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 ($O_2$, $\Delta H_2{}^*$) 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, $[CoCl(Ph_3P)_3]$, reportedly *tetrahedral*,[8] is relatively inactive toward $H_2$ and $O_2$.[22]

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[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 ($d^6$) Octahedral Ferrous Complexes

*Sir:*

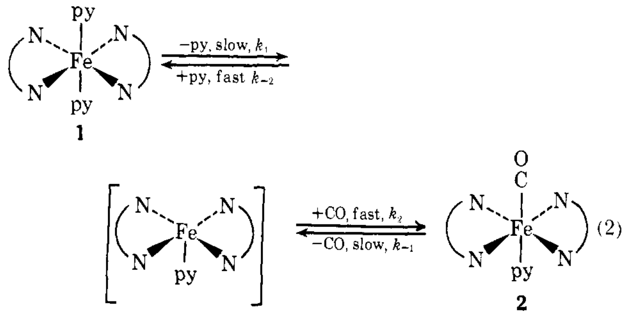
In search for simple inorganic imitators for some naturally occurring iron derivatives, we have prepared a new series of Fe(II) complexes **1** (**1** = *trans*-$[Fe(DPGH)_2L_2]$, where DPGH = bidentate diphenylglyoximato univalent anion; L = pyridine (py) and substituted pyridines, piperidine, imidazole, nicotine, or $Ph_3P$) 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

$$trans\text{-}[Fe(DPGH)_2L_2]\ (\mathbf{1}) + CO \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} trans\text{-}[Fe(DPGH)_2L(CO)]\ (\mathbf{2}) + L \quad (1)$$

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, $\nu_{CO}$ = 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 addition 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



N–N = DPGH

$$\text{rate} = -d[\mathbf{1}]/dt = \{k_1/[1 + (k_{-2}/k_2)([py]/[CO])]\}[\mathbf{1}] \quad (3)$$

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

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[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) ($d^7$).[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 ≃ 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, $[Fe(DPGH_2)(CH_3CO_2)_2]$ ($DPGH_2$ = *neutral* diphenylglyoxime), contains spin-free Fe(II), $\mu$ = 4.2 BM.

[5] In light of the overwhelming available data on the substitution mechanisms involving octahedral low-spin ($d^6$) 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.[6,7] 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 $Hb_4(CO)_4 \rightarrow Hb_4(CO)_3 + CO$ ($k_{-1}$) (19°, $H_2O$, pH 9.1): $k_{-1}$, $2.9 \times 10^{-2}$; $\Delta H_{-1}{}^*$, 23 kcal/mol: Q. H. Gibson, *Progr. Biophys. Chem.*, **9**, 1 (1959).

addition of pyridine to the intermediate (eq 2) is *ca.* four times faster than that of CO to the same species.

The kinetic and activation data, summarized in Table I, are in accord with the proposed reaction paths (eq 2). (1) The entropies ($\Delta S^*$) are positive, as expected for a dissociative type mechanism. (2) The rates of CO addition ($k_1$) increase with decreasing basicity of L, implying that the rate-determining step depends on the removal of the amine (L) from **1**. Furthermore, the activation energies, $\Delta H_1^*$ (Table I), are proportional to the squares of the Fe–N stretching frequencies in **1** ($\nu_{\text{FeN}}$: *m*-Clpy, 347; py, 350; *p*-$CH_3py$, 368 $cm^{-1}$, Nujol) which, altogether, relate the dynamics of the substitution to the Fe–L bond properties in **1** (eq 1). The rate constants ($k_1$) also show a dependence on the electronic excitation energies of the reactant complexes **1** (*E*, Table I), and the latter have been found to increase linearly with the p$K_B$ of the corresponding pyridines. (3) In contrast, the rate and activation parameters for decarbonylation of **2** are nearly invariant, which is compatible with a dissociative mechanism for this reaction in view of the closeness of the spectral data for the three carbonyl complexes, *E* (Table I) and $\nu_{\text{CO}}$: *p*-$CH_3py$, 1995; py, 1996; *m*-Clpy, 2000 $cm^{-1}$ (Nujol). It is to be noted that these CO stretching frequencies are somewhat higher than those found in analogous CO–heme–pyridine derivatives (1970–1980 $cm^{-1}$)[9] which appears to reflect a basicity difference between the two types of planar ligand systems, heme > bis-DPGH.

**Table I.** Electronic Spectral Data and Kinetic and Activation Parameters[a] for the Dissociation of Base (L) and Carbon Monoxide from **1** and **2**, Respectively (Eq 1, 2), in Chlorobenzene at 25°

| Reactant | | | $\Delta H^*$, | |
|---|---|---|---|---|
| L | *E*, kK[b] | $10^5k$, $sec^{-1}$ | kcal/mol | $\Delta S^*$, eu |
| | **1** $[Fe(DPGH)_2L_2] \xrightarrow{k_1} L$ | | | |
| *p*-$CH_3py$ | 17.8 | 228 | 24.7 | 21 |
| py | 18.1 | 422 | 23.6 | 19 |
| *m*-Clpy | 18.7 | 1810 | 23.2 | 20 |
| | **2** $[Fe(DPGH)_2L(CO)] \xrightarrow{k_{-1}} CO$ | | | |
| *p*-$CH_3py$ | 24.2 | 2.62 | 26.3 | 19 |
| py | 24.2 | 2.50 | 26.0 | 17 |
| *m*-Clpy | 24.3 | 5.33 | 26.8 | 21 |

