than static. ^{1}H NMR data[16] indicate that the ring current in isobacteriochlorins is lower than in bacteriochlorins, chlorins, or porphyrins in accord with a lower degree of aromaticity and thus with tautomers in which the conjugation is interrupted (**2b** and **c**). The bond distances observed in **2** (Figure 3) support such a disruption.

The emerging structural data for chlorins,[9,17] bacteriochlorins,[18] and isobacteriochlorins[13,14] indicate that the reduced rings of the macrocycles are flexible and can assume a wide range of conformations, influenced in part by the occupancy of the porphyrin pocket. Zn(II) complexes exhibit[13] only moderate deviations of the macrocycles from planarity whereas nickel(II) chlorins[9] and isobacteriochlorins[14] are particularly distorted. ESR results for cation radicals of **2** and its Zn and hexacoordinated Fe(II) complexes, which probe the β protons of the reduced rings and their spatial interactions with the α carbons, reveal no major differences between the three compounds.[12,19] This constancy implies that the average conformations of the ligands in solution are similar. Extrapolation of the model studies to the biological pigments suggests therefore that sirohydrochlorin and low-spin iron(II) siroheme should exhibit comparable conformational profiles.

In a different context, the present results may also be relevant to the "special pairs" of bacteriochlorophylls that act as light traps and primary electron donors in bacterial photosynthesis.[20] As in iBC cation radicals,[12] the HOMOs of bacteriochlorophyll cations localize unpaired spin at the reduced rings with the result that the observed ESR and ENDOR parameters of the radicals depend heavily on the orientations of these rings.[21] Conformational changes in the *flexible* reduced rings, induced by the "special pair" packing and/or protein interactions, thus provide an attractive structural explanation for the variety of ESR and ENDOR data observed for bacteriochlorophyll radicals in vivo.[20-22]

Note Added in Proof. The structure of another isobacteriochlorin, 3,3′,7,7′-tetrahydro-2,2′,8,8′,12,13,17,18-octamethylporphyrin, has recently been solved.[23] As in the present work, the central protons are delocalized, and an interrupted conjugative path is indicated. In sharp contrast to the results presented here, the molecule is planar and thus further illustrates the wide range of conformations that reduced porphyrins can assume.

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Registry No. 2a, 80106-11-2; **2b**, 80106-12-3; **2c**, 72218-67-8.

Supplementary Material Available: Crystallographic details, selected bond angles, bonds distances in the side chains, least-squares planes, atom coordinates and anisotropic vibrational parameters for the nonhydrogen atoms, coordinates of the hydrogen atoms, and a listing of structure amplitudes (20 pages). Ordering information is given on any current masthead page.

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Trans Lengthening of M-H Bonds and Steric Modification of M-P Bond Lengths in Chloro- and Hydrido-Transition-Metal-Phosphine Complexes

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In addition to primary metal and ligand types, metal-ligand distances in transition-metal complexes are dependent on a variety of factors, including metal and/or ligand oxidation state, coordination number and geometry, cis- and trans-bond lengthening effects, intramolecular nonbonded interactions, and in the solid state, intermolecular interactions of various types. Recent X-ray and (in some cases) neutron diffraction analyses of members of the series of complexes $L_3H_{3-n}Cl_nIr^{III}$ [L = PMe_2Ph; n = 0-3] provide valuable new insight into the relative importance of some of these factors. Relevant bond length data for *mer*-[$L_3Cl_3Ir^{III}$][1] (**1**), *mer*-[L_3-*trans*-Cl_2HIr^{III}] (**2**), *mer*-[L_3-*cis*-Cl_2HIr^{III}] [monoclinic (**3a**), and orthorhombic (**3b**), modifications], *mer*-[L_3Cl-*cis*-H_2Ir^{III}] (**4**), *fac*-[$L_3Cl_3Ir^{III}$] (**5**), and *fac*-[$L_3H_3Ir^{III}$][2] (**6**) are shown in Table I.[3] Even in this series, and for given ligand type, variable factors will include (as a minimum) the specific nature of the trans ligand, the differing steric requirements of the anionic ligands (Cl or H), ligand-ligand nonbonding interactions, and the intermolecular force fields. Because these factors are interdependent, we are unable to rationalize the variations indicated in Table I in detail. We are able, however, to derive some useful estimates of the *relative* magnitudes of the various effects.

Complexes **1**, **3a**, and **5**, each crystallize with two molecules per asymmetric unit, and despite the differing crystalline environments of pair members, chemically equivalent metal-ligand bond lengths do not differ significantly.[4] These data suggest an upper limit of ca. 0.005 Å for the effect of the intermolecular force field on the metal-ligand bond lengths. Other effects are much more substantial. Thus, for any particular complex, we observe that the trans influence on metal-ligand bond lengths is marked and that the order (H > PMe_2Ph > Cl) is as expected.[5] As the trans ligand is changed from chloride to phosphine and from phosphine to hydride, Ir-Cl is increased by ca. 0.07 and 0.05 Å respectively. The corresponding increases in Ir-P are ca. 0.10 and 0.04 Å. Trans lengthening of the Ir-H bond is also evident, with substitution of phosphine for chloride, causing an increase in Ir-H of ca. 0.05 Å. The Ir-H lengthening is only a little less than that observed for Ir-Cl with the same ligands. So far as we are aware, the present results provide the first quantitative measure of this effect in simple octahedral systems.

