with the molecular axis system this question of co-planarity is an important one. However, we do not feel that the question is readily resolved. From the above considerations, it appears as though deviations from coplanarity may arise as a result of crystal packing forces and other crystal-associated forces not found in the gas and liquid phases. On the other hand angular departures from ideal tetrahedral values are not uncommon in strained ring systems such as the tetramethylpiperidines. In the present case observed deviations from ideal angle values may result from the fact that the piperidine ring is not in a perfect chair conformation but rather a chair–twist or skew form. We believe, however, that our treatment is consistent in many respects with not only a plausible molecular geometry but also with prior data concerning binding of sulfonamides to carbonic anhydrase.

Direct experimental observation of the components of T' and g' for the rotating label would, of course, provide additional evidence for our model. An experiment was tried in which the label–enzyme complex in water was added to a highly viscous aqueous solution of sugar. The presumption in this experiment was that the molecular size of the sucrose disaccharide in high concentration would prevent the bulk rotation of the enzyme but would be too large to enter the active site cleft and interfere with the independent motion of the nitroxide. A rigid glass-like spectrum was observed which yielded values of $T_{||}$ and $T_{\perp}$ of 89.3 and 27.5 Mcps, respectively. These are intermediate between the values obtained for the frozen solution (where all motion is restricted) and those obtained from the enzyme–label complex where rapid anisotropic rotation is occurring. It seems likely that although the freedom of motion of the enzyme has been restricted, one has also affected the rotational freedom of the label itself about the ester linkage. A preferrable experiment would be one in which the enzyme–label complex acts as a substrate on an immobile surface. Preliminary work along this line is now under way.

The salient feature behind the rotational analysis is that the piperidine ring is relatively free to rotate while the aromatic nucleus is not. Since Strandberg's results indicate a tight fit of the aromatic nucleus within the enzyme cleft, the only feasible explanations of the rotation of the piperidine ring are (1) the cleft "opens up" so that the nitroxide experiences a wider, less restricting protein environment than does the aromatic nucleus, or (2) the piperidine ring projects out beyond the enzyme surface and experiences essentially an aqueous buffer environment. The length of the extended conformation of the SSL is about[33] 11 Å. Since evidence exists indicating that the sulfonamide group is within the coordination sphere of the zinc atom situated near the center of the enzyme, it appears unlikely that this projection beyond the enzyme surface occurs. Experimental confirmation of this is provided in the value of the isotropic hyperfine coupling constant, a_N. The value of a_N for the bound label is 17.2 G, while the value of a_N for the label in an aqueous Tris-HCl buffer solution is 16.8 G. Briere, et al.,[13] have demonstrated that various solvents perturb the nitroxide moiety causing a redistribution of the spin density on both the nitrogen and oxygen atoms. The more polar the solvent the greater is the spin density on the nitrogen. The shift of density toward the nitrogen arises because of the hydrogen bonding of the oxygen with the solvent molecules. These authors show that the hyperfine splitting may vary by as much as 1.7 G on going from benzene (virtually no ability to form hydrogen bonds) to water (strongly hydrogen bonded). Thus, a difference of 0.4 G in our studies is approaching significance. We conclude that the nitroxide does not see a purely aqueous environment and is therefore situated inside the protein cleft. Accordingly, while many studies[4,23,34] characterize the cleft as hydrophobic we are here mapping a region of the cleft that is highly polar. Use of dilute enzyme solutions (ca. 10^{-4}–10^{-5} M) virtually negates the possibility of the nitroxide moiety bound to one enzyme molecule interacting with a neighboring enzyme molecule. Our results show nevertheless that the nitroxide is influenced appreciably by a protein structure of hydrogen bonding capacity. Our results would not be inconsistent with the presence of NH- and NH₂-containing amino acid residues (histidine and tryptophan) in the vicinity of the NO group.

(33) This length is derived based on X-ray crystallographic work of B. H. O'Connor and E. N. Maslen, *Acta Crystallogr.*, **18**, 363 (1965), on sulfonanilide, G. A. Sim, J. M. Robertson, and T. H. Goodwin, *ibid.*, **8**, 157 (1955), on benzoic acid, and work by P. J. Lazerowicz-Bonneteau, cited previously, on 2,2,6,6-tetramethylpiperidine-1-oxyl-4-ol.

(34) R. W. Henkens, G. D. Watt, and J. M. Sturtevant, *Biochemistry*, **8**, 1874 (1969).

