calculated by combining Eqs. 2′ to 8;

$$\ln D = -U/kT \qquad (9)$$

From Eq. 9, one finds ln D is linear with ϵ^2 $(1 + \epsilon/\gamma)$. By plotting the observed values of D logarithmically against ϵ^2 $(1 + \epsilon/\gamma)$. reasonably straight lines are obtained (Figs. 5 and 6). The observed values for KCl are in good agreement with the calculated values (Fig. 6 and Table 2). The case of $NaNO_3$ presents the straight line in Fig. 5, but the "observed" line disagrees considerably from the calculated one.

The model discussed is primarily an application of that presented in the theory of lattice defects (*2*). This model can be applied only in the case where the substituting ion is larger than the host ion. The experimental evidence suggests that this model can be used for the approximate calculation of trace element partition coefficients in ionic crystals. The calculation could also be applied to the distribution of the chemically similar trace elements, such as rare-earth elements, in minerals to provide a relation between the partition coefficients and the ionic radii.

HIROSHI NAGASAWA
Faculty of Science, Gakushuin
University, Mejiro, Toshima-ku,
Tokyo, Japan

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7. I thank Professors K. Kigoshi, A. Okawa, and Y. Nakagawa for their advice and encouragement. Supported by grants of Matsunaga Science Foundation.

9 March 1966

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Reversible Combination of Carbon Monoxide with a Synthetic Oxygen Carrier Complex

Abstract. *Chlorocarbonyl-*bis*(triphenylphosphine)iridium(I), in solution, reacts reversibly with carbon monoxide under normal conditions, one molecule per metal atom. Formation of a 1 : 1 metal complex—CO adduct is verified by CO absorption measurements and the infrared spectrum of the adduct measured* in situ. *The spectrum suggests that the metal—C—O bonding is of the type found in conventional metal carbonyl.*

Although the reversible combination of carbon monoxide with the iron atom in hemoglobin and in related natural molecules has been extensively investigated (*1*), there appear to be no previously reported examples of *synthetic* transition metal complexes reacting in the same manner (*2*). The discovery of reversible oxygenation (*3*) of a synthetic metal complex, chlorocarbonyl-*bis*(triphenylphosphine)iridium(I) (*4*), shown in equation 1 (*5*),

$$[IrCl(CO)(Ph_3P)_2] + O_2 \rightleftarrows [O_2IrCl(CO)(Ph_3P)_2] \qquad (1)$$

immediately led us to consider other possible analogies between this inorganic system and biological oxygen carriers. As a result of these efforts, I wish to report the reversible carbonylation of the same parent compound,

$$[IrCl(CO)(Ph_3P)_2] + CO \underset{k_1}{\overset{k_2}{\rightleftarrows}} [(CO)IrCl(CO)(Ph_3P)_2] \qquad (2)$$

and the probable molecular configuration of the carbon monoxide adduct as deduced from gas absorption and spectroscopic measurements, structural properties of other adducts of the carrier complex, and a reported study of CO exchange in related metal complexes (*6*).

When a solution of $[IrCl(CO)(Ph_3P)_2]$ in benzene, toluene, or chloroform is flushed with carbon monoxide at room temperature and atmospheric pressure, the characteristic yellow color of the complex disappears, and the solution becomes nearly colorless within minutes. When the CO is allowed to escape from the solution, the original color reappears rapidly, and yellow crystals of the starting material can be recovered by precipitation with alcohol or by evaporation of the solvent. The CO adduct, $[(CO)IrCl(CO)(Ph_3P)_2]$, can be synthesized in white crystalline form by evaporating to dryness a CO-saturated solution of the metal complex in chloroform by means of a vigorous flow of carbon monoxide through the solution at room temperature. Both the crystals and the solutions of the adduct appear to be stable in an atmosphere of CO. Exposure to air causes both the reverse reaction (Eq. 2) and a reaction of the adduct with oxygen (*7*).

