_4$	5.89 (26.4)	156.4	113.5	235	10
$\{ADPO\}_2$•$Fe(CO)_3$	5.58 (7.4)	143.8	111.6	172	10
	5.94 (7.0)	152.9	110.6		
ADPO•$Mn(CO)_2Cp$	5.74 (24.3)	155.2	113.3	256	4
ADPO•$RuCp^*(NCCH_3)_2^+$	5.79 (24.1)	155.6	125.3	198	3
$(ADPO)_2$•$RuCp^*(NCCH_3)^+$	5.82 (m)	155.9	125.5	201	3
$(ADPO)_4$•Ag^+	7.70 (14.4)	171.6	113.3	166	7
ADPO•$Cr(CO)_5$	5.81 (24.9)	155.4	113.1	231	this work
ADPO•$W(CO)_5$	5.76 (24.9)	154.8	112.7	180	this work
$Ni(ADPO)_4$	5.4 (m)	153.5	112.5	200	this work
$(\{ADPO\}_2)_2Pd^{++}$	6.15 (4.7)	144.3	111.1	90.3	this work
	6.31 (4.6)	153.6	113.0		
$\{ADPO\}_2$	5.60 (5.08)			133.9	this work
	5.71 (2.30)				

[a] Couplings in Hz.

With *bis*(cyclooctadiene)nickel as a source of nickel(0), a homoleptic complex can be obtained with 4 ADPO units (eq. 2)



(2)

COD ≡ 1,5-cyclooctadiene

ADPO **Ni(ADPO)$_4$**

The NMR chemical shift of the ring protons in Ni(ADPO)$_4$ of δ 5.4 again suggests a folded geometry for the ADPO units. The *t*-butyls appear as a singlet so that "dimerization" of the ADPO subunits (*vide infra*) as observed in Fe{ADPO}$_2$(CO)$_3$[27] can be ruled out.[10] The ADPO subunits occupy a tetrahedral geometry about nickel and are thus too far apart to dimerize. The average P-P distance in Ni(ADPO)$_4$ is 342 pm with a closest approach of 329 pm. These distances are longer that the 304 pm closest approach between phosphorus atoms of an idealized trigional bipyramidal (tbp) structure for {ADPO}$_2$Fe(CO)$_3$, in which dimerization of the ADPO subunits was observed (eq 3).[10] The monomeric ADPO subunits and tetrahedral geometry are evident in the KANVAS[28] drawing of the X-ray structure of Ni(ADPO)$_4$ (Figure 1). The average ring fold in Ni(ADPO)4 is 116.8° (Table II) and is representative of other 8-P-4 ADPO•metal complexes.

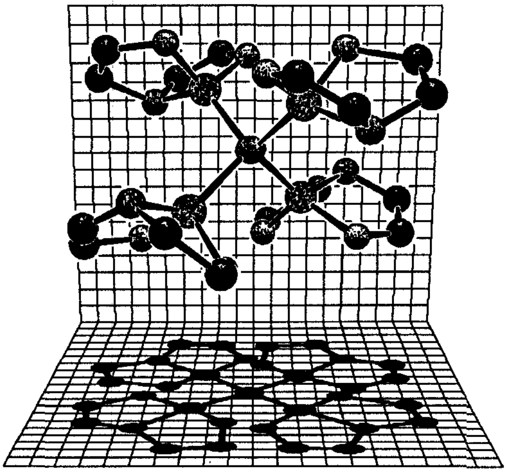
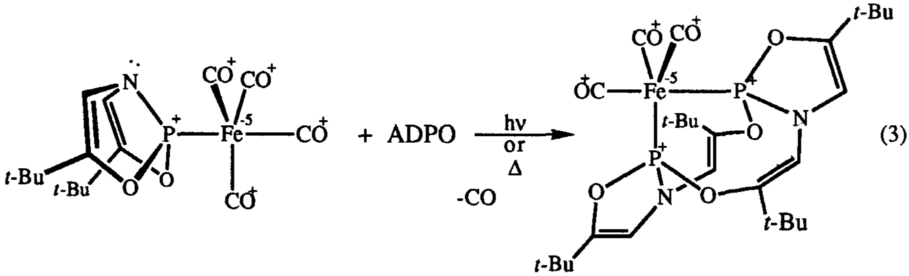