Communications to the Editor

Oxygenation and Related Addition Reactions of Isostructural d⁸ Complexes of Cobalt, Rhodium, and Iridium. A Quantitative Assessment of the Role of the Metal

Sir:

We have synthesized a new series of univalent cationic complexes, [M(2=phos)₂]A (M = Co, Rh, and Ir; 2= phos = cis-(C₆H₅)₂PCHCHP(C₆H₅)₂;[1] A = Cl, I, BF₄,

(1) This bidentate ligand, cis-1,2-bis(diphenylphosphino)ethylene, is

and/or B(C₆H₅)₄), whose reactions with covalent molecules (XY, eq 1) provide the first direct comparison of

$$[M(2=phos)_2]A + XY \underset{k_{-1}}{\overset{k_2}{\rightleftarrows}} [(XY)M(2=phos)_2]A \quad (1)$$

$$XY = O_2, HCl, H_2, CO, SO_2$$
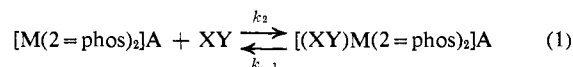
the reactivities of planar d⁸ complexes of *three different*

abbreviated as 2=phos throughout this paper. Occasional references are made also to a closely related ligand, 1,2-bis(diphenylphosphino)ethane, abbreviated as 2-phos.

transition metals in the same periodic group. The results show an unexpected[2-4] reactivity order, Co > Ir > Rh (Table II), which, however, may be understood by a novel observation relating the energy of activation of these addition reactions to the energy of an electronic transition in the reacting complexes.

The knowledge of the precise role of the metal in compounds which "carry" molecular oxygen, "fix" molecular nitrogen, undergo "oxidative additions," and participate in homogeneous catalysis is of fundamental importance for the understanding of these phenomena. In simple addition reactions (*e.g.*, eq 1), the reactivity of the activator complex and the stability of the resulting adduct are generally observed to show the sequence third- > second-row transition metal,[2-6] but a comparison with the first-row metal has apparently not been possible thus far because of an absence of a suitable series of *isostructural* and isoelectronic (valence shell) complexes of all three metals, *i.e.*, compounds which differ only in the metal, exhibit the same reaction path, and react at measurable rates.

The univalent complexes (Table I) are synthesized by the same method as the related "diphos" compound, [Ir(2-phos)₂]BPh₄ [2-phos = (C₆H₅)₂PCH₂CH₂P(C₆-

Table I. Electronic Spectral Data[a] for [M(2=phos)₂][B(C₆H₅)₄][b]

M	Color	E₁	a₁	E₂	a₂	E₃	a₃
				Energy, E, kK, and molar absorptivity, a, M^{-1} cm^{-1}			
Co[c]	Green	13.5	1290	(16.7)	(830)	(25.0)	(3080)
Rh[c]	Yellow	24.7	6160	(29.4)	(6650)	31.9	10900
Ir[d]	Orange	19.1	762	22.7	3810	26.4	4350

[a] Spectra measured in degassed chlorobenzene solutions (10⁻⁴ and 10⁻² *M* in complex) at 20° (M = Co, Rh) and 30° (M = Ir) between 280 and 1000 nm. [b] See ref 1. [c] Data in parentheses correspond to absorption bands appearing as shoulders. [d] A fourth transition is observed at $E_4 = 31.7$ kK, $a_4 = 7900$ M^{-1} cm⁻¹.

H₅)₂][1,7] (for Co, the starting material is [CoCl-(Ph₃P)₃][8]). The new derivatives, [M(2=phos)₂]⁺,[9] are, in general, somewhat less reactive (eq 1) than their known 2-phos analogs,[7,10,11a] but the behavior of the two cobalt complexes, [Co(2-phos)₂]⁺ [11] and [Co(2=phos)₂]⁺, toward molecular oxygen shows a qualitative difference. The former, on exposure to air, decomposes instantly to 2-phos oxide and other oxidation products, while the new 2=phos complex, which is also very sensitive to atmospheric oxygen, both in the solid state and in solution, yields a well-defined oxygen adduct.[11b]

The diamagnetism and electronic spectra of the four-coordinated complexes (Table I) strongly suggest that all three have a planar MP₄ configuration. The spectra in and near the visible region show three absorption bands which are typical of many planar d⁸ complexes.[12-18] In particular, the spectrum of each complex is nearly identical with that of its 2-phos analog, and planar structures have been established for [M-(2-phos)₂]⁺, M = Ir and Rh, by X-ray diffraction.[19]

The iridium and cobalt complexes readily undergo addition reactions, yielding five- and six-coordinated compounds (eq 1). The isoelectronic rhodium complex is decidedly less reactive, and its adducts, when observable, appear to be less stable than those of the Co and Ir analogs. Thus, [Rh(2=phos)₂]⁺ does not react measurably with H₂, CO, or SO₂, and its crystalline HCl adduct dissociates (eq 1) at 25°, while those of Co and Ir do not. Hence, the *qualitative* sequence of reactivity and adduct stability is Co ∼ Ir > Rh.