Next, comparison between *different* mer complexes (**1**-**4**) shows that whereas the Ir-Cl (and Ir-H) bond length trans to a given ligand is approximately constant, the Ir-P bond length trans to a given ligand is certainly not constant. There is a clear trend that, as the degree of hydride substitution is increased by unity, the Ir-P bond length (for any given trans ligand) is decreased by ca. 0.04 Å.[6] The same effect is illustrated dramatically in the fac complexes (**5**, **6**) where, despite the marked difference in the

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(1) A redetermination of the structure originally reported by: Aslanov, L.; Mason, R.; Wheeler, A. G.; Whimp, P. O. *J. Chem. Soc., Chem. Commun.* **1970**, 30.

(2) Bau, R., private communication, 1978. Bau, R. "Transition Metal Hydrides"; American Chemical Society: Washington, DC, 1978; *Adv. Chem. Ser.* No. 167.

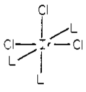
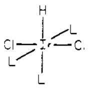
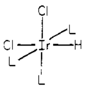
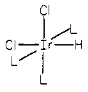
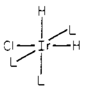
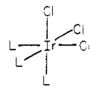
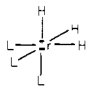
(3) M-H distances are from neutron diffraction data collected at the Australian Atomic Energy Commission (Lucas Heights) with the support of the Australian Institute for Nuclear Science and Engineering and at the Institute Laue-Langevin (Grenoble) with support from the Science Research Council of Great Britain.

(4) Except for Ir-Cl (trans to H) in **3a**. The inequivalence is apparent in both X-ray and neutron refinements. Its origin is not yet clear.

(5) McWeeny, R.; Mason, R.; Towl, A. D. C. *Discuss. Faraday Soc.* **1969**, *47*, 20.

(6) We have already noted (Robertson, G. B.; Tucker, P. A.; Whimp, P. O. *Inorg. Chem.* **1980**, *19*, 2307) that Ir-P bond lengths in hydride complexes of that metal lie at the shorter end of the observed range.

Table I. Iridium–Ligand Bond Lengths (Å) in $L_3H_{3-n}Cl_nIr^{III}$ Complexes [L = PMe_2Ph][a]

	 1[b]	 **2**	 **3a**	 **3b**	 **4**	 **5**	 6[c]
Ir-P (trans to Cl)	2.280 (2)		2.249 (1)	2.234 (1)		2.289 (2)	
Ir-P (trans to P)	2.366 (2) 2.381 (2)	2.329 (2)	2.335 (2) 2.343 (2)	2.344 (2) 2.352 (2)	2.292 (2)		
Ir-P (trans to H)		2.365 (2)			2.331 (2)		2.294 (3)
Ir-Cl (trans to Cl)	2.366 (1)	2.364 (2) 2.402 (2)					
Ir-Cl (trans to P)	2.437 (2)		2.453 (2)	2.449 (2)		2.463 (2)	
Ir-Cl (trans to H)			2.518 (2) 2.492 (2)	2.503 (2)	2.505 (1)		
Ir-H (trans to Cl)[d]			1.56 (1) 1.58 (1)		1.557 (9)		
Ir-H (trans to P)[d]		1.616 (7)			1.603 (8)		

[a] Average values are given where two or more measurements do not differ significantly. Bracketed values refer to notionally equivalent bond lengths which vary as a result of differing inter and/or intramolecular contacts. A discussion of these variations and details of the crystallographic work will be given elsewhere. [b] Results agree, within experimental error, with those reported in ref 1. [c] Results from ref 2. [d] See ref 3.

trans influences of chloride and hydride ligands, both molecules exhibit near identical Ir–P distances. There seems little doubt that the effect is due to the small steric requirement of the hydride ligand;[7] indeed, bond-angle changes at the metal atom, on substituting hydride for chloride, confirm a significant shift of ligands toward the hydride site.[8] However, since the Ir–Cl distances are effectively invariant to hydride substitution, we are certainly not seeing something as simple as first-coordination sphere ligand–ligand repulsion effects.[9] Rather, the determining factor would appear to be a rebalancing of bonding forces and the nonbonding interactions due to anionic ligand/phosphine substituent and phosphine substituent/phosphine substituent contacts.[10]

