# Synthesis Using Transition Metal Diatomic Molecules. Dirhodium Octacarbonyl, $Rh_2(CO)_8$, and Diiridium Octacarbonyl, $Ir_2(CO)_8$

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**Abstract:** Using transition metal diatom synthetic techniques the elusive binuclear carbonyl complexes $Rh_2(CO)_8$ and $Ir_2(CO)_8$ are shown by infrared spectroscopy to be the products (along with the respective mononuclear complexes $Rh(CO)_4$ and $Ir(CO)_4$) of the 15°K matrix cocondensation reactions of Rh and Ir atoms with pure CO, under conditions of high metal concentrations. The binuclear octacarbonyl complexes are also formed in the matrix dimerization reactions $2Rh(CO)_4 \rightarrow Rh_2(CO)_8$ and $2Ir(CO)_4 \rightarrow Ir_2(CO)_8$ at 45-50°K. A simple analysis of the statistical and surface reaction pathways to $M_2(CO)_8$ and $M(CO)_4$ is presented and leads to binuclear–mononuclear concentration ratios which are proportional to the metal/CO matrix ratio. Using these techniques, the effect of varying the metal/CO matrix ratio on the relative absorbances of the appropriate spectral bands was investigated for the Rh–CO reaction in the range 1/10 to 1/1000. The results provide convincing evidence for the binuclear octacarbonyl formulation. By comparison with dicobalt octacarbonyl, the complexes $Rh_2(CO)_8$ and $Ir_2(CO)_8$ are found to exist in the bridge bonded form, $Rh_2(CO)_8$ disproportionating under dynamic vacuum conditions to bridge bonded $Rh_4(CO)_{12}$ at about −48°C and $Ir_2(CO)_8$ similarly to bridged bonded $Ir_4(CO)_{12}$ at about −58°C, indicating that under comparable conditions $Ir_2(CO)_8$ is somewhat less stable than $Rh_2(CO)_8$. Evidence for the nonbridged (by analogy with $Co_2(CO)_8$, high temperature) isomer was not obtained for $Rh_2(CO)_8$ or $Ir_2(CO)_8$, probably because of the instability of the bridge bonded (low temperature) isomer with respect to disproportionation to the tetranuclear cluster complex. The low temperature stability of $Rh_2(CO)_8$ and $Ir_2(CO)_8$ is certainly consistent with the difficulties previously experienced by various groups of workers who attempted to synthesize and characterize the complexes by room temperature techniques.

Until very recently, dicobalt octacarbonyl, in its bridged and nonbridged isomeric forms, was the only well-defined "parent" binuclear carbonyl complex of the Co, Rh, and Ir group of metals.[1-3] In brief, the synthesis of $Ir_2(CO)_8$ and $Rh_2(CO)_8$ was first claimed in 1940–1943 by Hieber and Lagalles[4,5] by the action of CO on the freshly prepared metal at high CO pressures and temperatures (*ca.* 450 atm, 200°). Since then many groups of workers[6,7] have tried various different approaches, without success, to substantiate the authenticity of $Rh_2(CO)_8$ and $Ir_2(CO)_8$. However, in 1970 Whyman[8] reported infrared spectroscopic data for paraffin hydrocarbon solutions of $Rh_4(CO)_{12}$ under conditions of high CO pressure (*ca.* 430 atm) and low temperatures (*ca.* −19°). Aside from the CO absorptions associated with $Rh_4(CO)_{12}$, *new* CO absorptions were observed which by comparison with the bridge bonded form of $Co_2(CO)_8$ were assigned to the bridge bonded form of $Rh_2(CO)_8$ (Table I), presumably arising from the disproportionation equilibrium

$$Rh_4(CO)_{12} + 4CO \rightleftharpoons 2Rh_2(CO)_8$$
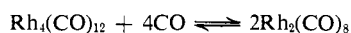
The only criticism of this study is that one cannot eliminate the possibility that the spectral changes might simply arise from the freezing out of one or more un-

### Table I. Infrared Spectra of $M_2(CO)_8$ (where M = Co, Rh, or Ir)

| $Co_2$-$(CO)_8^{b,c}$ | $Co_2$-$(CO)_8^{b,d}$ | $Rh_2$-$(CO)_8^{a,c}$ | $Ir_2$-$(CO)_8^{a,c}$ | $Rh_2$-$(CO)_8^{b,c}$ |
|---|---|---|---|---|
| 2071 vs | | 2060 s | 2095 m s | 2086 s |
| | 2069 vs | | | |
| 2044⎫vs 2042⎭ | | 2043 s sh⎫ᵉ 2038 s ⎭ | 2068 s br | 2061 s |
| | 2031 m s | | | |
| | 2022 vs | | | |
| 1866 sh | | 1852 w sh | 1848 w sh | 1860 w |
| 1857 s | | 1830 m w | 1822 m | 1845 m |

