

the ground-state configuration. On the other hand, some molecular orbitals display drastic alterations in their spacial charge distribution on passing from a ground to an excited electronic state configuration. For the  $\text{Ag}_5^{2+}$  and  $\text{Ag}_5^{4+}$  clusters, these molecular orbitals are the filled  $e'$  and  $e''$  states. Their charge distribution changes significantly when an electron is excited from these orbitals to a HOMO as illustrated in Table VI. Consequently, the use of charge distributions for the  $e''$  and  $e'$  in the ground and excited states yields different values for the  $g_{xx}$  and  $g_{yy}$  components in the  $\text{Ag}_5^{q+}$  clusters. Thus extreme caution must be exercised in cases similar to those described above, when utilizing charge distributions of molecular orbitals obtained from ground-state calculations. The appropriate excited states should be computed and their resulting charge distributions used in numerical estimations of the spin Hamiltonian  $g$  tensor components. Finally, one should note that, in all of our calculations of EPR parameters, the energy differences occurring in the denominator of eq 6 were estimated by the Slater transition-state procedure.<sup>3,12</sup>

### Conclusion

The SCF- $X\alpha$ -SW-MO method has been used to calculate the ground- and excited-state wave functions, charge distributions, and molecular orbital energies of trigonal-bipyramidal isotopically pure  $^{109}\text{Ag}_5^{q+}$  clusters ( $q = 0-4$ ). One goal of this study was to gain an insight into the effect of gradually depleting valence electronic charge from the neutral parent cluster  $\text{Ag}_5^0$  on the electronic and magnetic properties of the resulting cationic  $\text{Ag}_5^{q+}$  clusters. The problem was approached by calculating the optical transition energies and EPR spin Hamiltonian tensor components for selected  $\text{Ag}_5^{q+}$  clusters. In the case of their optical spectra, significant changes were predicted on passing from  $\text{Ag}_5^0$  to  $\text{Ag}_5^{2+}$  to  $\text{Ag}_5^{4+}$ . Specifically, certain dipole-allowed transitions found for one cluster were not allowed for another. Also, transitions that were common to two, or all three clusters, were predicted to blue shift with increasing positive charge on the cluster. This behavior paralleled the monotonic relaxation of all molecular orbital levels with increasing positive charge on the cluster. Trends

of this type are expected to be important when attempting to analyze optical absorption, reflectance, or fluorescence spectra of neutral and/or cationic silver clusters entrapped in, for example, rare gas solid, zeolite, or aqueous glassy matrices.

The electronic ground states of these pentaatomic silver clusters are also found to change on passing from  $\text{Ag}_5^0$  ( $^2E$ ) to  $\text{Ag}_5^{2+}$  ( $^2A_1'$ ) to  $\text{Ag}_5^{4+}$  ( $^2A_2''$ ). This is found to have a dramatic effect on their predicted magnetogyric  $g$  tensor components and hyperfine-splitting patterns. In the case of  $\text{Ag}_5^{4+}$ , the calculated EPR spectrum comprises essentially an isotropic set of quartets whose lines are separated by 121.287 G and are centered around  $g_{zz} = 2.01497$  and  $g_{xx} = g_{yy} = 2.04670$ , arising from coupling of the unpaired electron with three magnetically equivalent equatorial silver centers. Each line is further split into a triplet by coupling to two similarly equivalent axial silver centers whose lines are separated by 70.73 G, thereby yielding a 24-line hyperfine pattern (Figure 9). This spectrum is quite distinct from the EPR spectrum predicted for  $\text{Ag}_5^{2+}$ . The latter is best described as a set of two triplets centered around  $g_{xx} = g_{yy} = 1.9713$  and split by 228.08 and 227.48. The two center lines of these triplets coincide with one another, thus leading to apparently five resonances (Figure 10). A similar splitting pattern exists for the  $g_{zz} = 2.0023$ . Thus the superhyperfine splitting from the axial silver centers is predicted to yield 10 resonance lines. When the parallel and perpendicular components of the equatorial silver superhyperfine tensors are taken into account, every one of the 10 resonances is further split into two quartets with 0.7248 and 3.7 G splittings. Consequently one predicts an 80-line powder stick spectrum as shown in Figure 10.