Figure 1. KANVAS[28] drawing of Ni(ADPO)$_4$. Hydrogens and *t*-butyls have been omitted for clarity



ADPO•Fe(CO)$_4$ {ADPO}$_2$Fe(CO)$_3$ (3)

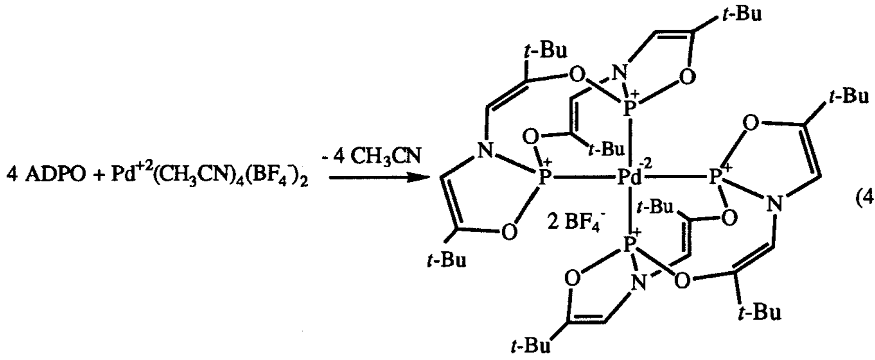
Table II

Average Bond Lengths (pm) and Angles (°) in selected ADPO•Metal Complexes.

	compound			
property	Ni(ADPO)$_4$	Pd^{+2}({ADPO}$_2$)$_2$	(ADPO)•Fe(CO)$_4$	{ADPO}$_2$•Fe(CO)$_3$
P→M	209.3	229.3	215.8	213.3 (ax), 212.0 (eq)
P-O	166.3	159.9^{a} 158.7^{b}	163.5	162.8^{a} 162.1^{b}
P-N	177.9	165.5	170.4	168.6
C-O	141.6	143.7^{a}, 142.0^{b}	142.9	140.8^{a}, 140.2^{b}
C-C$_{ring}$	132.7	131.1^{a}, 131.2^{b}	129.5	132.9^{a}, 132.3^{b}
C-N	146.4	142.4^{a}, 141.8^{b}	145.7	141.4^{a}, 141.8^{b}
P-M-P	109.5	90.7, 165.0	---	83.9
M-P-O	113.8	121.9^{a}, 115.2^{b}	114.6	120.5^{a}, 118.3^{b}
M-P-N	128.5	112.1	124.6	118.0 (ax), 121.0 (eq)
O-P-O	110.8	105.4	108.3	100.9
P-O-C	110.9	110.6^{a}, 128.8^{b}	108.7	111.1^{a}, 127.1^{b}
P-N-C	104.9	108.4^{a}, 130.4^{b}	106.3	108.7^{a}, 125.4^{b}
C-N-C	114.4	120.0	115.8	120.2
O-C-C$_{ring}$	113.8	111.3^{a}, 119.3^{b}	115.0	112.0^{a}, 120.7^{b}
C-C-N	114.6	113.1^{a}, 128.2^{b}	113.0	112.8^{a}, 126.7^{b}
O-P-N	93.4	94.6^{a}, 104.5^{b}	95.8	93.0^{a}, 99.8^{b}
N-P (fold)	116.8	---	116.5	---
reference	this work	this work	10	10

[a] Value for atom(s) in 5-membered ring.
[b] Value for atom(s) in 10-membered ring.