*ᵃ This study. ᵇ Whyman's study (ref 8). ᶜ Bridge bonded form. ᵈ Nonbridge bonded form. ᵉ Appears as a doublet or a singlet (2040 cm⁻¹) depending on the deposition conditions.*

stable isomers of $Rh_4(CO)_{12}$ (see for example the fluxional behavior of carbonyl cluster complexes and $Rh_4(CO)_{12}$ in solution).[9]

More recently, Whyman[10] has tried a number of similar approaches in an attempt to substantiate the existence of $Ir_2(CO)_8$, but as yet without success, and prior to this study the parent binuclear complex, $Ir_2(CO)_8$, remained elusive.

We and other groups of workers[11] have recently shown that a useful route to the synthesis of binary $ML_n$ compounds that would be difficult if not impossible to prepare by conventional means involves the matrix stabilization of the products of metal atom–ligand cocondensation reactions. In this way com-

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(6) L. Malatesta, C. Caglio, and M. Angoletta, *Chem. Commun.,* 532 (1970).
(7) P. Chini and S. Martinengo, *Inorg. Chim. Acta,* 3, 21 (1969), and references therein.
(8) R. Whyman, *Chem. Commun.,* 1194 (1970); *J. Chem. Soc., Dalton Trans.,* 1375 (1972).

(9) F. A. Cotton, L. Kruczynski, B. L. Shapiro, and L. F. Johnson, *J. Amer. Chem. Soc.,* 94, 6191 (1972); J. Bullitt, F. A. Cotton, and T. J. Marks, *ibid.,* 92, 2155 (1970).
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(11) G. A. Ozin and A. Vander Voet, *Accounts Chem. Res.,* 6, 313 (1973), and references therein.

pounds such as $Pt(CO)_4$,[12] $Pd(N_2)_3$,[13] $(N_2)_2Ni(O_2)$,[14] etc., have been synthesized and characterized using matrix isolation infrared and Raman spectroscopy.

More recently[15-17] we have shown that it is possible to control the dimerization process of metal atoms, M, to the respective diatomic molecule, $M_2$, by using a combination of carefully monitored metal deposition and matrix diffusion techniques.

In this paper we apply the diatom matrix technique and show that it provides a direct route to the synthesis of the parent binuclear carbonyl complexes $Rh_2(CO)_8$ and $Ir_2(CO)_8$.

## Experimental Section

Monatomic Rh vapor was generated by directly heating a thin (0.010 in.) ribbon filament of Rh with alternating current. Monatomic Ir vapor was obtained by directly heating with alternating current a 0.030-in. tungsten rod around the center of which were wound several turns of 0.010-in. Ir wire. The rhodium (99.99%) was supplied by McKay Inc., New York, N. Y., and the iridium (99.99%) by Johnson and Mathey, England. Research grade $^{12}C^{16}O$ (99.99%) was supplied by Matheson of Canada.

The furnace used for the evaporation of the metals has been described previously.[18] The rate of metal atom depositions was continuously monitored using a quartz crystal microbalance.[19]

To obtain quantitative data for the Rh/CO and Ir/CO matrix cocondensation reactions, it was necessary to carefully calibrate the rate of deposition of both metal and gas onto the CsI sample window. In the case of the metal flows, the system was initially calibrated by setting a quartz crystal in place of the CsI sample window in addition to the standard crystal behind the source of metal.[18,19] As the relationship between the frequency change and mass change of the quartz crystal is accurately known,[19] it is a simple matter to determine the rate of deposition of metal onto the sample window from the rate of change of frequency of the quartz crystal positioned to receive the backward flux of metal. The true rate of deposition of carbon monoxide onto the sample window was determined from its apparent rate of deposition out of a bulb system of known volume and pressure. This was achieved from infrared absorbance measurements of CO deposited onto the sample window (of known surface area) at 15°K and by making use of the known extinction coefficient of CO. The temperature of the CsI window was monitored with an accuracy of 0.1°K using a standard chromel vs. gold 0.07% iron thermocouple in conjunction with a Fluka digital microvoltmeter. The thermocouple was embedded into the center of the CsI sample window using the recommended cryogenic epoxy Hysol 1C.

In the infrared experiments matrices were deposited on a CsI plate cooled to 15°K by means of an Air Products Displex closed cycle helium refrigerator or a liquid helium transfer system. Spectra were recorded on a Perkin-Elmer 180 spectrophotometer. Typical deposition conditions which favored the matrix reactions of Rh and Ir atoms and the formation of mononuclear complexes $M(CO)_4$ were $M/CO \leq 1/1000$. Deposition conditions which favored the formation of appreciable quantities of binuclear complexes $M_2(CO)_8$ were $1/1000 \leq M/CO \leq 1/10$ (where M = Rh or Ir).