**Acknowledgment.** The generous financial assistance of the Natural Sciences and Engineering Research Council of Canada's Operating and Strategic Grants Programmes and the Connaught Foundation of the University of Toronto are both gratefully acknowledged.

Registry No.  $\text{Ag}_5$ , 64475-46-3.

## Unusual Macrocyclic Biphenyls Containing the Dihydropyrene Nucleus. An Observation of Aryl Group Transfer from Phosphine to Aryl Halide Using Nickel Complexes<sup>1</sup>

Reginald H. Mitchell,\* Mahima Chaudhary, Thomas W. Dingle, and Richard Vaughan Williams

Contribution from the Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada V8W 2Y2. Received May 14, 1984

**Abstract:** Coupling of 2-bromo-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**5**) by using bis(triphenylphosphino)nickel(II) chloride yielded not only the expected biaryl **2** but also the phenyldihydropyrene **3**. The latter must have arisen through an aryl transfer from the phosphine ligand. The UV and <sup>1</sup>H NMR spectra of **2** and **3** are discussed relative to those of **4** and biphenyl and analyzed with respect to calculated  $\pi$ -SCF bond orders of these molecules. Reduction in ring current of **2** and **3** relative to **4** is minimal, whereas substantial inter-ring interaction is indicated by UV spectroscopy.

Biphenyls have been of interest to organic chemists for more than half a century because of their interesting stereochemistry.<sup>2</sup>

More recently a huge amount of synthetic effort appears to have been made to develop efficient aryl coupling methods,<sup>3</sup> which in

(1) Benzannulated Annulenes. 10. For part 9 see: Mitchell, R. H.; Williams, R. V.; Mahadevan, R.; Lai, Y. H.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2571-2578.

(2) For reviews see: (a) Adams, R.; Yuan, H. C. *Chem. Rev.* **1933**, *12*, 261-338. (b) Hall, D. M. "Progress in Stereochemistry"; Aylett, B. J., Harris, M. W., Eds.; Butterworths: London, 1969; Vol. 4, p 1.

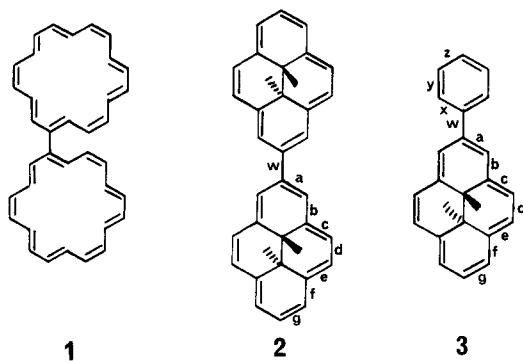
Table I. Principal Absorption Spectra Bands<sup>a</sup> [ $\lambda_{\max}$  (log  $\epsilon_{\max}$ )] for Dihydropyrenes 2-4 and Pyrenes 7-9

compd	ref	$\alpha$	$p$	$\beta$	$\beta'$
pyrene 7	13	356 (2.71)	333.5 (4.71)	272 (4.67)	241 (4.90)
1-phenylpyrene 8	14	375 (2.53)	337.5 (4.50)	276 (4.64)	242 (4.81)
1-(1'-pyrenyl)pyrene 9	15	ca. 410	350 (4.67)	280 (4.85)	244 (5.09)
dihydropyrene 4		641 (2.52)	463 (3.78)	377 (4.57)	337.5 (4.94)
phenyldihydropyrene 3		648 (2.51)	493 (4.18)	390 (4.52)	348 (5.15)
dihydropyrenyldihydropyrene 2		(in tail to 700)	577 (4.20)	400 (4.12)	368 (4.72)