Table II summarizes some kinetic and activation data for the reactions with H₂ and O₂.[20] The unmistakable order of attraction of the univalent cations to molecular oxygen, Co ≫ Ir > Rh, holds also for the hydrogenation of these complexes (Co > Ir ≫ Rh). Except for [O₂Rh(2=phos)₂]⁺ (footnote *c*, Ta-

Table II. Kinetic and Activation Parameters[a] for the Addition of Molecular Oxygen and Hydrogen (XY) to [M(2=phos)₂][B(C₆H₄)₄][b] (Eq 1) in Chlorobenzene at 25°

XY	M	k_2, M^{-1} sec⁻¹	ΔH_2^*, kcal/mol	ΔS_2^*, eu	ΔG_2^*, kcal/mol
O₂	Co	1.7 × 10⁴	3.4	−28	10.3
O₂	Rh[c]	0.12	11.6	−24	18.8
O₂	Ir	0.47	6.5	−38	17.8
H₂	Co	1.2 × 10⁵	3.6	−23	11.0
H₂	Ir	6.7 × 10³	5.0	−24	12.2

[a] Determined by spectrophotometric methods (*cf.* Table I) at four temperatures between 10 and 40°: Rh, Ir + O₂, conventional; others, stopped flow. Subscript 2 refers to the second-order addition reactions (eq 1). *Maximum* standard deviations: k_2, ±3%; ΔH_2^*, ±0.3 kcal; ΔS_2^*, ±3.5 eu. [b] See ref 1. [c] The reaction is readily reversible (eq 1). At 25°: k_{-1}, 3.4 × 10⁻⁴ sec⁻¹; ΔH_{-1}^*, 23.5 kcal/mol; ΔS_{-1}^*, 4 eu; $\Delta H_2°$, −11.9 kcal/mol; $\Delta S_2°$, −28 eu.

ble II), the rates of O₂ or H₂ dissociation from [(XY)-M(2=phos)₂]⁺ (k_{-1}, eq 1) are too low for reliable measurements below 70°. Thus, the thermodynamics of these reactions are presently unknown, but estimates for lower limits for the values of the equilibrium constants (eq 1) at 25° give these data: (O₂) Co, 10⁹; Ir, 10⁶; Rh, 350 (Table II); (H₂) Co, Ir, 10¹⁰ M^{-1}. It

(2) R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 5337 (1965).

(3) (a) J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, 7, 53 (1968); (b) J. P. Collman, *Accounts Chem. Res.*, 1, 136 (1968).

(4) (a) J. Halpern, *Advan. Chem. Ser.*, No. 70, 1 (1968); (b) *Accounts Chem. Res.*, 3, 386 (1970).

(5) (a) R. Ugo, *Coord. Chem. Rev.*, 3, 319 (1968); (b) S. Carrà and R. Ugo, *Inorg. Chim. Acta Rev.*, 1, 49 (1967).

(6) (a) L. Vaska, *Accounts Chem. Res.*, 1, 335 (1968), and references quoted; (b) L. Vaska, *Inorg. Chim. Acta*, 5, 295 (1971).

(7) L. Vaska and D. L. Catone, *J. Amer. Chem. Soc.*, 88, 5324 (1966).

(8) M. Aresta, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, 3, 227 (1969).

(9) Satisfactory elemental analyses and conductivity data have been obtained for M = Ir and Rh; the Co derivative is too air sensitive for reliable analysis, but its O₂ adduct analyzes satisfactorily.

(10) A. Sacco and R. Ugo, *J. Chem. Soc.*, 3274 (1964).

(11) (a) A. Sacco, M. Rossi, and C. F. Nobile, *Chem. Commun.*, 589 (1966); (b) N. W. Terry, III, E. L. Amma, and L. Vaska, *J. Amer. Chem. Soc.*, in press.

(12) *trans*-[IrA(CO)L₂][13] show similar spectra: L. Vaska and J. Peone, Jr., unpublished results.