## Results

### Dirhodium Octacarbonyl, $Rh_2(CO)_8$. An insight into the binuclear rhodium and iridium problem first came

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(18) E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Mol. Struct.*, **14**, 137 (1972).
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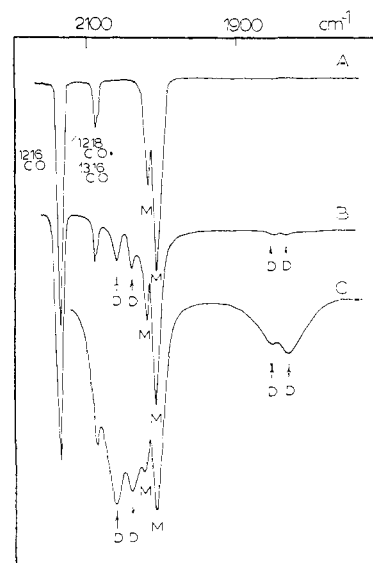


Figure 1. Matrix infrared spectrum of the products of the Rh atom CO cocondensation reaction at 15°K: (A) Rh:CO $\simeq$ 1:10,000, (B) Rh:CO $\simeq$ 1:1000, and (C) Rh:CO $\simeq$ 1:100, where the M indicates lines belonging to $Rh(CO)_4$ and the D indicates lines belonging to $Rh_2(CO)_8$. (On allowing the CO matrix to slowly pump away (ca. 50°K) the lines associated with $Rh_2(CO)_8$ remain up to 225°K, at which temperature $Rh_2(CO)_8$ is observed to disproportionate to $Rh_4(CO)_{12}$ and at room temperature to $Rh_6(CO)_{16}$; see text and Table II.)

from a detailed study of the Co–CO cocondensation reaction.[11,17,20] Using conditions designed to favor only Co atoms, we initially synthesized and characterized the $Co(CO)_4$ radical. The authenticity of $Co(CO)_4$ was independently corroborated by Crichton's, *et al.*,[21] matrix photolysis of $Co(CO)_3(NO)$ in dilute CO–Ar matrices, which also produces $Co(CO)_4$, the infrared data of which were identical with ours, showing two CO stretching modes at 2029 m and 2010 s $cm^{-1}$.

At higher rates of Co atom deposition, we were able to exclusively synthesize $Co_2(CO)_8$.[22] By carefully controlling the Co–CO concentration ratio, the conditions which favored either $Co(CO)_4$ or $Co_2(CO)_8$ could be ascertained.

Previously we had synthesized the radicals $Rh(CO)_4$ and $Ir(CO)_4$ from the matrix reactions of Rh and Ir atoms with pure CO.[23] The complexes were characterized using $^{12}C^{16}O$–$^{13}C^{16}O$ mixed isotopic substitution experiments which defined the complexes as pseudo tetrahedra.

Using Rh atom deposition rates which favor binuclear matrix reactions, the infrared spectra of the products in pure CO show, in addition to the absorptions assigned to $Rh(CO)_4$ (Figure 1A), *four* new CO absorptions. Inspection of Tables I and II shows that the new absorptions are very similar in terms of frequency and intensity to the infrared absorptions of the bridged form of $Co_2$-$(CO)_8$ as well as Whyman's bridged form of $Rh_2(CO)_8$ (Tables I and II). The close correspondence of these sets of data is quite striking and serves to authenticate the existence of $Rh_2(CO)_8$ in its bridge bonded form.

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**Table II.** Infrared Spectra[a] of Rh(CO)₄, Rh₂(CO)₈, Rh₄(CO)₁₂, and Rh₆(CO)₁₆

| Rh-(CO)₄ | Rh₂-(CO)₈ | Rh₄-(CO)₁₂[b] | Rh₆-(CO)₁₆[c] |
|---|---|---|---|
| | | | 2070 s br |
| | | 2064 s | |
| | 2060 s | | |
| | 2040 s sh[d] | | 2040 w sh |
| | | 2035 ms | |
| 2020 m | | | 2020 w sh |
| 2010 s | | | |
| | | 1870 s | |
| | 1852 w sh | | |
| | 1830 m w | | |
| | | | 1798 m |