<sup>a</sup> Clar band nomenclature.<sup>16</sup>Table II. Bond Orders ( $\pi$ -SCF) and Calculated<sup>1</sup> Ring Current Shieldings for Compounds 2-4

bond	bond orders ( $\times 10^3$ )			biphenyl
	4	3	2	
a	647	605	598	
b	639	654	658	
c	636	628	625	
d	650	654	655	
e		633	632	
f		640	641	
g		646	646	
w		344	367	326
x		624		629
y		675		674
z		661		662
$\delta_{\text{CH}_3}$ (calcd) <sup>1</sup>	-4.42	-4.21	-4.15	
$\delta_{\text{CH}_3}$ (found)	-4.25	-4.00	-3.68	
		-4.03	-3.77	
$\Delta\delta$ (compd,4) calcd	0.21	0.27		
$\Delta\delta$ (compd,4) found	0.25, 0.22	0.57, 0.52		

turn has led to a number of papers concerned with the mechanism of aryl couplings.<sup>4</sup> Most of this work has been restricted to benzenoid compounds; however, Sondheimer and Storie recently reported<sup>5</sup> the novel bi[18]annulenyl 1, the first example of a



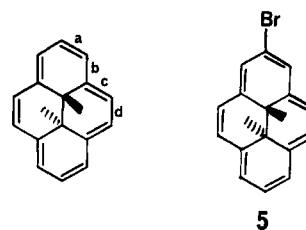
(3) For example see: (a) Whitesides, G. M.; San Filippo, J.; Casey, C. P.; Panek, E. J. *J. Am. Chem. Soc.* **1967**, *89*, 5302-5303. (b) Wittig, G.; Klar, G. *Annalen* **1967**, *704*, 91-108. (c) Whitesides, G. M.; Fischer, W. F.; San Filippo, J.; Basche, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871-4882. (d) Semmelhack, M. F.; Helquist, P. M.; Jones, L. D. *J. Am. Chem. Soc.* **1971**, *93*, 5908-5910. (e) Nakaya, T.; Arabori, H.; Imoto, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1422-1423. (f) Kende, A. S.; Liebeskind, L. S.; Braitsch, D. *Tetrahedron Lett.* **1975**, 3375-3378. (g) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G. *J. Chem. Soc., Chem. Commun.* **1977**, 203-204. (h) Zembayashi, M.; Tameo, K.; Yoshida, J.; Kumada, M. *Tetrahedron Lett.* **1977**, 4089-4092. (i) Negishi, E.; King, A. O.; Okukado, N. *J. Org. Chem.* **1977**, *42*, 1821-1823. (k) Tamura, Y.; Chun, M. W.; Inque, K.; Minamikawa, J. *Synthesis* **1978**, 822. (l) Schwartz, R. H.; San Filippo, J. *J. Org. Chem.* **1979**, *44*, 2705-2712. (m) Cornforth, J.; Sierakowski, A.; Wallace T. W. *J. Chem. Chem. Soc. Commun.* **1979**, 294-295. (n) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4992-4998. (o) Takagi, K.; Hayama, N.; Inokawa, S. *Chem. Lett.* **1979**, 917-918. (p) Mori, M.; Hashimoto, Y.; Ban, Y. *Tetrahedron Lett.* **1980**, *21*, 631-634. (q) Taylor, S. K.; Bennett, S. G.; Heinz, K. J.; Lashley, L. K. *J. Org. Chem.* **1981**, *46*, 2194-2196. (r) Han, B. H.; Boudjouk, P. *Tetrahedron Lett.* **1981**, *22*, 2757-2758. (s) Semmelhack, M. F.; Helquist, P.; Jones, L. D.; Keller, L.; Mendelson, L.; Yono, L. S.; Smith, J. G.; Stauffer, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 6460-6471.

(4) (a) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319-6332, 7547-7560. (b) Michman, M.; Kaufman, V. R.; Nussbaum, S. *J. Organomet. Chem.* **1979**, *182*, 547-559. (c) Lewin, M.; Aizenshtat, Z.; Blum, J. *J. Organomet. Chem.* **1980**, *184*, 255-261.

macrocyclic non-benzenoid biphenyl. This paper describes our results on the second such species, the bidihydropyrenyl 2, together with the mixed biphenyl 3, in which we had interest not only because they are novel biphenyls, which have very sensitive<sup>6</sup> internal NMR probes to test conjugation between the aryl rings, but also because they were model compounds for our studies on benzannelated dihydropyrenes.<sup>7</sup>