[a] The first-order kinetic constants were determined spectrophotometrically under these conditions: 20, 25, 30, 35°; $3 \times 10^{-5}$ *M* solutions in complex; $k_1$, $p_{\text{CO}}$ (constant) = 190–750 mm; $k_{-1}$, $p_{\text{CO}}$ (constant) $\simeq$ 0 mm, [py] = $(1\text{–}6) \times 10^{-2}$ *M*. Maximum standard deviations: $k_1$, $k_{-1}$, $\pm 2\%$; $\Delta H_1^*$, $\pm 0.5$, $\Delta H_{-1}^*$, $\pm 1.5$ kcal/mol; $\Delta S_1^*$, $\pm 1.7$, $\Delta S_{-1}^*$, $\pm 5$ eu. [b] The energy corresponding to the longest wavelength absorption band in the visible spectra of the complexes; $a_{\max} = 8110\text{–}17{,}500$ $M^{-1}$ $cm^{-1}$.

**Acknowledgment.** This research was supported by the National Institutes of Health and the Environmental Protection Agency.

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(9) (a) J. H. Wang, A. Nakahara, and E. B. Fleischer, *J. Amer. Chem. Soc.*, 80, 1109 (1958); (b) J. O. Alben and W. S. Caughey, *Biochemistry*, 7, 175 (1968).

(10) Teijin, Ltd. Predoctoral Fellow; on leave of absence from Teijin, Ltd., Tokyo, Japan.

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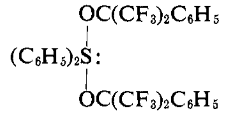
## Sulfuranes. IV. The X-Ray Crystal Structure of a Diaryldialkoxysulfurane

*Sir:*

We report the results of a single-crystal X-ray structure determination on the recently described[1] first example of a tetracoordinate sulfur(IV) compound lacking halogen atom ligands, sulfurane **1**. The $^{19}F$ nmr evidence that the alkoxy ligands of **1** occupy geometrically equivalent positions in the solution phase is confirmed in the crystal and these positions are identified as the apical positions of a trigonal bipyramid.



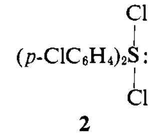
$$(C_6H_5)_2\overset{OC(CF_3)_2C_6H_5}{\underset{OC(CF_3)_2C_6H_5}{S}}:$$

**1**

Multiple recrystallizations of moisture-sensitive[1,2] **1** from ether–pentane were carried out using vacuum-line techniques. The transparent, colorless crystals were sealed in thin-walled glass capillaries in a nitrogen atmosphere. The following crystal data were obtained for $C_{30}H_{20}O_2F_{12}S$: mol wt 672.1; triclinic; $a = 10.026$ (3), $b = 14.268$ (3), $c = 10.802$ (3) Å; $\alpha = 109°\ 50'$ (2′), $\beta = 92°\ 52'$ (2′), $\gamma = 95°\ 20'$ (2′); $V = 1447$ Å$^3$; $Z = 2$; $\rho_{\text{calcd}} = 1.54$ g $cm^{-3}$; $F(000) = 680$; space group, $P1$ or $P\bar{1}$, the latter choice being established by the results of the analysis.

Two crystals were used to obtain the intensity data on a Picker FACS-1 diffractometer. As the sulfurane reacted with or dissolved in the solvents in every glue that we tried, the crystals had to be wedged between the walls of the capillary, and consequently they frequently moved and had to be realigned (on the order of 20 times). A total of 3364 nonzero reflections was obtained using Cu K$\alpha$ radiation. The structure was solved by Patterson heavy-atom methods involving sulfur, and at the present stage of refinement (hydrogen atoms located and anisotropic thermal parameters for the nonhydrogen atoms) the crystallographic *R* factor is 0.070. A view of the structure is shown in Figure 1.

Among the tetracoordinate sulfur(IV) compounds which have been isolated and characterized are $SF_4$ and a number of its derivatives[3] and several analogous compounds with S–Cl bonds.[4,5] A preliminary X-ray investigation[6] of a compound postulated to have the structure of a spirodiaryldiacyloxysulfurane showed that the molecule had $C_2$ molecular symmetry in the crystal. This would be consistent with the sulfurane structure, as is the reported chemical evidence.



$$(p\text{-}ClC_6H_4)_2\overset{Cl}{\underset{Cl}{S}}:$$

**2**

Of the halosulfuranes, the unstable adduct of chlorine and 4,4′-dichlorodiphenyl sulfide is perhaps most

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(1) J. C. Martin and R. J. Arhart, *J. Amer. Chem. Soc.*, 93, 2339, 2341 (1971).

(2) J. C. Martin and R. J. Arhart, *ibid.*, 93, 4327 (1971).

(3) For a review, see E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, 20, 245 (1966).

(4) I. B. Douglass, K. R. Brower, and F. T. Martin, *J. Amer. Chem. Soc.*, 74, 5770 (1952).

(5) N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson, *ibid.*, 91, 5749 (1969).

(6) I. Kapovits and A. Kálmán, *Chem. Commun.*, 649 (1971).