[a] Recorded under dynamic vacuum (10⁻⁶ Torr). [b] The reported infrared spectrum of Rh₄(CO)₁₂ shows CO absorptions at 2076, 2071 vs, 2045 s, 1886 m cm⁻¹ (in solution, ref 8). [c] The reported infrared spectrum of Rh₆(CO)₁₆ shows CO absorptions at 2070 s, 2043 w, 2021 mw, and 1798 s cm⁻¹ (in solution, ref 6) and 2077, 2074 s, 2041 m, 2016 m, and 1770 s cm⁻¹ (solid, W. P. Griffith and A. J. Wickham, *J. Chem. Soc. A*, 834 (1969)). [d] Appears as a doublet (2043, 2038 cm⁻¹) depending on the deposition conditions.
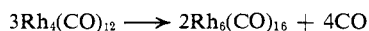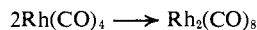
On allowing the CO matrix to warm up slowly to temperatures where the CO matrix is slowly being pumped away (*ca.* 50°K) the Rh₂(CO)₈ could be retained on the optical plate and its infrared spectrum observed as a function of temperature upwards from 10°K. In this way the stability of Rh₂(CO)₈ with respect to decomposition or disproportionation can in principle be established.

During the procedure when the CO matrix begins to break up, the Rh(CO)₄ present is observed to diffuse and dimerize, as *only* Rh₂(CO)₈ was observed at 50°K. Furthermore, the absorbances of the four new CO stretching modes are *all* observed to increase in a parallel fashion. The infrared spectrum of Rh₂(CO)₈ remains essentially unchanged up to about −48° at which temperature a spectacular transformation occurs to yield Rh₄(CO)₁₂ (Table II), presumably by loss of CO under the high vacuum conditions used in these experiments, that is

$$2Rh_2(CO)_8 \longrightarrow Rh_4(CO)_{12} + 4CO$$

At about room temperature a further transformation is observed in which Rh₄(CO)₁₂ disproportionates to Rh₆(CO)₁₆ by further loss of CO (Table II) where the bridge bonded form of Rh₆(CO)₁₆ is found to be indefinitely stable under high vacuum conditions.

In essence, the transformations

$$2Rh(CO)_4 \longrightarrow Rh_2(CO)_8$$

$$2Rh_2(CO)_8 \longrightarrow Rh_4(CO)_{12} + 4CO$$

$$3Rh_4(CO)_{12} \longrightarrow 2Rh_6(CO)_{16} + 4CO$$

have been observed in a single warm-up experiment from 15°K to room temperature. In contrast to Co₂(CO)₈, and in agreement with Whyman's observations,[8] we obtained *no* evidence for the nonbridged (high temperature) form of Rh₂(CO)₈, presumably a reflection of its instability with respect to disproportionation to the more stable Rh₄(CO)₁₂ complex.

**The Dependence of the Concentration of Binuclear Species on Metal/Matrix Gas Ratio. Further Evidence for M₂(CO)₈.** One technique that has been used

successfully by us[16] to establish the presence of binuclear reaction products in metal atom cocondensation reactions is to investigate the relative absorbances of bands as a function of metal/matrix gas ratio. Binuclear species can arise in the matrix in two ways. The first is statistical, that is, metal dimers arising from the finite and calculable probability that in one of the nearest neighbor sites about a metal atom there resides another metal atom, while the second is due to reactions in the surface region of the matrix during the first few moments following deposition and before the kinetic energy of the reagents has been accommodated, hence while the molecules are still fairly mobile.

We will now show that both of these mechanisms give rise, at least in the case of metal atoms deposited into a "reactive CO matrix" and under such circumstances that mononuclear species still predominate, to binuclear species whose concentration is proportional to the square of the metal/matrix gas ratio, while the concentration of mononuclear species is directly proportional to that ratio.

Consider the matrix reaction between a metal atom M and CO which gives rise to mononuclear carbonyls M(CO)ₙ where n = 1, 2, 3, or 4 and binuclear species M₂(CO)ₘ where, for example, m = 1–8 as in the case of the Rh–CO system. Species containing higher aggregates of metal are in general also possible. We will assume, however, that the matrix ratio, [M]₀, never becomes high enough to result in the formation of appreciable quantities of these. Let us now consider the surface reaction and the statistical factor separately.

**Surface Reaction.** We assume that only CO and M are mobile species. Accordingly only those reactions which involve at least one mobile species will be admitted. This implies that reactions of the form

$$M(CO)_n + M(CO)_{n'} \longrightarrow M_2(CO)_{n+n'}$$
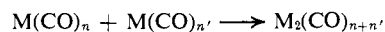
are inadmissable. The total reaction scheme for the formation of M(CO)₄ and M₂(CO)₈ is therefore as shown in Scheme I. The backward steps in these re-

**Scheme I**
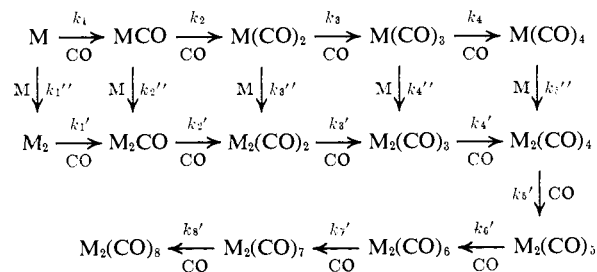


actions are assumed to be negligibly slow and are thus not considered.