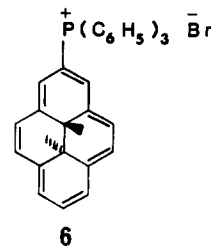
## Results

Of the numerous coupling procedures suitable for biaryl preparation,<sup>3</sup> that of Kende et al.<sup>3f</sup> by using in situ generated zerovalent nickel complex looked most attractive. We thus first developed a procedure to convert dimethyldihydropyrene 4 into its green bromide 5 by using NBS in DMF.<sup>8</sup> However, when



4

5 was subjected to the coupling procedure of Kende,<sup>3f</sup> we obtained two coupled products, both purple. The structures of these were readily shown by <sup>1</sup>H NMR and mass spectra to be the desired biphenyl 2 together with the unexpected phenyldihydropyrene 3 in about 41% and 16% yields, respectively. Unfortunately these were coeluted with triphenylphosphine on chromatography over silica gel and could only be separated from Ph<sub>3</sub>P by using reverse-phase HPLC. They were identical however with samples prepared below without using phosphine coupling methods. Others have also noted this phosphine removal problem for some hydrocarbons.<sup>31</sup> The formation of 3 is interesting since this compound must have arisen by an aryl transfer from the phosphine ligand.<sup>9</sup> From previous work<sup>4,10</sup> this may involve the phosphonium salt 6<sup>4,10</sup>



6

or an Ar-Ar'<sup>9</sup>Ni(Ph<sub>3</sub>P)<sub>2</sub> species.<sup>9</sup> from which ultimately Ar-Ar'

(5) Storie, I. T.; Sondheimer, F. *Tetrahedron Lett.* **1978**, 4567-4570.

(6) Mitchell, R. H.; Carruthers, R. J.; Mazuch, L.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2544-2551.

(7) Mitchell, R. H.; Williams, R. V.; Mahadevan, R.; Lai, Y. H.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2571.

(8) Mitchell, R. H.; Lai, Y. H.; Williams, R. V. *J. Org. Chem.* **1979**, *44*, 4733-4735.

(9) Nakamura, A.; Otsuka, S. *Tetrahedron Lett.* **1974**, 463-466. Fahey, D. R.; Mahan, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 4499-4503.

(10) Cassar, L.; Foa, M. *J. Organomet. Chem.* **1974**, *74*, 75-78.

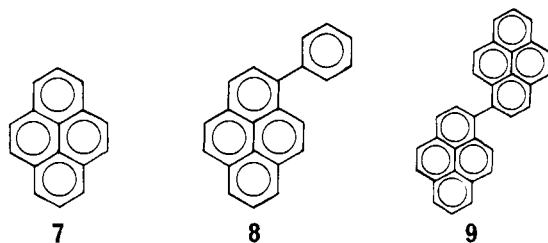
is formed. Kochi however does not indicate<sup>4a</sup> any ethyl transfer in his work using triethylphosphine. He does however note that the problem is complex and the biaryl cycle appears to be locked to the phosphonium salt cycle. Reversible formation of the salt **6** however would provide at least one means of transferring a phenyl group from phosphorus to nickel<sup>9</sup> to allow biaryl coupling. It would be interesting to know whether the process is more general.

Few of the recognized aryl coupling methods yielded much **2** from **5**, the best yield (35%) being obtained by using the TIBr method<sup>11</sup> on the lithio derivative **4**, derived by treating **5** with *n*-butyllithium. Biaryl **2** was thus obtained as dark greenish crystals that formed purple solutions. In its mass spectrum **2** gave a molecular ion at *m/e* 462 with fragment ions corresponding to loss of one, two, three, and four methyl groups, and in its <sup>1</sup>H NMR spectrum, the internal methyls appeared characteristically shielded for a dihydropyrene at  $\delta$  -3.68 and -3.77 (those of **4** appear at  $\delta$  -4.25).<sup>12</sup> The hydrogen 1,3 protons appeared as a singlet at  $\delta$  9.48, strongly deshielded from those of **4** ( $\delta$  8.57)<sup>12</sup> by the adjacent ring, analogous to the corresponding ones in **1** ( $\delta$  9.84).<sup>5</sup> The phenyldihydropyrene **3** was obtained in 16% yield from **5** by reaction with lithium phenylcuprate<sup>3c</sup> as yellow-green needles, mp 118–119 °C, which also form purple solutions; the structure was confirmed by a mass spectrum molecular ion at *m/e* 308, and its <sup>1</sup>H NMR spectrum, which showed internal methyl protons at  $\delta$  -4.00 and -4.03 and hydrogen 1,3 at  $\delta$  8.91 as a singlet. The ortho protons (hydrogen 2',6') of the phenyl rings were also substantially deshielded from benzene to about  $\delta$  8.1.