Volumetric measurements of carbon monoxide uptake by the parent compound in toluene solution indicate a 1 : 1 attachment of CO to the metal complex. At 16°C and 700 mm-Hg of CO (constant), the equilibrium concentration of the adduct is 93 mole percent of the total iridium concentration present in solution (1.87×10^{-3} mole/liter), and the value of the equilibrium constant (K_C) is 1.91×10^5 liter $mole^{-1}$ (*8*). Under the same conditions, the rate constant for the bimolecular synthetic reaction, k_2, is 43.4 liter $mole^{-1}$ sec^{-1}; for the dissociative reaction, calculation from K_C and k_2 gives $k_1 = 2.27 \times 10^{-4}$ sec^{-1}, the reverse rate constant (Eq. 2). Repeated cycling of carbonylation-decarbonylation does not measurably affect the pertinent properties of the reacting complexes. In a quantitative experiment, after the CO-uptake measurement the gas was completely removed from the system which was then resaturated under the original conditions (16°C, 700 mm-Hg of CO); the results of the two absorptions were identical.

The data of the infrared spectra of the CO adduct are given in Table 1 (*9*), together with those for the parent compound which are listed for comparison. The spectrum of the crystalline adduct, measured immediately after it was synthesized, showed no absorption bands attributable to the starting material. After 20 minutes in air, the appearance of the 1956 cm^{-1} band (Table 1) indicated that some desorption of CO had occurred, and after 40 hours, about one-half of the sample had been converted to the oxygen adduct $[O_2IrCl(CO)(Ph_3P)_2]$ (*7*).

The solutions of the CO adduct to be measured were prepared in the absence of oxygen, and a CO pressure of 1 atm or more was maintained above the solution in the infrared cell as the spectrum was obtained. Under these conditions, the presence of the parent compound was not detectable. After 5 days under carbon monoxide, the same solution gave a spectrum that was essentially identical with the original.

The interpretation of the infrared spectrum of the CO adduct is related to the coincidental fact that the parent compound $[IrCl(CO)(Ph_3P)_2]$ already contains one carbon monoxide ligand. Hence, the adduct is expected to repre-

Table 1. Carbonyl and iridium-chlorine vibrational frequencies (in cm^{-1}) in the parent compound $[IrCl(CO)(Ph_3P)_2]$ and its reversible CO adduct $[(CO)IrCl(CO)(Ph_3P)_2]$. vs, Very strong; s, strong; m, medium; w, weak.

Medium	$[IrCl(CO)(Ph_3P)_2]$	$[(CO)IrCl(CO)(Ph_3P)_2]$
	ν_{CO} Vibrational mode	
Crystals*	1956 vs	1923 s, 1976 vs
Chloroform	1967 vs	1934 s, 1988 vs
Toluene	1968 vs	1933 s, 1982 vs
	δ_{CO} Vibrational mode	
Crystals*	602 m	562 m
Chloroform	605 m	570 m
	ν_{IrCl} Vibrational mode	
Crystals*	320 m	234 w (?)
Chloroform	325 m	235 w (?)

*Measured as a Nujol mull.

sent a dicarbonyl complex and to exhibit two infrared-active absorption bands derived from C—O stretching motions (ν_{CO}). The observed spectrum (Table 1) agrees with this proposition, and the two new bands in the 1900 to 2000 cm^{-1} region confirm that the added CO molecule is bonded to the central metal atom (*11*). Comparison of the infrared spectra of the solutions and crystals of $[(CO)IrCl(CO)(Ph_3P)_2]$ shows that the complex has the same molecular configuration in both environments (*12*).

Important information regarding the molecular structure of the new five-coordinated dicarbonyl complex of iridium emerges from a carbon monoxide exchange study on $[RhCl(CO)(Ph_3P)_2]$ (Eq. 3) (*6*), a compound which is isoelectronic and isostructural with the CO carrier complex $[IrCl(CO)(Ph_3P)_2]$ (*13*).

$$[RhCl(CO)(Ph_3P)_2] + {}^{14}CO \rightarrow [RhCl({}^{14}CO)(Ph_3P)_2] + CO \qquad (3)$$

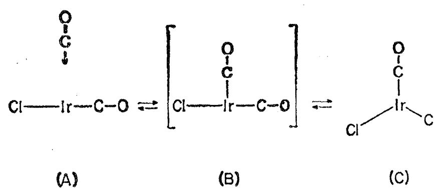

Fig. 1. Proposed mechanism for the reversible carbonylation of $[IrCl(CO)(Ph_3P)_2]$, Eq. 2. Two-dimensional idealized diagrams of the starting compound (*A*), the activated complex (*B*), and the CO adduct (*C*). The two *trans*-Ph_3P groups, present in all three species but not shown in the diagrams, are normal to the plane of the paper; that is (*A*) is a tetragonal plane, (*B*) is a tetragonal pyramid, and (*C*) is a trigonal bipyramid.