**Mononuclear Species.** The rate equations for formation of mononuclear species can be written directly

$$\frac{d[MCO]}{dt} = k_1[M][CO] - k_2[MCO][CO] - k_2''[MCO][M] \quad (1)$$

$$\frac{d[M(CO)_2]}{dt} = k_2[MCO][CO] - k_3[M(CO)_2][CO] - k_3''[M(CO)_2][M] \quad (2)$$

$$\frac{d[M(CO)_3]}{dt} = k_3[M(CO)_2][CO] -$$
$$k_4[M(CO)_3][CO] - k_4''[M(CO)_3][M] \quad (3)$$

$$\frac{d[M(CO)_4]}{dt} = k_4[M(CO)_3][CO] - k_5''[M(CO)_4][M] \quad (4)$$

Since the reaction is carried out in pure CO all species of the form $M(CO)_n$ will become $M(CO)_4$ upon quenching; hence the final concentration of $M(CO)_4$ is given by

$$[M(CO)_4] = \int_0^{\tau_q} \left\{ \frac{d[MCO]}{dt} + \frac{d(M(CO)_2]}{dt} + \frac{d[M(CO)_3]}{dt} + \frac{d[M(CO)_4]}{dt} \right\} dt + [M]_{\tau_q} \quad (5)$$

where $\tau_q$ is the average quenching time, *i.e.*, the average lifetime of a species before it is immobilized within the matrix.

Substituting from eq 1–4 into eq 5 one obtains

$$[M(CO)_4] = [M]_{\tau_q} + \int_0^{\tau_q} [M]\{k_1[CO] -$$
$$(k_2''[MCO] + k_3''[M(CO)_2] + k_4''[M(CO)_3] +$$
$$k_5''[M(CO)_4])\}dt \quad (6)$$

where $k_2'' \simeq k_3'' \simeq k_4'' \simeq k_5''$ if the reactions are assumed to be diffusion limited. Integral 6 can therefore be written

$$[M(CO)_4] = [M]_{\tau_q} + \int_0^{\tau_q} [M]\{k_1[CO] -$$
$$k_2''[(M(CO)] + [M(CO)_2] + [M(CO)_3] + [M(CO)_4])\}dt$$

Under the experimental conditions considered the CO concentration far exceeds the sum of concentrations of all mononuclear species. Moreover, $k_2''$ is not expected to be markedly different from $k_1$. Accordingly integral 6 reduces to

$$[M(CO)_4] \simeq \int_0^{\tau_q} k_1[M][CO]dt + [M]_{\tau_q} \quad (7)$$

The rate of change of concentration of metal can also be written down as

$$\frac{-d[M]}{dt} = k_1[M][CO] + k_1''[M]^2$$

which reduces, for the same reasons stated above, to

$$\frac{-d[M]}{dt} \simeq k_1[M][CO]$$

which has the following solution

$$[M] = [M]_0 e^{-k_1[CO]t} \quad (8)$$

in which [CO] being in great excess is taken to be a constant and where $[M]_0$ is the initial metal concentration, hence proportional to the metal/CO ratio.

Substituting eq 8 into eq 7 and integrating, one obtains

$$[M(CO)_4] = [M]_0$$

**Binuclear Species.** The kinetic equations governing the production of binuclear species may also be written down as follows

$$\frac{d[M_2]}{dt} = \frac{1}{2}k_1''[M]^2 - k_1'[M_2][CO] \quad (9)$$

together with eight other equations of the form

$$\frac{d[M_2(CO)_n]}{dt} = k_n'[M_2(CO)_{n-1}][CO] +$$
$$k_{n+1}''[M][M(CO)_n] - k_{n+1}'[M_2(CO)_n][CO] \quad (10)$$

for $n \le 4$ and deleting the term in $k''$ for $n > 4$.

Using similar arguments as those stated for production of mononuclears the concentration of $M_2(CO)_8$ is given by

$$[M_2(CO)_8] = \frac{1}{2}k_1'' \int_0^{\tau_q} [M]^2 dt +$$
$$k_2'' \int_0^{\tau_q} [M]\left( \sum_{n=1}^4 [M(CO)_n] \right) dt \quad (11)$$

We have assumed throughout that the concentration of binuclear species is always smaller than that of mononuclears, consequently the quantity

$$\sum_{n=1}^4 [M(CO)_n] \simeq [M]_0 - [M] \quad (12)$$

Substituting eq 12 into eq 11 and eq 8 into the resulting expression and integrating, we obtain

$$[M_2(CO)_8] = K_2[M]_0^2$$

where

$$K_2 = \frac{k_1''}{4k_1[CO]} (1 - e^{-2k_1[CO]\tau_q}) +$$
$$\frac{k_2''}{2k_1[CO]} [1 + e^{-2k_1[CO]\tau_q} - 2e^{-k_1[CO]\tau_q}]$$

The result of this analysis indicates, therefore, that the ratio of the concentration of binuclear species to that of mononuclear should increase proportionately to the matrix ratio $[M]_0$. A similar analysis for metal trimers indicates that the analogous ratio involving trinuclears increases as the square of the metal-to-CO ratio.