## Discussion

**UV Spectra.** The question of conjugation between the rings in biphenyls has always been of interest.<sup>2b</sup> This conjugation at least in the past has most readily manifested itself in their UV spectra.

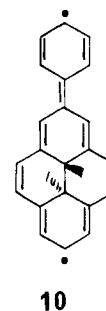
The  $\lambda_{\max}$  of the principle bands for **2**, **3**, and **4** are given in Table I, together with those for pyrene (**7**),<sup>13</sup> 1-phenylpyrene (**8**)<sup>14</sup> and 1-(1'-pyrenyl)pyrene (**9**)<sup>15</sup> for comparison. It appears that the



effects in both series of compounds in passing from **4**  $\rightarrow$  **3**  $\rightarrow$  **2** and **7**  $\rightarrow$  **8**  $\rightarrow$  **9** are amazingly similar. The bands of **7**, **8**, and **9** readily fit Clar's  $\alpha$ ,  $\beta$ , and  $\beta'$  notation,<sup>16</sup> though the "conjugation band" of biphenyl<sup>17</sup> is masked not only by the intense pyrene bands themselves but also by the fact that **8** and **9** are effectively 1-arylnaphthalene derivatives and these have higher energy barriers to become planar and hence show less conjugation than the 2 derivatives.<sup>18</sup> Unfortunately the 2-arylpirenes that would make better comparisons do not appear to have been reported. The bands of **2**, **3**, and **4** in Table I can also be assigned as above; however, in these cases the conjugation band is intense and undoubtedly overlaps the  $\beta$  band and, in the case of **2** sub-

sumes the  $\alpha$  bands as well. The effect of the conjugation band however can be clearly seen on the  $\epsilon$  values of the  $\beta$  bands for **3** and **2** that are considerably enhanced, being more than 3 times that of **4**. Note that this does not occur for their  $\beta$  bands or for the  $\beta$  or  $\beta'$  bands of **7**  $\rightarrow$  **9**. This enhancement leaves no doubt that conjugation between the macrocyclic rings occurs. Determining the extent of this conjugation is, however, far from trivial.

**<sup>1</sup>H NMR Spectra.** We have previously shown that the chemical shifts of the internal methyl protons of dihydropyrenes are sensitive probes for the extent of delocalization of the macroring.<sup>1</sup> Thus since conjugation between the rings of a "biphenyl" such as **2** or **3** would be expected to reduce the delocalization within any one of the rings because of participation of neutral or charged canonical structures of type **10**, this should manifest itself in a change of