In contrast with the homoleptic Ni(ADPO)$_4$ complex, a homoleptic complex of Pd(II) and 4 ADPO units shows dimerization of the sets of ADPO subunits. The reaction of tetrakis(acetonitrile)palladium(II) tetrafluoroborate with four equivalents of ADPO gave Pd^{+2}[{ADPO}$_2$]$_2$(BF$_4^-$)$_2$ (eq. 4).



(4)

$Pd^{+2}[\{ADPO\}_2]_2(BF_4^-)_2$

The dimerization of the two sets of ADPO subunits in $Pd^{+2}[\{ADPO\}_2]_2(BF_4^-)_2$ is evident from the two sets of *t*-butyl and vinyl proton resonances for substituents on the 5 and 10-membered rings. The vinyl protons appear to be quintets with apparently identical couplings to all four phosphorus atoms, thus exhibiting the same type of virtual coupling that has been observed for $Fe\{ADPO\}_2(CO)_3$ (*vide supra*). The proton and carbon NMR chemical shifts are fairly similar to those observed for $Fe\{ADPO\}_2(CO)_3$. The dimerization of ADPO subunits around a square planar palladium center is possible because of the close approach of adjacent phosphorus atoms. In a square planar arrangement, assuming the average P-Pd distance in $Pd^{+2}[\{ADPO\}_2]_2(BF_4^-)_2$, adjacent phosphorus atoms approach within 324 pm. This distance is the largest P-P separation at which dimerization of ADPO subunits is observed. The geometry at palladium in $Pd^{+2}[\{ADPO\}_2]_2(BF_4^-)_2$ is square planar as indicated in Figure 2. The ring internal angles in the 10-membered rings are larger than their counterparts in the 5-membered rings (Table II) as would be expected.

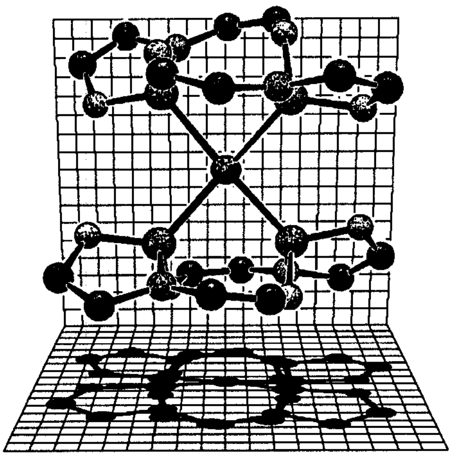
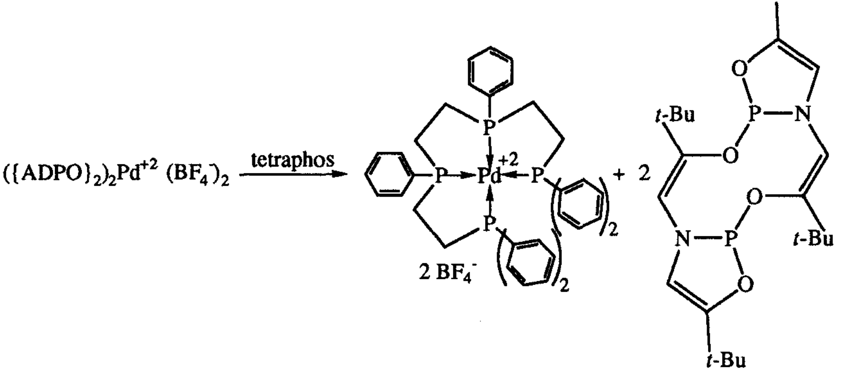


Figure 2. KANVAS[28] drawing of $Pd^{+2}[\{ADPO\}_2]_2$. Hydrogens and *t*-butyls have been omitted for clarity.

