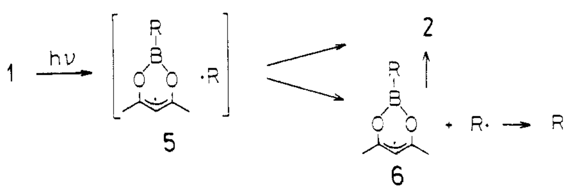
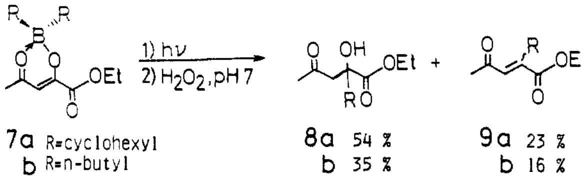


(3)

The singlet excited state of **1** gives the radical pair **5** in the solvent cage, which mainly rearranges intramolecularly to the noncrossed borane complex **2** and partly dissociates into free radicals. The free radicals, **6** and cyclohexyl, may recombine to yield crossed **2** or give typical free radical products, such as cyclohexane and cyclohexene.[11]

The reaction was successfully extended to ethyl acetopyruvate borane complexes **7a,b**. The alkyl group migrates regiospecifically on the α-carbon to the ester yielding **8** and **9** (eq 4). This result



(4)

may reflect a larger spin density on the α-carbon of the ester group in the radical pair **5**. The hypothesis is supported by an analogy with allyl radicals, which have a larger ESR coupling constant to the proton α to electron-withdrawing groups (carbomethoxy and cyano).[12]

Application of this reaction to the borane complex **1c** which has optically active isopinocampheyl as the migrating alkyl group is interesting. Photolysis and successive neutral hydrolysis of **1c**, however, resulted in an equimolar diastereomeric mixture of the aldols and no diastereoselectivity was observed.

Further study is currently in progress in our laboratory.

Acknowledgment. We thank Prof. P. de Mayo (University of Western Ontario, Canada) for useful discussions.

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[11] The CIDNP experiment is interesting in this context, though we have not yet succeeded in it. We thank Dr. S. K. Wong (the University of Western Ontario, Canada) for the CIDNP experiment.

[12] (a) Sustmann, R.; Trill, H.; Brandes, D. *Chem. Ber.* **1977**, *110*, 245. (b) Sustmann, R.; Trill, H.; Vahrenholt, F.; Brandes, D. *Ibid.* **1977**, *110*, 255.

Reversible Transformation of 10-P-3 ADPO[1] to an 8-P-3 ADPO·PtI$_2$ Adduct

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We have synthesized a phosphorus–platinum complex containing an 8-P-4 center which is formally derived from the 8-P-3 ADPO electromorph.[2] This provides the first evidence that the ADPnO (Pn = pnictogen: P, As, Sb) systems may exhibit electromorphism between 8-Pn-3 and 10-Pn-3[2-4] structures. Multinuclear NMR spectra (^1H, ^{13}C, and ^{15}N) indicate a dramatic electronic and geometric reorganization of the ring system between free and complexed ADPO. Ligand substitution affords the first reversible reorganization between normal and hypervalent bonding arrangements (vide infra).[5]

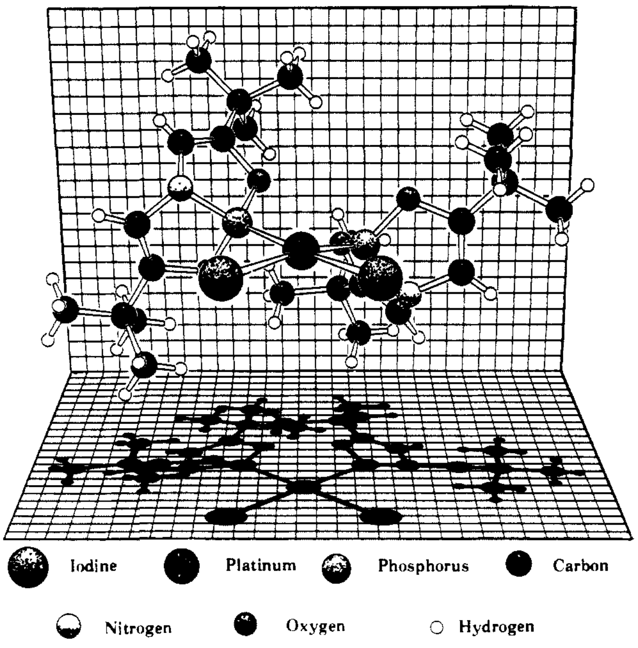
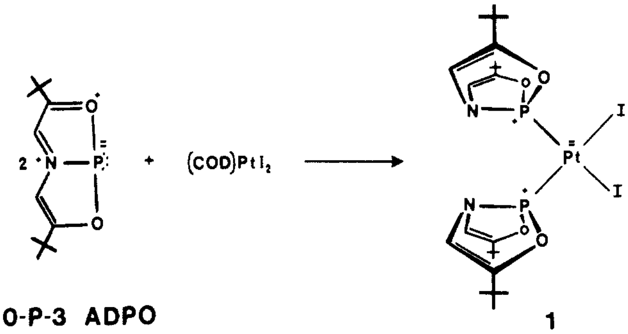


Figure 1. KANVAS[9] drawing of **1**.