the readily observed chemical shifts of the internal methyl protons of the molecule under study from those of **4**. The large distance between the internal methyl protons of **3** and the center of the other ring ensures that any diamagnetic deshielding of these protons through space is small, and it is also relatively easily calculated,<sup>19</sup>  $<0.1$  ppm; that for **2** should also be relatively small though larger than **3** but is not so readily calculated because of the shape of the dihydropyrene framework. Calculated<sup>1</sup>  $\pi$ -SCF bond orders for **2**–**4** and biphenyl are shown in Table II, together with the calculated and observed chemical shifts of the internal methyl protons of **2**–**4**. The calculated and observed chemical shift differences between the internal methyl protons of **3** and **4** agree very closely and support our hypothesis that anisotropic effects are minimized. The actual reduction in shielding of 0.2 ppm is rather small and indicates that the magnetic ring current is hardly perturbed at all by conjugation between the rings, unlike the effect on the UV spectra. While the calculated reduction of shielding (0.3 ppm) for **2** is somewhat larger than for **3**, the agreement with the experimental value of 0.5 ppm is not quite as good, probably because of the increased anisotropic effect of the larger ring (as can be readily seen by its huge effect on the external hydrogen 1,3 protons and of the corresponding ones of **1**). Nevertheless, despite the substantial  $\pi$  bond character for the aryl–aryl bond  $w$  of **2** and **3**, the bond localization that occurs around the remainder of the periphery, i.e., bonds  $b$ – $g$  is surprisingly minimal with its consequent small effect on ring current. Clearly calculation and experiment agree on this aspect. Comparison of calculated bond orders  $w$  for **2**, **3**, and biphenyl indicates that most interaction occurs for **2** and least for biphenyl. This greater interaction is consistent with the larger number of canonical structures available to **2** and its lower resonance energy per electron. It also appears consistent with the UV spectra, which clearly **2** shows the largest bathochromic shift of its  $\beta$  band.

Whereas ring current effects are related to  $\pi$ -electron delocalization and hence to average  $\pi$ -bond orders, which in turn reflect all the  $\pi$ -orbital energies of a molecule, UV spectra are more concerned with energy difference between specific orbitals and hence in the case of biphenyls interaction between the aryl–aryl bond carbon orbitals. This interaction can thus have a substantial effect on the UV spectrum, even if most of the remainder of the  $\pi$  system is not much perturbed. Clearly, considering molecules

(11) McKillop, A.; Elsom, L. F.; Taylor, E. C. *Tetrahedron* **1970**, *26*, 4041–4050.

(12) Boekelheide, V.; Phillips, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 1695–1704.

(13) Clar, E. "Polycyclic Hydrocarbons"; Academic Press-Springer Verlag: London, 1964; Vol. 2, 116.

(14) Lang, K. F.; Buffleb, H. *Chem. Ber.* **1957**, *90*, 2894–2897.

(15) Clar, E.; Kuhn, O. *Annalen*, **1956**, *601*, 181–192.

(16) Clar, E. "Polycyclic Hydrocarbons"; Academic Press-Springer Verlag: London, 1964; Vol. 1, Chapter 9.

(17) Wheland, G. W. "Resonance in Organic Chemistry"; Wiley: New York, 1955; p 263.

(18) Jones, R. N. *J. Am. Chem. Soc.* **1945**, *67*, 2127–2150.

(19) Johnson, C. E.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012–1014. Emsley, I. W.; Feeny, J.; Sutcliffe, L. H. "High resolution nuclear magnetic resonance spectroscopy"; Pergamon Press: Oxford, 1965; Vol. 1, p 595.

such as **2** are expected to be the *most* sensitive of aromatics to ring current effects, for normal biphenyl-type aromatics interaction between the rings will be more readily observed through UV spectra than nuclear magnetic resonance data.

### Experimental Section

<sup>1</sup>H NMR spectra were determined in CDCl<sub>3</sub> on a Perkin-Elmer R32 (90 MHz) spectrometer and are reported in parts per million downfield from tetramethylsilane as internal standard. UV spectra were determined in cyclohexane on a Cary 17 spectrophotometer. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-7 (high-resolution) or Finnigan 3300 (low-resolution) mass spectrometer at 70 eV. Microanalyses were performed by this department and by Canadian Micro-analytical services Ltd. All evaporations were carried out under reduced pressure on a rotary evaporator at ca. 40 °C. Extracts were dried with anhydrous sodium sulfate.