Separation of the effects of these two nonbonding interaction types is not possible for the present series of complexes. Anionic ligand/phosphine substituent interactions are certainly very important. Thus, observed Pt–P distances in *trans*-$[(P\text{-}i\text{-}Pr_3)_2Cl_2Pt^{II}]$ (**7**), and *trans*-$[(P\text{-}i\text{-}Pr_3)_2HClPt^{II}]$ (**8**), are 2.340 (2) and 2.287 (1) Å,[11] and in *trans*-$[(PPh_3)_2Cl(CH_2CN)Pt^{II}]$ (**9**), and *trans*-$[(PPh_3)_2H(CH_2CN)Pt^{II}]$ (**10**), are 2.309 (3) and 2.274 (4) Å, respectively.[12] Phosphine substituent/phosphine substituent interactions are apparently of similar importance since (a) replacement of monodentate by chelating phosphines (hence reducing the number of substituent/substituent contacts in otherwise similar complexes) is generally accompanied by M–P bond length compression[13] and (b) comparison of the Pt–P distances in $[(PPh_3)_3HPt^{II}][(CF_3CO_2)_2H]$ (**11**), [2.312 (6) Å trans to P][14] with those in **9** [2.309 (3) Å] and **10** [2.274 (4) Å] shows the effects of the substitutions H for Cl and PPh_3 for CH_2CN to be largely self-cancelling.

Steric modification of metal–phosphine distances is already well established.[7,15,16] We believe it important, however, to draw attention to the *magnitude* of the effect even in complexes with small phosphine ligands. Both in the complexes discussed here and in the cationic species $[(PEt_3)_3XPt^{II}]^+$ (X = Cl, F, H) described in ref 16, the M–P compression due to H for Cl substitution is fairly constant at ca. 0.04 Å. The near equivalence is probably fortuitous, reflecting a balance between phosphine size and number of ligands coordinated. Clearly, however, the frequently made assumption that trans and particularly cis electronic effects on bond lengths are large relative to steric effects in octahedral and square-planar phosphine complexes requires validation.

Registry No. 1, 15664-86-5; **2**, 12099-72-8; **3**, 32914-89-9; **4**, 12099-74-0; **5**, 21919-29-9; **6**, 12099-83-1.

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(7) Tolman, C. A. (*Chem. Rev.* **1977**, *77*, 313) has estimated cone angles of 75° for H, 102° for Cl, and 122° for PMe_2Ph.

(8) Except for the fac-complexes **5** (with mean P-Ir-P angle = 100°) and **6** (with mean P-Ir-P angle = 101°)[2].

(9) Because the variations in Ir–Cl and Ir–P bond lengths with changes in trans ligand are similar it seems unlikely that the Ir–Cl bond is much less easily deformed than the Ir–P bond.

(10) Even though these contacts are not exceptionally short. In **2** the shortest nonbonding contacts to anionic ligands are H···H (2.63 Å), H···Cl (2.77 Å) and in **4** are H···H (2.56 Å) and H···Cl (2.59 Å).

(11) Robertson, G. B.; Tucker, P. A., unpublished results.

(12) Ros, R.; Michelin, R. A.; Belluco, U.; Zanotti, G.; Del Prā, A.; Bombieri, G. *Inorg. Chim. Acta* **1978**, *29*, L 187.

(13) For example, $RhCl(PPh_3)_3$ Bennett, M. J.; Donaldson, P. B. *Inorg. Chem.* **1977**, *16*, 655] [Rh–P (trans to Cl) 2.214, 2.225 Å, Rh–P (trans to P) 2.304–2.338 Å] and $RhCl(Ph_2PC_3H_6PPhC_3H_6PPh_2)$ [Nappier, T. E.; Meek, D. W.; Kirchener, R. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 4194] [Rh–P (trans to Cl) 2.201 Å, Rh–P (trans to P) 2.288 Å); $RhCl(PPh_3)_2(C_2F_4)$ [Hitchcock, P. B.; McPartlin, E. M.; Mason, R. *J. Chem. Soc., Chem. Commun.* **1969**, 1367] (Rh–P 2.372 Å) and $RhCl(PPh_2C_6H_4CHCHC_6H_4PPh_2)$ [Robertson, G. B.; Tucker, P. A.; Whimp, P. O. *Inorg. Chem.* 1980, *19*, 2307] (Rh–P 2.285 Å); *cis*-$PdCl_2(PMe_2Ph)_2$ [Martin, L. L.; Jacobson, R. A. *Inorg. Chem.* **1971**, *10*, 1795] Pd–P 2.260 Å) and $PdCl_2(PPh_2(CH_2)_nPPh_2)$ [n = 1–3: Steffen, W. L.; Palenik, G. *Inorg. Chem.* **1976**, *15*, 2432] (Pd–P 2.226–2.250 Å).

(14) Caputo, R. E.; Mak, D. K.; Willet, R. D.; Roundhill, S. G. N.; Roundhill, D. M. *Acta Crystallogr., Sect. B* **1977**, *B33*, 215.

(15) Mason, R.; Meek, D. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 183.

(16) Mazid, M. A.; Russell, D. R.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1737.

Regiospecific Cleavage of Strained Tri- and Tetraquinane β-Diketones via Retro-Claisen Reaction[1]

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We have been interested for some time[2a-f] in the synthesis of polyquinane ring systems, some of which contain reactive β-di-

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(1) A brief report on part of the subject matter of the present communication has been incorporated into a recent review: Mitschka, R.; Oehldrich, J.; Takahashi, K.; Cook, J. M.; Weiss, U. *Tetrahedron*, in press.

0002-7863/82/1504-0318$01.25/0