Gray and Wojcicki (*6*) report that the carbonyl group in the rhodium complex exchanges immeasurably quickly with radiocarbon monoxide at −20°C in chloroform (Eq. 3). This result, together with my observations, strongly suggests that the exchange occurs via a five-coordinated CO adduct (*14*) in which the two carbonyls are equivalent (Fig. 1*C*). In other words, the observed rapid CO exchange in $[RhCl(CO)(Ph_3P)_2]$ requires an intermediate complex in which the entering and leaving CO molecules are indistinguishable (or nearly so), and such a configuration can readily be proposed on the basis of the data presented here (Fig. 1).

Of the numerous possible geometrical isomers (*16*) of $[(CO)IrCl(CO)(Ph_3P)_2]$ (*17*), the one shown in Fig. 1*C* agrees best with all the available evidence. This structure allows the two CO ligands to occupy equivalent positions, and it represents a minimum modification of the parent structure (Fig. 1*A*) (*16*). It thus best explains the facile reversibility of the carbonylation reaction. Furthermore, the proposed configuration is fully compatible with the established structural properties of other adducts of the carrier complex; for example, the two triphenylphosphine ligands have been found to retain their *trans* positions (*16*) in $[O_2IrCl(CO)(Ph_3P)_2]$ (*3, 18*), $[H_2IrCl(CO)(Ph_3P)_2]$ (*13*), and $[(SO_2)IrCl(CO)(Ph_3P)_2]$ (*15, 19*). Finally, the observed infrared spectral bands can be readily assigned to the normal modes of vibration of the planar $\{IrCl(CO)_2\}$ unit (Fig. 1*C*) having C_{2v} symmetry (*20*) (frequencies, in cm^{-1}, are of the spectra of the crystals; Table 1) as follows: 1923, symmetric C—O stretch (A_1); 1976, antisymmetric C—O stretch (B_2); 562, C—O bend (A_1); 234, Ir-Cl stretch (A_1) (*21*).

According to the properties of the reversible CO adduct described in this note, the iridium—C—O bonding is of the same type as found in conventional transition metal carbonyl. Hence, this study suggests a link between the latter class of compounds and the CO adducts of some important biological molecules, such as hemoglobin, which, because of their complexity, often escape direct observation of their structures and the metal-substrate bonding. It should be noted that in our proposed configuration (Fig. 1*C*) the orientation of carbon monoxide relative to the metal atom is analogous to that suggested for the hemoglobin-CO complex (*22*). In conclusion, I wish to point out that the present results and their interpretation are also contributing to our understanding of the nature of intermediates in catalytic reactions, homogeneous (*23*) and heterogeneous (*24*), involving carbon monoxide as a reactant. Analogous suggestions have previously been made for the reversible reactions of the same parent compound with hydrogen (*13, 25*) and oxygen (*3*).

L. VASKA

Mellon Institute, Pittsburgh, Pennsylvania, and Department of Chemistry, Clarkson College of Technology, Potsdam, New York