**Statistical Concentrations of Dimers.** Assuming that aggregates larger than dimers are in negligible abundance and that there are 12 nearest neighbor sites associated with every substitutional site in the CO matrix, one can write down the metal dimer and metal monomer concentrations directly

$$[M_2(CO)_8] = 12([M]^2)(1 - [M])^{11}$$
$$[M(CO)_4] = [M](1 - [M])^{12}$$
$$[M_2(CO)_8]/[M(CO)_4] = 12[M]/(1 - [M])$$

which reduces to approximately $12[M]$ for [M] not too large.

We see therefore that both the statistical and surface reaction pathways lead to binuclear–mononuclear concentration ratios which are proportional to the matrix ratio while the appropriate ratios related to species containing larger metal aggregates vary as some higher power of the matrix ratio. It is therefore apparent that one can distinguish binuclear species from both higher aggregates and mononuclears by observing the effect of varying the matrix ratio on the relative absorbances of the appropriate spectral bands.

Using these techniques we undertook a study of the Rh/CO matrix reaction as a function of the Rh/CO ratio in the range 1/10 to 1/1000. The results of such a series of experiments showed quite clearly that at low Rh/CO ratios ($\le 1:1000$) Rh(CO)$_4$ is the only observ-
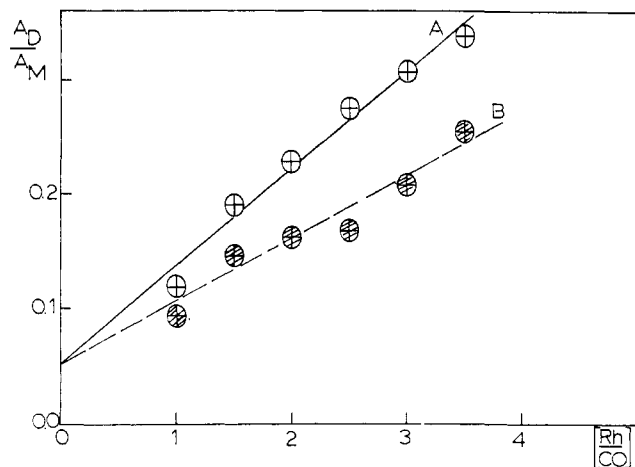
**Figure 2.** Graphical plot of the absorbance ratio, (A) $A_D^{2060}/A_{Rh(CO)_4}^{2010}$ and (B) $A_D^{2040}/A_{Rh(CO)_4}^{2010}$ vs. Rh/CO proving that D is best formulated as the binuclear species $Rh_2(CO)_8$. Abscissa is in arbitrary units.



**Figure 3.** The matrix infrared spectrum of the products of the Ir atom CO cocondensation reaction at 15°K: (A) Ir:CO $\simeq$ 1:10,000 showing well-isolated $Ir(CO)_4$, (B) the spectrum obtained in the range 15–215°K, after allowing the CO matrix (Ir:CO $\simeq$ 1:100) to slowly pump away (ca. 50°K) showing the presence of spectroscopically pure $Ir_2(CO)_8$ in the bridge bonded form, (C) the spectrum obtained on warming $Ir_2(CO)_8$ above 215°K, showing the disproportionation of $Ir_2(CO)_8$ to the bridge bonded form of $Ir_4(CO)_{12}$. The asterisk indicates a small amount of $Ir_6(CO)_{16}$ growing in (see text and Table III).

able species on deposition. However, at higher Rh/CO ratios ($\geq 1:1000$) four new lines begin to grow in at 2060, 2040 and 1852, 1830 cm$^{-1}$, coincident with the lines ascribed to $Rh_2(CO)_8$ (D) formed in the dimerization of $Rh(CO)_4$ (M).

The results of the above experiments for Rh–CO are plotted graphically in Figure 2 where a proportional increase in the absorbance ratio D/M is observed with increasing Rh concentrations. These results provide convincing evidence for the binuclear formulation $Rh_2(CO)_8$ for species D.

In summary, the infrared spectra, the Rh concentration dependence, and the formation of the new rhodium carbonyl species on allowing $Rh(CO)_4$ to dimerize are consistent with a process in which a binuclear $Rh_2(CO)_8$ complex is formed having a bridge-bonded structure analogous to the bridge-bonded form of $Co_2(CO)_8$.