Contrary to the situation with {ADPO}$_2$•Fe(CO)$_3$, liberation of the intact dimer ADPO unit, {ADPO}$_2$, from Pd^{+2}({ADPO}$_2$)$_2$ was possible (eq 5). Reaction of [Pd({ADPO}$_2$)$_2$]$^{+2}$[BF_4^-] with tetraphos ([$(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2]_2$) afforded free {ADPO}$_2$ as evidenced by ^{31}P and ^{1}H NMR spectra. The liberated {ADPO}$_2$ exhibited a ^{31}P chemical shift of δ 133.9 and ^{1}H chemical shifts at δ 1.191 (s, t-Bu), 1.130 (s, t-Bu), 5.599 (pseudo t, 5.08 Hz), and 5.714 (pseudo t, 2.36 Hz). This ^{31}P resonance is similar to the dimers of saturated ADPO analogs studied by Wolf and co-workers.[29, 30] The isolation or further characterization of {ADPO}$_2$ was prevented by the rapid conversion to 10-P-3 ADPO at room temperature.



{ADPO}$_2$

(5)

The facile reversion of {ADPO}$_2$ to 10-P-3 ADPO contrasts the more vigorous conditions required to split the dimers of saturated ADPO analogs.[29, 30] The tendency of ADPO-like ring systems to dimerize appears only when an 8-P-3 folded geometry can be achieved and then only if the folded rings can approach sufficiently close to allow the formation of the necessary P-O bonds. For discrete ADPO units coordinated to a single metal center, the furtherest distance between adjacent phosphorus atoms which leads to dimerizartion is about 324 pm. The consideration of only the P-P distance in regard to ADPO dimerization is undoubtedly simplistic as other geometric orientation factors are also likely to be important in some cases. None-the-less this simple criterion distinguishes all 8-P-4 ADPO metal complexes in which dimerization occurs from those where the ADPO units remain discrete.

EXPERIMENTAL PROCEDURES

General Methods. All solvents were freshly distilled and dried before use according to established procedures.[31] Melting points were measured on a Thomas Hoover capillary apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a General Electric QE-300 spectrometer. ^{13}C and ^{31}P NMR spectra were recorded on a Nicolet NT-300WB spectrometer. All NMR spectra are reported in ppm δ (positive shifts downfield of the reference). NMR references are: ^{1}H: TMS, ^{13}C: TMS, ^{31}P: 85% H_3PO_4.

Mass spectra were obtained on a VGMM 7070 double focusing high resolution mass spectrometer. UV spectra were recorded on a Varian Cary 2300. Infrared spectra were obtained on a Perkin-Elmer 983G spectraphotometer.

Manipulations of air sensitive samples were performed in a Vacuum Atmospheres drybox under nitrogen. Ultraviolet photolyses were carried out in quartz vessels using a Sylvania 275 Watt mercury-arc sunlamp and cooled by a fan.

Elemental analyses were performed by Galbraith Laboratories, Inc. Knoxville, TN, and Oneida Research Services, Whitesboro, NY, and are within 0.4% of theoretical values unless otherwise indicated.

$ADPO{\bullet}Cr(CO)_5$. ADPO (0.050 g, 0.207 mmol) and $Cr(CO)_6$ (0.091 g, 0.413 mmol) were mixed in thf (20 mL) and photolyzed for 6 h at room temperature. The volatiles were removed from the resulting yellow solution under vacuum. The NMR indicates the quantitative formation of $ADPO{\bullet}Cr(CO)_5$. The same product resulted under identical conditions with 1:1 ADPO and $Cr(CO)_6$. NMR (CD_2Cl_2), ^1H: δ 1.14(s, $(CH_3)_3C$, 18 H), 5.81 (d, $^3J_{PH}$ = 24.9 Hz, 2 H). $^{13}C\{^1H\}$: δ 27.4 (s, CH_3), 32.6 (d, J_{PC} = 5.4 Hz, CC_4), 113.1 (d, J_{PC} = 2.0 Hz, NC), 155.4 (d, J_{PC} = 5.6 Hz, COP), 214.3 (d, J_{PC} = 21.4 Hz, *cis*-C≡O), 220.1 (d, J_{PC} = 2.8 Hz, *trans*-C≡O). $^{31}P\{^1H\}$: δ 231.