**Bi(2,2'-trans-10b,10c-dimethyl-10b,10c-dihydropyrenyl) (2).** A solution of *n*-butyllithium (0.2 mmol in hexane, 0.1 mL) was added under N<sub>2</sub> to a stirred solution of 2-bromo-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**5**)<sup>8</sup> (50 mg, 0.16 mmol) in dry ether (2 mL) in a flamed flask. After 5 min this solution was added under N<sub>2</sub> to a slurry of TlBr (0.08 g, 0.3 mmol) in benzene (2 mL) and ether (2 mL). The mixture was then heated under reflux with stirring for 4 h. It was then cooled, poured into water, and extracted with dichloromethane. The extract was washed, dried, and evaporated and the residue was chromatographed over silica gel. Pentane eluted first the green dimethyldihydropyrene **4**, ca. 10 mg, and then the purple bipyrene **2**, 13 mg (35% yield), as very dark greenish black crystals from methanol that formed purple solutions; mp ca. 195–199 °C dec; <sup>1</sup>H NMR δ 9.46 (s, 4 H, H-1,3), 8.8–8.5 (m, 14 H, other ArH), –3.68 and –3.77 (s, 6 H each, CH<sub>3</sub>); MS, M<sup>+</sup> at *m/e* 462 (24%), 447 (M – CH<sub>3</sub>, 38), 432 (M – 2CH<sub>3</sub>, 26), 417 (M – 3CH<sub>3</sub>, 100), 402 (M – 4CH<sub>3</sub>, 55) plus many doubly charged ions; UV λ<sub>max</sub> (log ε<sub>max</sub>) 577 nm (4.20), 544 (sh, 4.13), 480 (sh, 3.80) 436 (3.83), 400 (4.12), 368 (4.72), 345 (4.42), 332 (sh, 4.35). Anal. Calcd for C<sub>36</sub>H<sub>30</sub>: C, 93.46; H, 6.54; mol wt., 462.23. Found: C, 92.91; H, 6.06; mol wt, 462.24 (MS). When anhydrous CoCl<sub>2</sub> (0.8 g) was used as oxidant (reflux, 4 h) from bromide **5** (800 mg), there was obtained bipyrene **2** (150 mg, 25% yield), identical with the above sample.

**trans-10b,10c-Dimethyl-2-phenyl-10b,10c-dihydropyrene (3).** A solution of phenyllithium (3.2 mmol in hexane 1.8 mL) was added to a

stirred slurry of CuBr (0.23 g 1.6 mmol) in dry ether (5 mL) at 0 °C under N<sub>2</sub>. After 30 min the solution was allowed to warm to ca. 20 °C and a solution of the bromodihydropyrene **5**<sup>8</sup> (100 mg, 3.2 mmol) in dry ether (5 mL) was added. The mixture was kept at ca. 20 °C for 8 days. Nitrobenzene (0.2 mL) was then added and stirring maintained for ca. 15 min, after which the mixture was poured into water and extracted with dichloromethane. The extract was washed, dried, and evaporated, and the residue was chromatographed over silica gel using pentane as eluant. Eluted first was some parent dihydropyrene **4** (10–20 mg) followed by the purple biphenyl **3**, which on recrystallization from methanol–water gave yellow-green needles: 16 mg (16% yield); mp 118–119 °C, which on dissolution form purple solutions; <sup>1</sup>H NMR δ 8.91 (s, 2 H, H-1,3), 8.8–8.5 (m, 6 H, H-4,5,6,8,9,10), 8.3–7.9 (m, 3 H, H-7,2',6'), 7.8–7.4 (m, 3 H, H-3',4',5'), –4.00, –4.03 (s, 3 H each, CH<sub>3</sub>); MS, M<sup>+</sup> at *m/e* 308 (30%), 293 (M – CH<sub>3</sub>, 97), 278 (M – 2CH<sub>3</sub>, 100); UV λ<sub>max</sub> (log ε<sub>max</sub>) 648 nm (2.51), 620 (sh, 2.35), 493 (4.18), 390 (4.52), 366 (4.41), 348 (5.15), 330 (4.56), 279 (4.08), 246 (4.11). Anal. Calcd for C<sub>22</sub>H<sub>20</sub>: C, 93.46; H, 6.54; mol wt, 308.16. Found: C, 93.25; H, 6.75; mol wt, 308.17 (MS).