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2. I refer here to the reversible formation of a 1 : 1 adduct of the central metal atom of a complex with carbon monoxide in which the CO is bonded to the transition metal and to no other atom or group. The reversible reaction of $Co_2(CO)_8$ with carbon monoxide at elevated temperatures and CO pressures has been reported to occur, but the resulting adducts have not been interpreted as 1 : 1 complexes [S. Metlin, I. Wender, H. W. Sternberg, *Nature* **183**, 457 (1959)].
3. L. Vaska, *Science* **140**, 809 (1963).
4. ——— and J. W. DiLuzio, *J. Amer. Chem. Soc.* **83**, 2784 (1961).
5. Ph_3P is $(C_6H_5)_3P$,(triphenylphosphine).
6. H. B. Gray and A. Wojcicki, *Proc. Chem. Soc.* **1960**, 358 (1960).
7. Decarbonylation in solution when exposed to air is followed by oxygenation of the parent compound, and the final product is $[O_2IrCl(CO)(Ph_3P)_2]$ (*3*). The same sequence of reactions occurs with the crystals of the CO adduct, but there also appears to be a concurrent direct reaction of the adduct with oxygen, and the over-all product is a complex mixture. Owing to these properties, elemental analysis of the solid CO adduct is impractical at present. [Note also that the calculated values (percent by weight) of the elements in the adduct differ only slightly from those of the starting material; the theoretical molecular weights are 808 and 780, respectively; see Eq. 2.]
8. Calculated from the molar concentrations of the three reacting species at equilibrium; the concentration of CO was obtained by a separate measurement of the solubility of CO in toluene.
9. In addition to the absorptions represented in Table 1, the spectra of the complexes (200 to 4000 cm^{-1}) show bands derived from the triphenylphosphine ligands (*10*, note 17).
10. L. Vaska, *J. Amer. Chem. Soc.* **86**, 1943 (1964).
11. This spectroscopic evidence eliminates the rather unlikely possibility that the reversible CO is attached to a ligand. (The quantitative CO-uptake measurements and the accompanying color change do not, of course, by themselves provide unequivocal information about the metal complex—CO bonding.)
12. The relatively small frequency shifts (crystals → solutions) of all spectral bands (Table 1) parallel one another and also those of the parent compound.
13. L. Vaska and R. E. Rhodes, *J. Amer. Chem. Soc.* **87**, 4970 (1965), and references quoted therein.
14. Although no measurable CO uptake by $[RhCl(CO)(Ph_3P)_2]$ was found under the conditions reported for the iridium analog, this observation does not contradict the proposed CO-exchange (Eq. 3) mechanism (compare Fig. 1); the experimental finding implies that

the equilibrium is far in the direction of the starting complex (Eq. 2). The two isostructural Ir and Rh complexes usually appear to undergo analogous reversible addition reactions, but [$RhCl(CO)(Ph_3P)_2$] is considerably more stable (*15*) which renders its adduct often undetectable (*13*).

15. L. Vaska and S. S. Bath, *J. Am. Chem. Soc.* **88**, 1333 (1966).
16. On the basis of two commonly encountered configurations there are eleven possible geometrical isomers of the five-coordinated complex: five isomers are based on trigonal bipyramidal and six on tetragonal pyramidal configurations. Of the 11 possible isomers, there are five isomers in which the two CO ligands are equivalent, three in which the two Ph_3P groups are *trans* to one another, and two structures in which both of these conditions are met: (i) a *trans*-$(Ph_3P)_2$—*trans*-$(CO)_2$ tetragonal pyramid with Cl at the apex and (ii) the configuration in Fig. 1*C*. The formation of the latter from the starting complex (Fig. 1*A*) involves less structural change than the formation of (i).
17. According to the evidence presented here, the two carbon monoxide ligands in the CO adduct appear to occupy equivalent positions. Hence, the formula of the adduct should be written as [$IrCl(CO)_2(Ph_3P)_2$]. The alternative expression which is used in text and in Table 1 emphasizes the reversibility of the carbonylation reaction (Eq. 2 and Fig. 1), and its use is thus appropriate in the context of this report.
18. S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.* **87**, 2581 (1965).
19. ———, *Inorg. Chem.* **5**, 405 (1966).
20. For interpretation of vibrational spectra of carbonyl complexes, see, for example, K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds* (Wiley, New York, 1963), pp. 176–182. See also Vaska (*10*) and references quoted therein.
21. This assignment is uncertain at present because of the low intensity of the band and because it occurs near the lower end of the available frequency range of the spectrophotometer used (200 cm^{-1}, Beckman IR-12). It is certain, however, that the original ν_{IrCl} in the spectrum of the parent compound (Table 1) is absent in the spectrum of the CO adduct, and that it has probably shifted to a lower frequency, in agreement with the increase of the coordination number of iridium from four to five.
22. J. S. Griffith, *Proc. Roy. Soc. London Ser. A* **235**, 23 (1956), and earlier papers cited therein.
23. H. W. Sternberg and I. Wender, in *International Conference on Coordination Chemistry* (Chemical Society, Special Publication No. 13, London, 1959), p. 35.
24. R. P. Eischens, *Science* **146**, 486 (1964).
25. L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.* **84**, 679 (1962).
26. This is part III of a series, "Activation of molecular oxygen and related molecules by transition metal complexes." (Part II is reference *15*.) I thank R. E. Rhodes and W. V. Miller for technical assistance. Supported in part by NIH grant HE 09678.