$ADPO{\bullet}W(CO)_5$. Tungsten hexacarbonyl (0.292 g, 0.830 mmol) was dissolved in thf (30 mL) and photolyzed for 4 h to obtain a yellow solution. ADPO (0.100 g, 0.415 mmol) in thf (10 mL) was added to this mixture at room temperature and stirred for a further 2 h. The color became lighter. The volatiles were removed under vacuum and the residue was extracted into diethylether, and filtered through celite. The NMR spectra indicated the formation of $ADPO{\bullet}W(CO)_5$ in quantitative yield. NMR (CD_2Cl_2), ^1H: δ 1.15 (s, $(CH_3)_3C$, 18 H), 5.76 (d, $^3J_{PH}$ = 24.9 Hz, 2H). $^{13}C\{^1H\}$: δ 27.4 (d, J_{PC} = 0.6 Hz, CH_3), 32.5 (d, J_{PC} = 4.6 Hz, CC_4), 112.7 (d, J_{PC} = 1.5 Hz, NC), 154.8 (d, J_{PC} = 5.7 Hz, COP), 194.4 (d, J_{PC} = 10.6Hz, J_{CW} = 125.5 Hz, *cis*-C≡O), 199.3 (d, J_{PC} = 43.1 Hz, *trans*-C≡O). $^{31}P\{^1H\}$: δ 180 ($^1J_{PW}$ = 398 Hz)

$Ni(ADPO)_4$. ADPO (0.400 g, 1.66 mmol) and *bis*(cyclooctadiene)nickel (0.114 g, 0.415 mmol) were mixed in diethylether and stirred for 6h at room temperature. The volatiles were pumped off and the residue was redissolved in minimum amount of diethylether, hexane was added and cooled to -25 °C to obtain colorless crystals, 0.268 g, 63% yield. m.p. > 270 °C. NMR (CD_2Cl_2), ^1H: δ 1.09 (s, $(CH_3)_3C$, 18 H), 5.4 (m, 2 H). ^{13}C: δ 27.8 (s, CH_3), 32.1 (s, Me_3C), 112.5 (s, CN), 153.5 (s, CO). $^{31}P\{^1H\}$: δ 200. Anal. Calc'd for $C_{48}H_{80}N_4O_8P_4Ni{\bullet}{}^1/_2((C_2H_5)_2O)$; C 56.68, H 8.01, N 5.4, O 12.33, P 11.93, Ni 5.65. Found C, 56.53; H, 8.57, N, 5.42.

$Pd^{+2}[\{ADPO\}_2]_2(BF_4^-)_2$. $Pd^{+2}(CH_3CN)_4(BF_4^-)_2$ (0.200 g, 0.450 mmol) and ADPO (0.435 g, 1.80 mmol) were mixed in CH_2Cl_2 and stirred for 6 h at room temperature. Red-brown colored solution was obtained. The volatiles were removed and the residue was dissolved in CH_3CN, concentrated and cooled at -25 °C. Dark red crystals were obtained, 0.319 g, 57% yield. m.p. 187-189 °C. NMR (CD_2Cl_2), ^1H: δ 1.12 (s, 9 H), 1.26 (s, 9 H), 6.15 (*pseudo*-quintet, J_{PH} = 4.7 Hz), 6.31 (*pseudo*-quintet, J_{PH} = 4.6 Hz). $^{13}C\{^1H\}$: δ 27.5 (s, CH_3), 27.9 (s, CH_3), 33.1 (s, CC_4), 35.6 (s, CC_4), 111.6 (*pseudo*-quintet, J_{PC} = 2.4 Hz, NC), 113.0 (*pseudo*-quintet, J_{PC} = 1.8 Hz, NC), 144.3 (*pseudo*-quintet, J_{PC} = 2 Hz, CO), 153.6 (*pseudo*-quintet, J_{PC} = 2.4 Hz, CO). $^{31}P\{^1H\}$ δ 90.3. Anal. Calc'd for $C_{48}H_{80}N_4O_8B_2F_8P_4Pd$; C, 46.30; H, 6.48; N, 4.50; Found; C, 46.10; H, 6.54; N, 4.55.