(13) L. Vaska and J. Peone, Jr., *Chem. Commun.*, 418 (1971).

(14) M. C. Browning, J. R. Mellor, D. J. Morgan, S. A. J. Pratt, L. E. Sutton, and L. M. Venanzi, *J. Chem. Soc.*, 693 (1962).

(15) W. R. Mason and H. B. Gray, *J. Amer. Chem. Soc.*, 90, 5721 (1968).

(16) J. R. Preer and H. B. Gray, *ibid.*, 92, 7306 (1970).

(17) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, New York, N. Y., 1968, p 132.

(18) According to previous interpretations of the spectra of related d⁸ systems,[15,16] the lowest energy absorption, E_1, corresponds to either $xy \rightarrow x^2 - y^2$ or $xz, yz \rightarrow x^2 - y^2$ transition.

(19) M. C. Hall, B. T. Kilbourn, and K. A. Taylor, *J. Chem. Soc. A*, 2539 (1970).

(20) For comparison with the data for the oxygenation of Co(II) complexes, see R. G. Wilkins, *Advan. Chem. Ser.*, No. 100, 111 (1971).

is also interesting to compare the reactivities or "acidities" of the two reacting gases: for Co and Ir, $H_2 > O_2$, but for Rh, $O_2 > H_2$.

An examination of the data in Tables I (E_1) and II (O_2, ΔH_2*) shows that the activation enthalpy for oxygenation is proportional to the electronic excitation energy E_1 of the three complexes. If the latter is related to the $xy \rightarrow x^2 - y^2$ transition,[18] and the correlation is not fortuitous, it seems that the reactivity of the d^8 M(I) complexes is directly dependent on their ligand-field stabilization energies, perhaps suggesting a new guide for predicting the relative energetics of analogous addition reactions.[21]

It should be finally noted that this study also demonstrates the paramount importance of the *structure* of the metal complex in these addition reactions (eq 1): the *univalent* d^8 complex, [CoCl(Ph₃P)₃], reportedly *tetrahedral*,[8] is relatively inactive toward H_2 and O_2.[22]

(21) Some qualitative reactivity differences are compatible with this suggestion, e.g., E_1 Ni(II)[16] > Co(I) (Table I), Pt(II)[15] > Ir(I); in each case, the *univalent* d^8 complex is more reactive than its *bivalent* analog.

(22) No H_2 or O_2 uptake is observed in toluene solution under 700 mm of the gas for 24 hr at 25, 45, or 65°.

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Reversible Coordination of Carbon Monoxide to Bivalent Iron. Dissociative Mechanism for Monosubstitution in Spin-Paired (d⁶) Octahedral Ferrous Complexes
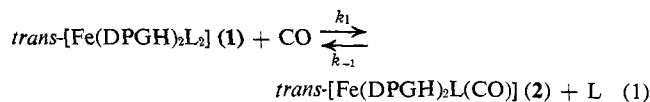
Sir:

In search for simple inorganic imitators for some naturally occurring iron derivatives, we have prepared a new series of Fe(II) complexes 1 (1 = trans-[Fe(DPGH)₂-L₂], where DPGH = bidentate diphenylglyoximato univalent anion; L = pyridine (py) and substituted pyridines, piperidine, imidazole, nicotine, or Ph₃P) based on the planar Fe(DPGH)₂ unit.[1] These dark purple compounds[4] readily undergo substitutions of one or both of their axial ligands (L) by small covalent molecules. Of particular interest are the reversible reactions with carbon monoxide (eq 1) in nonaqueous

(1) No di*phenyl*glyoximato (D*P*GH) complexes of iron have been reported previously, and the reactions of the corresponding *methyl* derivatives (D*M*GH), analogous to 1, have been only cursorily described.[2] This is in contrast to the extensive and detailed studies of the related oxime complexes of cobalt(II) (d⁷).[3]

(2) (a) J. F. Drake and R. J. P. Williams, *Nature (London)*, 182, 1084 (1958); (b) B. A. Jillot and R. J. P. Williams, *J. Chem. Soc.*, 462 (1958); (c) L. F. Lindoy and S. E. Livingstone, *Coord. Chem. Rev.*, 2, 173 (1967), and references therein.

(3) (a) G. N. Schrauzer, *Accounts Chem. Res.*, 1, 97 (1968), and references quoted therein; (b) G. N. Schrauzer and L. P. Lee, *J. Amer. Chem. Soc.*, 92, 1551 (1970).