**Coupling Using Bis(triphenylphosphino)nickel(II) Chloride as a Precursor to Ni<sup>0</sup>.** Preparation of **2** and **3**. Bis(triphenylphosphino)nickel(II) chloride<sup>20</sup> (105 mg, 0.16 mmol), triphenylphosphine (84.2 mg, 0.32 mmol), and zinc dust (10.6 mg, 0.16 mmol) were slurried in dry O<sub>2</sub>-free DMF (5 mL) in a flamed flask under N<sub>2</sub>. The mixture was then heated to 50 °C with stirring for 1 h, and then the bromopyrene **5**<sup>8</sup> (50 mg, 0.16 mmol) in DMF (2 mL) was added. After 24 h at 50 °C the reaction mixture was cooled, poured into dilute aqueous HCl, and extracted with ether. The extract was washed, dried, and evaporated. Chromatography on silica gel using pentane as eluant gave first dimethyldihydropyrene **4** (~10 mg, 27%), then the symmetrical dipyrene **2** (~15 mg, 41%), and finally the unsymmetrical biphenyl **3** (~8 mg, 16%) all contaminated with triphenylphosphine. The latter could only be removed by HPLC using a reverse-phase column with methanol as eluant. The biphenyl's **2** and **3** showed retention times identical with those of the samples previously described.

**Registry No.** **2**, 92720-01-9; **3**, 92720-02-0; **4**, 956-84-3; **5**, 71807-14-2; PhLi, 591-51-5; (Ph<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub>, 14264-16-5.

(20) Yamamoto, K. *Bull. Chem. Soc. Jpn.* **1954**, *27*, 501–505.

## Oxygenation Patterns for Iron(II) Porphyrins. Peroxo and Ferryl (Fe<sup>IV</sup>O) Intermediates Detected by <sup>1</sup>H Nuclear Magnetic Resonance Spectroscopy during the Oxygenation of (Tetramesitylporphyrin)iron(II)

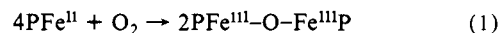
Alan L. Balch,\* Yee-Wai Chan, Ru-Jen Cheng, Gerd N. La Mar, Lechoslaw Latos-Grazynski, and Mark W. Renner

Contribution from the Department of Chemistry, University of California, Davis, California 95616. Received March 20, 1984

**Abstract:** The reaction between unligated (tetramesitylporphyrin)iron(II) (TMPFe<sup>II</sup>) and dioxygen in a toluene solution has been examined by <sup>1</sup>H NMR spectroscopy. At –70 °C, TMPFe<sup>II</sup> reacts with O<sub>2</sub> to yield TMPFe<sup>III</sup>OOFe<sup>III</sup>TMP that has spectroscopic properties similar to those of other peroxo-bridged complexes. On warming, TMPFe<sup>III</sup>OOFe<sup>III</sup>TMP decomposes to yield a second intermediate (identified as TMPFe<sup>IV</sup>O) and TMPFe<sup>III</sup>OH, the final, stable product. TMPFe<sup>III</sup>OOFe<sup>III</sup>TMP reacts with *N*-methylimidazole (*N*-MeIm) to produce (*N*-MeIm)TMPFeO<sub>2</sub> and (*N*-MeIm)<sub>2</sub>TMPFe<sup>II</sup>. The former has been independently prepared from (*N*-MeIm)<sub>2</sub>TMPFe<sup>II</sup> and dioxygen at –50 °C. TMPFe<sup>IV</sup>O reacts with *N*-MeIm to form (*N*-MeIm)TMPFe<sup>IV</sup>O that has been identified by comparison with other Fe<sup>IV</sup>O complexes. TMPFe<sup>IV</sup>O reacts with triphenylphosphine at –50 °C to yield triphenylphosphine oxide while TMPFe<sup>III</sup>OOFe<sup>III</sup>TMP is unreactive toward triphenylphosphine under these conditions. TMPFe<sup>II</sup> is a catalyst for the oxidation of triphenylphosphine by dioxygen. <sup>1</sup>H NMR spectra and resonance assignments for each species are described.

### Introduction

The autoxidation of iron(II) porphyrins, PFe (P is a porphyrin dianion), in the absence of other axial ligands generally leads to the formation of an oxo-bridged species as shown in eq 1.<sup>1</sup> This



transformation represents a simple case of dioxygen activation by a transition metal system, and it is one where it is possible to