**Diiridium Octacarbonyl, $Ir_2(CO)_8$.** Using methods similar to those described for the synthesis of $Rh_2(CO)_8$, we investigated the iridium–carbon monoxide cocondensation reaction. In Figure 3A and Table III the

**Table III.** Infrared Spectra[a] of $Ir(CO)_4$, $Ir_2(CO)_8$, and $Ir_4(CO)_{12}$

| $Ir(CO)_4$ | $Ir_2(CO)_8$ | $Ir_4(CO)_{12}$[b,c] |
|---|---|---|
| | 2095 m s | |
| | | 2068 s |
| | 2060 s | |
| | | 2035 m s |
| 2022 m s | | |
| 2010 s | | |
| | | 1869 m |
| | 1845 w sh | |
| | 1822 m | |

[a] Recorded under dynamic vacuum conditions. [b] Assigned to bridged form of $Ir_4(CO)_{12}$ by analogy with $Rh_4(CO)_{12}$. The non-bridged form of $Ir_4(CO)_{12}$ shows CO absorptions at 2072 s and 2032 s cm$^{-1}$ (ref 10). [c] At room temperature, the strongest lines of $Ir_6(CO)_{16}$ are just beginning to grow in (by comparison with the spectra of ref 6)

matrix infrared spectrum of well-isolated $Ir(CO)_4$[21] is shown and is characterized by two CO stretching modes at 2022 m s and 2010 s cm$^{-1}$. On increasing the rate of deposition of Ir atoms to those values which favor
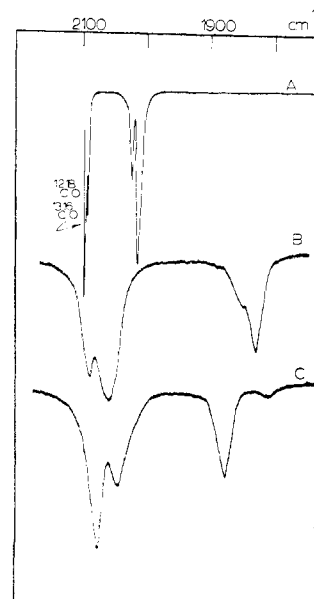
binuclear matrix reactions (Ir:CO $\simeq$ 1:100), the infrared spectra of the products in pure CO show, in addition to the absorptions assigned to $Ir(CO)_4$, four new CO absorptions (Table III) at 2095 m s, 2060 s, 1845 w sh, and 1822 m cm$^{-1}$. On allowing the CO matrix to slowly pump away (ca. 50°K) as described earlier for the Rh–CO reaction, the absorbances of the four new CO stretching modes are all observed to increase in a parallel fashion with the concomitant disappearance of $Ir(CO)_4$ (Figure 3B), a result which parallels very closely those for the bridged forms of $Co_2(CO)_8$ and $Rh_2(CO)_8$ (Table III). The spectra remain unchanged up to about $-58°$. The close correspondence of these three sets of data is again quite striking, and serves to authenticate the existence of $Ir_2(CO)_8$ in a low temperature bridge bonded form.

When $Ir_2(CO)_8$ is allowed to warm up above $-58°$ under condition of dynamic vacuum, a transformation entirely analogous to that for $Rh_2(CO)_8$ but at $-48°$ is observed (Table III). Presumably loss of CO is occurring, as the spectrum so obtained is virtually identical with that of the bridged form of $Rh_4(CO)_{12}$. This suggests that we are monitoring the disproportionation reaction

$$2Ir_2(CO)_8 \longrightarrow Ir_4(CO)_{12} + 4CO$$
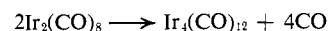
On warming the bridged form of $Ir_4(CO)_{12}$ to room temperature, the onset of another transformation can just be observed (Table III), indicating that $Ir_4(CO)_{12}$ is slowly disproportionating to $Ir_6(CO)_{16}$.

The results of this study[24] prove, therefore, that $Ir_2$-

(24) NOTE ADDED IN PROOF. We have now obtained the iridium concentration dependence of the absorbance ratio $A_D/A_M$ (as described for $Rh_2(CO)_8/Rh(CO)_4$) and find it to be linear in [Ir/CO], thereby providing convincing evidence for the binuclear formulation $Ir_2(CO)_8$.