The reaction of 2 equiv of ADPO with (1,5-cyclooctadiene)platinum(II) diiodide in toluene provides **1** in good yield (>85%).



10-P-3 ADPO **1**

Complex **1** is a yellow crystalline solid melting at 245 °C with decomposition. The 2:1 nature of the complex is consistent with elemental analysis (CHN) and NMR spectra.[6]

The ^{195}Pt NMR (CD_2Cl_2) exhibits a triplet at -3487 ppm (J_{PtP} = 5622 Hz) upfield from K_2PtCl_4 (D_2O). The ^{31}P NMR of **1** shows a single resonance at 126.5 ppm with ^{195}Pt satellites. This ^{31}P resonances is upfield of the 10-P-3 ADPO resonance (189 ppm) and is suggestive of the 8-P-4 nature of the phosphorus environment. In addition the ^{13}C resonance for the carbons attached to oxygen are substantially upfield relative to 10-P-3 ADPO ($\Delta\delta$ = 13.9). The ring proton on the ADPO moiety also shows a significant upfield shift ($\Delta\delta$ = 1.5) relative to the free ligand. Finally the ^{15}N NMR shows a doublet at -276 ppm with platinum satellites ($^1J_{PN}$ = 44.8, $^2J_{PtN}$ = 108 Hz) clearly indicative of the pyramidal (8-N-3) nature of the nitrogen environment.[7] These NMR data indicate the ADPO ring system has a bent structure

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[1] The *N*-X-*L* system has previously been described (Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753). *N* valence electrons about a central atom X, with *L* ligands.

[2] Culley, S. A.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1984**, *106*, 1164.

[3] Culley, S. A.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1985**, *107*, 1089.

[4] Stewart, C. A.; Harlow, R. L.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1985**, *107*, 5543.

[5] A referee indicated another type of ligand reorganization process different from that reported here; see: Vierling, P.; Riess, J. G. *J. Am. Chem. Soc.* **1981**, *103*, 2466.

[6] We have obtained the following NMR data on **1** in CD_2Cl_2. ^1H NMR δ 1.20 (s, 18 H), 5.95 (d and dd, J_{PH} = 29.0, J_{PtH} = 16.7 Hz, 2 H); $^{13}C\{^1H\}$ NMR δ 26.7 (CH_3), 32.1 ($C(CH_3)$), 113.9 (CH), 156.0 (CO); $^{31}P\{^1H\}$ NMR δ 126.5 (d and dd, J_{PtP} = 5622 Hz); ^{15}N NMR δ -276 (d and dd, $J_{P^{15}N}$ = 44.8, $J_{Pt^{15}N}$ = 108 Hz); $^{195}Pt\{^1H\}$ NMR δ -3487 (t, J_{PPt} = 5622 Hz). ^{15}N resonance relative to $NH_4{}^{15}NO_3$ in D_2O and ^{195}Pt resonance relative to K_2PtCl_4 in D_2O. Satisfactory elemental analysis were obtained (CHN).

[7] "Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy", Levy, G. C.; Lichter, R. L., Eds.; Wiley: New York, 1979; pp 84, 100.

0002-7863/86/1508-0322$01.50/0

Table I. Bond Lengths and Angles in **1**[a]

bond lengths, pm		bond angles,[b] deg	
P–O	161.1 (3)	O–P–O	113.0 (3)
		N–P–O	96.0 (2)
P–N	170.0 (7)	C–O–P	110.3 (7)
		C–N–P	106.2 (9)
		C–N–C	115.5 (7)
C–O	143.3 (6)	C–C–N	114.3 (14)
		C–C–O	112.7 (9)
$C–C_{ring}$	131.5 (11)	N–P–Pt	124.4 (24)
		O–P–Pt	112.8 (17)
C–N	144.5 (9)	P–Pt–I	86.8 (3)
		P–Pt–P	95.76 (8)
P–Pt	220.3 (2)	I–Pt–I	91.58 (2)
Pt–I	264.5 (3)		

[a] These numbers are averages from the two ADPO ligands. [b] The fold angle about the P–N bonds is 119°.

as a result of coordination to the platinum center to provide an 8-P-4 bonding scheme.

The structure of complex **1** has been verified by single-crystal X-ray structure determination.[8] The solid-state structure of the complex is illustrated in Figure 1.

The ADPO ring system has folded such that the angle between the two five-membered rings is 119°. The two ADPO ligands are essentially identical and representative bond lengths and angles are given in Table I.

It is interesting to note that the N–P bond in the complexed ligand is only 2-pm longer than in 10-P-3 ADPO (168 pm). Fixation of the π-bonds in the ligand rings is also evident from the lengthened C–O and C–N bonds and shortened C–C bonds.

