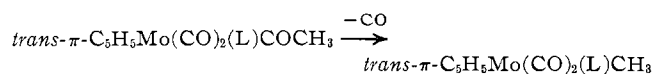


were collected at 30° and our current findings at 60° are in accord with these assignments. An X-ray diffraction study revealed that $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{COCH}_3$ possesses *trans* stereochemistry in the solid state.⁸ The methyl derivatives described here afford doublet C_6H_5 resonances (Table I) and two terminal CO bands (1935–1950 and 1845–1855 cm^{-1}) of which the lower frequency absorption is the more intense. Thus the over-all transformations may be described by



The detailed mechanism of these reactions must await further investigation, but certain features should be mentioned at present. The carbonyl group lost on decarbonylation is probably not the acetyl CO, but rather a terminal ligand, as found in acylmanganese⁹ and -cobalt¹⁰ carbonyl systems. Furthermore, we have found that a mixture of *cis*- and *trans*- $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{OC}_6\text{H}_5)_3]\text{CH}_3$ (synthesized from $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{OC}_6\text{H}_5)_3]^- \text{Na}^+$ and CH_3I ¹¹) maintains a constant *cis*:*trans* ratio under our reaction conditions for up to 48 hr as shown by nmr. Thus the *cis*-methyl complex should have been observed if formed during decarbonylation. We have as yet been unable to rigorously exclude the possibility of *cis*-*trans* equilibration of the corresponding acetyl derivative $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{OC}_6\text{H}_5)_3]\text{COCH}_3$ prior to decarbonylation owing to the unexpectedly complex reaction of the anion $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{OC}_6\text{H}_5)_3]^-$ with acetyl chloride.

Craig and Green have recently reported the solid-state (140°) decarbonylation of *trans*- $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{COCH}_2\text{C}_6\text{H}_5$ to the corresponding σ -benzyl complex, the latter of indeterminate stereochemistry.¹² The relationship of this finding to our results is not clear at present.

Experimental Section

Materials.—The complex $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CH}_3$ was prepared by the published method.¹³ Triphenylphosphine was used as received from Eastman Chemicals. Triphenyl phosphite, trimethyl phosphite, and tributylphosphine were obtained from Eastman, Bryant, and M and T, respectively, and distilled under nitrogen prior to use. Acetonitrile- d_3 was purchased from Dia- prep, inc., and used without further purification.

General Procedure.—In the drybox (Vacuum Atmospheres Corp), 0.2 g of $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CH}_3$ (0.77 mmol) and an equimolar amount of the ligand were dissolved in acetonitrile- d_3 (3.0 ml) and equal portions were charged to each of two nmr tubes. Tetramethylsilane was added as an internal marker and the tubes were capped immediately. The sample tubes were quickly brought out of the drybox and frozen immediately in liquid nitrogen. The tubes were then inserted into a standard vacuum line apparatus and sealed (while still frozen). The samples were allowed to warm slowly to room temperature and an

initial nmr spectrum was obtained (Varian Associates A-60 spectrometer). Thereafter, the sample tubes were thermostated at $60 \pm 2^\circ$ for the duration of the experiment. The spectra of the $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CH}_3\text{-}(\text{C}_6\text{H}_5)_3\text{P}$ reaction mixtures were obtained at 60° for reasons of solubility, but all other nmr spectra were obtained at ambient temperatures. Samples of the $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{L})\text{CH}_3$ compounds for infrared analysis (Beckman IR-4, cyclohexane solution) were obtained by refluxing the corresponding acetyl complex in acetonitrile (open system) for 50–60 hr. The identities of the products were further verified by recording their nmr spectra.

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Metal-Metal Frequencies and Force Constants of $\text{Ir}_4(\text{CO})_{12}$ ¹

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As part of a continuing study of frequencies and force constants associated with the vibrational modes of metal atom clusters^{2,3} we present here an analysis of the low-frequency Raman spectrum of $\text{Ir}_4(\text{CO})_{12}$. This molecule contains a tetrahedral cluster of iridium atoms, with all carbonyl ligands bound terminally,⁴ as shown in Figure 1. In a preliminary report,³ three intense Raman bands, at 208, 164, and 105 cm^{-1} , were identified with the anticipated cluster modes, of symmetries A_1 , T_2 , and E, respectively. The frequency ratios are not far from those predicted from a "simple cluster" model:³ $\nu_{A_1}:\nu_{T_2}:\nu_E = 2:\sqrt{2}:1$.