(4) Compounds 1 are prepared from Fe(II) acetate and L (L/Fe $\simeq$ 10) in methanol at 25° in 80–100% yields. The complexes have been fully characterized by their infrared and electronic spectra, diamagnetism, monomeric and nonconducting behavior in solution, and elemental analyses of most of the derivatives. A related complex, [Fe(DPGH₂)-(CH₃CO₂)₂] (DPGH₂ = *neutral* diphenylglyoxime), contains spin-free Fe(II), $\mu = 4.2$ BM.

$$\text{trans-[Fe(DPGH)₂L₂] (1) + CO} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$\text{trans-[Fe(DPGH)₂L(CO)] (2) + L} \quad (1)$$

solutions which disclose the first detailed mechanism of *monodentate* ligand substitution in low-spin six-coordinated iron(II).[5] It is also noteworthy that although the kinetics of the reversible carbonylation of hemoglobin (Hb) and myoglobin (Mb) have been extensively investigated,[8] no such studies seem to have previously been reported for a synthetic ferrous complex.

The stoichiometry of reaction 1 has been established by volumetric CO-uptake measurements (k_1, CO:Fe = 0.96, in toluene at 25°, p_{CO} = 714 mm), and a full characterization of the yellow carbonyl complex 2 [elemental analysis, ν_{CO} = 1996 cm⁻¹ (Nujol), diamagnetic (L = py)]. The reverse reaction (k_{-1}, eq 1) takes place on addition of L to 2 in the absence of (free) carbon monoxide. The electronic spectra of 1 show an absorption band in the 502–573-nm region which shifts to *ca.* 412 nm in the CO adducts 2 (Table I).

Both the carbonylation of 1 and decarbonylation of 2 are first order in the respective iron complexes, and the rates are independent of the concentrations of the addenda (k_1, $p_{CO} \geqslant 190$ mm; k_{-1}, [py] $\geqslant 10^{-2}$ M). These results suggest a *dissociative* (SN1) mechanism for both substitutions, as depicted in eq 2. If the addi-

1

2

$$N{-}N = DPGH$$
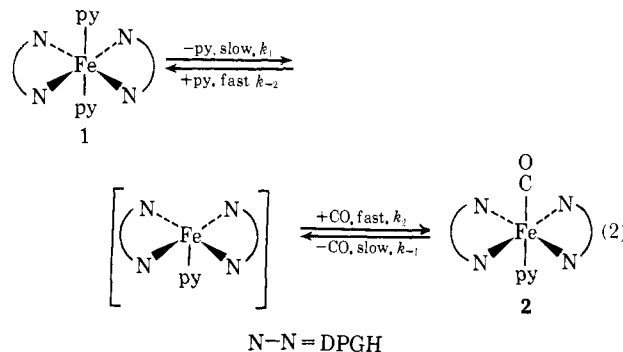
tion of CO (k_1) is carried out in the presence of an excess of pyridine, and a steady-state assumption is made for the postulated five-coordinated intermediate, and the slow reverse reaction (k_{-1}, Table I) is neglected, the predicted rate law for the carbonylation of 1 is

$$\text{rate} = -d[1]/dt = \{k_1/[1 +$$

$$(k_{-2}/k_2)([py]/[CO])]\}[1] \quad (3)$$

A variation of the pyridine–CO ratio (0–50) at constant concentration of carbon monoxide (p_{CO} = 487 mm) has confirmed this prediction: a plot of k_1/rate *vs.* [py]/[CO] gives a straight line with intercept equal to unity; the slope, k_{-2}/k_2, is 3.9 which shows that the

(5) In light of the overwhelming available data on the substitution mechanisms involving octahedral low-spin (d⁶) Co(III) complexes,[6] the analogous Fe(II) species have found only limited attention, and detailed mechanistic studies seem to have been confined to chelate complexes.[5,7] This must be due to the scarcity of *low-spin* iron(II) compounds with *monodentate* ligands.

(6) (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 4; (b) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, Chapter 3.

(7) J. Burgess, *Chem. Commun.*, 1422 (1969).

(8) *Cf.* the data in Table I with those for Hb₄(CO)₄ → Hb₄(CO)₃ + CO (k_{-1}) (19°, H₂O, pH 9.1): k_{-1}, 2.9 × 10⁻²; $\Delta H_{-1}*$, 23 kcal/mol: Q. H. Gibson, *Progr. Biophys. Chem.*, 9, 1 (1959).