Diplacement Reactions of $Pd^{+2}[(ADPO)_2]_2(BF_4^-)_2$ with $[Ph_2PCH_2CH_2P(Ph)CH_2]_2$ (tetraphos), $[Ph_2PCH_2]_2$ (diphos) and PPh_3. A sample of $Pd^{+2}[(ADPO)_2]_2(BF_4^-)_2$ (0.124 g, 0.10 mmol) was mixed with tetraphos

(0.067 g, 0.10 mmol), diphos (0.079 g, 0.20 mmol) and PPh_3 (0.104 g, 0.40 mmol) respectively in three separate glass vials and CD_2Cl_2 was added at room temperature. These reactions were followed by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy.

$Pd^{+2}[(ADPO)_2]_2(BF_4^-)_2$ with tetraphos: The reaction was immediate and after 1 hour almost quantitative yield of $Pd^{+2}(tetraphos)(BF_4^-)_2$ [^{31}P NMR: 103.2 (pseudo dd, 312.5 Hz, 26.3 Hz), 52.7 (pseudo dd, 312.5 Hz, 26.3 Hz)], the free $(ADPO)_2$ [^{31}P NMR: 133.9, ^{1}H NMR: 1.191 (s, t-Bu), 1.130 (s, t-Bu), 5.599 (pseudo t, 5.08 Hz), 5.714 (pseudo t, 2.36 Hz) and a minor amount of ADPO [^{31}P NMR: 187 (br s)] was obtained. Over a period of several days the amount of $(ADPO)_2$ slowly decreased with the formation of ADPO and a small amount of a new compound [^{31}P NMR: 143.6 (s)]. The identity of $Pd^{+2}(tetraphos)(BF_4^-)_2$ was confirmed by reacting $Pd^{+2}(CH_3CN)_4(BF_4^-)_2$ with tetraphos in CD_2Cl_2.

$Pd^{+2}[\{ADPO\}_2]_2(BF_4^-)_2$ with diphos: The diphos begins to react with $Pd^{+2}[(ADPO)_2]_2(BF_4^-)_2$ immediately and after 1 hour, $Pd^{+2}(diphos)_2\,(BF_4^-)_2$ [^{31}P NMR: 57.8 (s)] begins to precipitate. No significant amount of $Pd^{+2}[\{ADPO\}_2]_2(BF_4^-)_2$ was observed in the reaction mixture. Three new sets of signals due to ADPO, $\{ADPO\}_2$ and $Pd^{+2}[\{ADPO\}_2](diphos)(BF_4^-)_2$ [^{31}P NMR: δ 98.8 (d, 483 Hz), 67.3 (d, 483 Hz), ^{1}H NMR of coordinated $\{ADPO\}_2$; 0.759 (s, t-Bu), 0.841 (s, t-Bu), 6.375 (pseudo t, 9.9 Hz), 6.558 (pseudo t, 8.4 Hz) were observed in the NMR. Over a period of days the $Pd^{+2}[\{ADPO\}_2](diphos)(BF_4^-)_2$ gets completely converted to $Pd^{+2}(diphos)_2(BF_4^-)_2$, $\{ADPO\}_2$ and ADPO. A minor amount of a new compound was also detected [^{31}P NMR: δ 143.6(s)]. The formation of $Pd^{+2}(diphos)_2(BF_4^-)_2$ was confirmed by an independent reaction.