(CO)₈ can be prepared at low temperatures in an entirely analogous fashion to that used for Rh₂(CO)₈. Both complexes exist in the bridged form analogous to the bridged isomer of Co₂(CO)₈. By comparing the temperatures at which Rh₂(CO)₈ and Ir₂(CO)₈ disproportionate to the respective bridge forms of Rh₄(CO)₁₂ and Ir₄(CO)₁₂, one is led to believe that under comparable conditions Ir₂(CO)₈ is slightly less stable than Rh₂(CO)₈ although it is not possible to estimate the magnitude of this difference from the present data. The lower stability of Ir₂(CO)₈ compared to Rh₂(CO)₈ and their instability with respect to disproportionation to Ir₄(CO)₁₂ and Rh₄(CO)₁₂ above −58° are certainly consistent with the nonobservation of the nonbridged forms of the complexes and with the difficulties previously experienced by various groups of workers in attempting to synthesize and characterize Rh₂(CO)₈ and Ir₂(CO)₈, particularly the latter, by room temperature techniques.

# Reactions of Molecular Crystals with Gases. I. Reactions of Solid Aromatic Carboxylic Acids and Related Compounds with Ammonia and Amines[1,2]

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**Abstract:** Single crystals of carboxylic acids such as benzoic and 4-chlorobenzoic acid have been found to react quantitatively with ammonia gas to give microcrystalline aggregates preserving the shape of the original crystal. No accumulation of a 2:1 (acid–ammonia) ammonium salt was detected, and single crystals of this acid–ammonium salt were themselves found to react to form the 1:1 salt. *dl*-2-Butylamine vapor could be employed instead of ammonia in the reaction with *dl*-mandelic acid. The exchange of one base for another was found to be negligible under the reaction conditions as shown by the fact that ammonium *dl*-mandelate failed to react with *dl*-2-butylamine and *dl*-2-butylammonium mandelate was unreactive toward ammonia. Preliminary kinetic studies show no correlation of reaction rate with acidity (measured in aqueous solution), crystal density, or melting point. Microscopic observation of the reaction of single crystals suggests that such reactions may be highly anisotropic.

Although investigations of reactions believed to occur between molecular crystals and gases have been reported[3,4] for many years, there have been few studies of such reactions in depth, and it is sometimes[5] difficult to decide whether or not the reaction is complicated by the presence of melt produced in intermediate stages. The question of the generality of such reactions has not been answered; innumerable instances are known to the synthetic organic chemist in which a substance vulnerable to attack by air (oxygen and moisture) in solution or in the melt is indefinitely stable as the crystalline solid. Particularly striking examples of such nonreactivity are the behavior of the dimer of triphenylmethyl free radical, which in the solid state reacts with oxygen to form an outer coating of ditrityl peroxide that protects the crystal from further oxidation,[6] and the "molecular packaging" of unsaturated fatty acids which are protected from oxidation when incorporated into solid urea-inclusion complexes.[7] Of special interest have been attempts to induce a change in the course of a reaction by carrying it out in a way which should lead to direction of the reaction path by the rigid matrix of starting material. Thus, the orientation in nuclear bromination of aromatic compounds has been studied[8] as have the reactions of crystalline metal salts of phenol with methyl

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(2) We are indebted to the National Science Foundation (NSF-GH-33634) and to the Advanced Research Projects Agency of the Department of Defense (Contract ARPA-HC-15-67-0221) for support of this work.

(3) (a) For preliminary reports of the present work see R. S. Miller, D. Y. Curtin, and I. C. Paul, *J. Amer. Chem. Soc.*, 93, 2784 (1971); (b) *ibid.*, 94, 5117 (1972).

(4) In addition to the literature cited in ref 3a the following may be noted: (a) E. Hadjoudis, E. Kariv, and G. M. J. Schmidt, *J. Chem. Soc., Perkin Trans. 2*, 1056 (1972); (b) E. Hadjoudis and G. M. J. Schmidt, *ibid.*, 1060 (1972); (c) G. Friedman, C. Cohen, D. Wolf, and G. M. J. Schmidt, *Isr. J. Chem.*, 10, 559 (1972); (d) E. Hadjoudis, *ibid.*, 11, 63 (1973); (e) G. Adler, *ibid.*, 10, 563 (1972); (f) C. Ressler, *J. Org. Chem.*, 37, 2933 (1972); (g) J. R. Scheffer and M. D. Ouchi, *Tetrahedron Lett.*, 223 (1970); (h) J. P. Desvergne and J. M. Thomas, *Chem. Phys. Lett.*, 23, 343 (1973); (i) M. D. Cohen and B. S. Green, *Chem. Brit.*, 490 (1973); (j) H. W. Kaufman, D. Rabinovich, and G. M. J. Schmidt, *J. Chem. Soc., Perkin Trans. 2*, 433 (1974); (k) J. P. Desvergne, H. Bouas-Laurent, E. V. Blackburn, and R. Lapouyade, *Tetrahedron Lett.*, 947 (1974); (l) I. C. Paul and D. Y. Curtin, *Science*, in press.

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