21 March 1966 ■

Osmotic Pressure Influence in Germination Tests for Antibiosis

Abstract. *A common test for the presence of toxic organic substances in plant tissues, and therefore of the potential role of antibiosis (specifically allelopathy) in native plant communities, has been to apply a water extract of the tissues in germination tests of cultivated annuals. The observed osmotic pressure of the extracts can be high, and sucrose solutions of similar osmotic pressure result in a depression of germination and early development. Thus in the aforementioned type of test, extracts must be diluted to an osmotic pressure no greater than 0.5 atmospheres.*

The significance of chemical competition between higher plants, allelopathy, has been debated for many years (*1, 2*). The earliest studies were directed toward relieving the apparent "soil sickness" that followed cultivation of certain crops such as citrus fruits. Borner (*2*) concluded that the soil deterioration phenomenon was insufficiently investigated but that there was enough evidence to show that some soils could be made poisonous to other plants by organic compounds originating with a preceding plant cover. He noted also that in tests for the occurrence of toxic compounds, attention should be directed to their identification, as well as to the study of their physiological effects upon other plants or associated microorganisms.

The difficulty in isolating chemical constituents of water extracts from parts of plants growing both above and below ground has restricted study to a few of the most obvious examples (*3–5*) with readily distinguished toxic chemicals. More rapid survey techniques have been sought by investigators concerned with the occurrence of allelopathy among native plants, whether for pharmacological and medical studies (*6*), or as a factor in the distribution of plants in native vegetation (*7*). These methods have ranged from direct use of plant tissue remains, suspected of containing a toxic material, to application of a water extract from the plant parts. The plant materials or extracts usually are applied directly to potted plants or germinating seedlings (*4, 5, 8, 9*). In tests of germination and early seedling development, the responses are clear and readily measurable. With the wider acceptance of allelopathy as a fact, there have been increasing data purporting to show toxic materials in the water extracts from many native species.

Only a few of these papers consider that a moderate osmotic pressure in the extract could repress growth and germination through a direct influence on water uptake (*10, 11*). In general, either this influence has been ignored, or the assumption is made that since the materials are water extracts, there will be rapid build-up in osmotic value within the cell, and therefore normal uptake of water. Koller (*10*) found that a water extract of *Atriplex* fruit bracts had an osmotic pressure of 6.31 atm, but concluded that his data did not eliminate the possibility of an allelopathic substance being present. Torres *et al.* concluded that osmotic pressure was not a factor in germination inhibition by *Zinnia*. However, the osmotic concentration of their *Zinnia* extract was less than one atm.

In most of these studies the retarding of germination, and the depression of seedling growth, has been assessed by comparison with control seedlings cultured in distilled water. Since the object of the tests has been to demonstrate and measure the strength of allelopathic effects, a more suitable control would be a nontoxic substance, such as sucrose, giving osmotic concentrations in the same range as those of the diluted extracts. In this study a 0.05*M* sucrose solution in a simple columnar osmometer supported a column of water equal in height to that supported by a 1:10 extract of *Antennaria*. The osmotic pressures of the two solutions were 1:3 atm (*12*) and 2.4 atm respectively. The sucrose solutions were therefore adopted as controls against which to measure the degree of inhibition produced by the plant extracts. Additional controls cultured with distilled water were used as necessary.

Materials from five species of plants were used to prepare the plant extracts. *Lonicera tatarica* leaf tissue, whole *Antennaria neglecta* plants, and the rhizomes of *Aster macrophyllus*, *Pteridium aquilinum* and *Helianthus laetiflorus* were oven-dried and ground, and the water-soluble materials were extracted. Production of allelopathic substances had been suggested for *Aster*, *Antennaria*, *Helianthus*, and *Pteridium* (*3, 9*); *Lonicera* was suspected of producing a toxic substance because of its ability to invade native Wisconsin plant communities.

In the preparation of the extracts, ten parts by weight of hot, double-distilled water were poured into a beaker containing 1 part of plant tissue. The material was stirred for 10 minutes and then strained with light manual pressure through two layers of cheese