$Pd^{+2}[\{ADPO\}_2]_2(BF_4^-)_2$ with PPh_3: The reaction was slow and significant amounts of starting material was observed after 1 hour. In addition, ADPO [^{31}P NMR: 187 (br S)] and a major new compound possibly $Pd^{+2}[\{ADPO\}_2](PPh_3)_2(BF_4^-)_2$ [^{31}P NMR: δ 91.6 (d, 535 Hz), 26.3 (d, 26.3)] could be observed in the NMR. It is possible to identify several new minor products from the t-Butyl region of the ^{1}H NMR. These most likely represent the various combinations of ADPO, $\{ADPO\}_2$ and PPh_3 coordinated to Pd^{+2}. After several hours the signals due to $Pd^{+2}[\{ADPO\}_2]_2(BF_4^-)_2$ completely dissapears with the formation of free ADPO. Unlike in the tetraphos or diphos reactions, no free $\{ADPO\}_2$ was observed in the reaction mixture. Also, significant amounts of coordinated $\{ADPO\}_2$ and PPh_3 were observed even after several days.

X-ray Crystal Structure of Ni(ADPO)$_4$. Formula: $C_{48}H_{80}N_4O_8P_4Ni\bullet(C_2H_5)_2O$, monoclinic, space group $P2_1/n$ (No. 14), a = 1445.2(8), b = 2484.3(2), c = 1615.9(8) pm, β = 98.26(2)°; T = -70 °C, Z = 4, FW = 1097.92, D_c =1.270 g/cm^3, μ (Mo) = 5.00 cm^{-1}; Crystal Description: colorless, thin parallelopiped, (0.25 x 0.10 x 0.51 mm) grown from hexane/ether solution of Ni(ADPO)$_4$. A total of 5784 reflections were collected, 1.6° ≤ 2θ ≤ 40.0°, on an Enraf-Nonius CAD4 diffractometer with graphite monochromator using Mo-Kα radiation (λ = 71.073 pm). With 1164 unique reflections of intensity greater than 3.0σ, the structure was solved by direct methods (MULTAN) and standard difference Fourier techniques. The final R factors were R = 0.089, R_w = 0.075. The final difference Fourier showed the largest residual density to be 0.64 e/Å^3. Further details of the crystal structure are available in the supplementary material deposited with the Cambridge Crystallographic Data Centre.

X-ray Crystal Structure of $Pd^{+2}[\{ADPO\}_2]_2(BF_4^-)_2$. Formula: $C_{48}H_{80}N_4O_8P_4PdB_2F_8 \cdot {}^1/_2(C_6H_{14}) \cdot CH_2Cl_2$,monoclinic, space group $P2_1/n$ (No. 14), a = 1433.0(3), b = 3139.3(4), c = 1546.7(3) pm, β = 97.71(1)°; T = -70 °C, Z = 4, FW = 1382.11, D_c =1.331 g/cm³, μ (Mo) = 5.02 cm⁻¹; Crystal Description: deep red, irregular cube (0.40 x 0.35 x 0.36 mm) grown from hexane diffusion into a CH_2Cl_2 solution of $Pd^{+2}[\{ADPO\}_2]_2(BF_4^-)_2$. A total of 11591 reflections were collected, 1.3° ≤ 2θ ≤ 48.0°, on an Enraf-Nonius CAD4 diffractometer with graphite monochromator using Mo-Kα radiation (λ = 71.073 pm). With 6604 unique reflections of intensity greater than 3.0σ, the structure was solved by automated Patterson analysis (PHASE) and standard difference Fourier techniques. The final R factors were R = 0.051, R_w = 0.047. The final difference Fourier showed the largest residual density to be 0.76 e/Å³, near one of the fluorines. Further details of the crystal structure are available in the supplementary material deposited with the Cambridge Crystallographic Data Centre.

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28. This drawing was made with the *KANVAS* computer graphics program. This program is based on the program *SCHAKAL* of E. Keller (Kristallographisches Institute der Universitat Freiburg, Germany), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes. The planes bear a 50-pm grid and the lighting source is at infinity so that shadow size is meaningful.
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