The 10-P-3 ADPO could have provided a phosphorus lone pair to the platinum center without bending;[10] however, this would have two unfavorable consequences. First the planar 10-P-3 ADPO could only provide rather diffuse (low p-orbital character) lone pairs from the phosphorus center while the bent 8-P-3 ADPO provides a single fairly directional phosphorus lone pair (higher p-orbital character).[11] Second the planar 10-P-3 ADPO would yield a sterically congested 10-P-4 complex, whereas the bent 8-P-3 ADPO gives a less hindered 8-P-4 complex.

It should be noted that the existence of the platinum complex **1** shows that there is not inordinate ring strain associated with the bent structure in the ADPO system and that the preference for the planar 10-P-3 structure of the free ligand is largely based on electronic factors. The small energy difference between 8-P-3 and 10-P-3 ADPO is thus overcome by coordination of phosphorus to platinum. The ADPO group can be displaced from the platinum center with triethyl phosphite at −50 °C. However, we saw no evidence of free 8-P-3 ADPO in solution at this temperature. Apparently the geometrical reorganization of 8-P-3 ADPO to 10-P-3 ADPO is fast on the NMR time scale on concomitant reorganization to 10-P-3 ADPO occurs with displacement from the platinum center.

Work is continuing in this area to address the various factors which control the geometry of the ADPnO ligand in metal complexes.

Acknowledgment. The X-ray crystal structure analysis was performed by the Molecular Structures Corporation, College Station, TX.

Supplementary Material Available: A complete description of the X-ray crystallographic structure determination of **1** and tables of positional and thermal parameters (20 pages). Ordering information is given on any current masthead page.

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(8) Two equivalents of 10-P-3 ADPO in toluene were added to a suspension of $(COD)PtI_2$ (1 equiv) in toluene. The reaction was allowed to stir for 4 h. The toluene was removed in vacuo and the residue recrystallized from benzene. The crystal data (−108 °C) were as follows: $C_{24}H_{40}PtI_2N_2O_4P_2\cdot{}^1/_2C_6H_6$, monoclinic, space group $P2_1/n$, $a = 1955.6$ (4) pm, $b = 1137.0$ (6) pm, $c = 1668.2$ (6) pm, $\beta = 107.27$ (2)°, $Z = 4$, $D_c = 1.82$ g/cm^3, crystal size 0.15 × 0.15 × 0.25 mm. Only the 3745 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The structure was solved by direct methods. The final R factors were $R = 0.030$ and $R_w = 0.037$.

(9) This perspective drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institut der Universitat Freiburg, FRG), 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 with the lighting source at infinity so the shadow sizes are meaningful.

(10) Bicyclic 10-P-4 phosphoranides have been shown to coordinate to metal centers with minimal distortion of the idealized phosphoranide geometry; see: Wachter, J.; Mentzen, B. F.; Reiss, J. G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 284. We have recently synthesized a complex between 10-Sb-3 ADSbO and platinum in which the planar geometry of the ADSbO group is maintained. Details will be disclosed in subsequent publications.

(11) The two lone pairs in 10-P-3 ADPO can be thought of as essentially sp^2 orbital lone pairs whereas 8-P-3 ADPO has one phosphorus lone pair in an sp^3 orbital.

ESR and ENDOR of Bacteriopheophytin a Radicals. Implications for Bacteriochlorophylls in Vivo

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The model studies presented here seek to probe effects that the protein environment may induce or impose on the conformation and electronic configuration of photosynthetic chromophores. The cation radicals observed on photooxidation of bacterial reaction centers have been assigned previously to dimeric bacteriochlorophylls (BChl) a or b on the basis of comparisons of ESR and ENDOR characteristics in vivo with those observed for BChl$^+$ a and b in vitro.[1-5] Recent X-ray results of the *Rhodopseudomonas viridis* reaction center (BChl b) support the dimer formulation for its unoxidized primary donor, P960, and provide evidence of possible interactions between the magnesium and the oxygen of a nearby 2-acetyl group, as well as of ligation by neighboring protein residues.[6] Chlorophylls further interact with their environment by hydrogen bonding of their peripheral carbonyl groups, as evidenced by resonance Raman data.[7] To separate ligation and/or hydrogen bonding effects from the "intrinsic" unpaired spin distributions of BChl radicals, the ENDOR parameters of the cation radical of bacteriopheophytin a (BPheo, a demetalated BChl) have been measured as a function of solvent and temperature.

Comparisons of the BPheo a$^+$ results with BChl a$^+$ data suggest that ligation and hydrogen bonding do not significantly alter the unpaired spin distribution of BChl radicals and thus lend validity to the common use of coordinating solvents such as methanol in ENDOR spectroscopy to prevent aggregation and enhance resolution.[8] This insensitivity to ligation also supports theoretical predictions[4,9,10] that the two highest occupied orbitals in BChls

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(6) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385–398; private communication.

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(8) To our knowledge, all reported ENDOR investigations of BChl cations were carried out in the presence of methanol.

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