These frequencies have been corroborated by Abel, *et al.*,⁵ who found the 164- cm^{-1} band in the infrared as well, confirming its assignment to a T_2 mode. Abel, *et al.*, also reported higher frequency fundamentals for $\text{Ir}_4(\text{CO})_{12}$ and discussed them briefly. Our spectra (Raman and infrared) are in good agreement with theirs.

The representations of the T_d point group spanned by a complete set of internal coordinates are given in Table I. Below 250 cm^{-1} nine Raman bands are expected, from vibrations primarily involving metal-metal stretching (three) and metal-carbon deformation (six).

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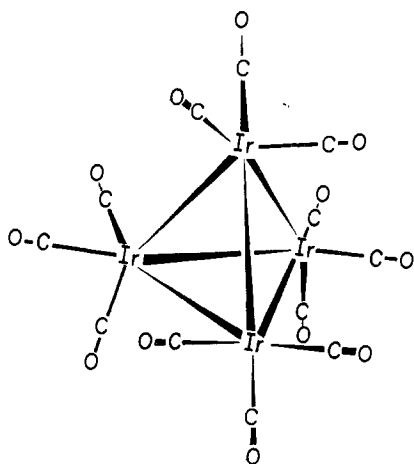


Figure 1.—Molecular configuration of $\text{Ir}_4(\text{CO})_{12}$ (redrawn from ref 4). Molecular parameters are: $d_{\text{Ir-Ir}} = 2.68 \text{ \AA}$; $d_{\text{Ir-C}} = 1.90 \text{ \AA}$; $d_{\text{C-O}} = 1.14 \text{ \AA}$; $\angle \text{Ir-C-O} = 180^\circ$; $\angle \text{Ir-Ir-C} = 95^\circ$.

TABLE I

SYMMETRIES OF VIBRATIONAL MODES FOR $\text{Ir}_4(\text{CO})_{12}$ (T_d)

$$\begin{aligned} \Gamma_{\text{vib}} &= 5A_1 + 2A_2 + 7E + 8T_1 + 11T_2 \\ \Gamma_{\nu(\text{M-M})} &= A_1 + E + T_2 \\ \Gamma_{\nu(\text{C-O})} &= A_1 + E + T_1 + 2T_2 \\ \Gamma_{\nu(\text{M-C})} &= A_1 + E + T_1 + 2T_2 \\ \Gamma_{\delta(\text{M-C-O})} &= A_1 + A_2 + 2E + 3T_1 + 3T_2 \\ \Gamma_{\delta(\text{C-M-C})}^a &= A_1 + E + T_1 + 2T_2 \\ \Gamma_{\delta(\text{M-M-C})}^a &= A_1 + A_2 + 2E + 3T_1 + 3T_2 \end{aligned}$$

^a Contain $A_1 + E + T_1 + 2T_2$ redundancies.

The low-frequency Raman spectrum is shown in Figure 2. Eight prominent bands are observed, assignable as fundamentals. In addition the emission at 40 cm^{-1} is broad and may be a superposition of two bands. Indeed the normal-coordinate analysis, described below, satisfactorily predicts two fundamentals close to this frequency. The site symmetry for $\text{Ir}_4(\text{CO})_{12}$ molecules in the crystals is only C_3^4 . Two shoulders can be discerned in the spectrum at about 112 and 68 cm^{-1} , which might arise from metal-carbon deformations forbidden in T_d symmetry. No distortions are detectable for the cluster vibrations, however, the T_2 mode at 160 cm^{-1} being unsplit and sharp. While the A_1 and T_2 cluster bands stand out clearly in Figure 2, the previous assignment of the E cluster mode to 105 cm^{-1} is called into question by the complexity of the spectrum in this region.

In order to assign the spectrum correctly and to examine the requisite force field, an approximate normal-coordinate analysis was performed. The G matrix was calculated by the method of Wilson, *et al.*,⁶ employing Schachtschneider's program GMAT.⁷ Molecular parameters, shown in Figure 1, were average values taken from the X-ray structure determination⁴ except that small deviations from 180° of the Ir-C-O angles were ignored. A valence force field was used to construct the F matrix. Both G and F matrices were factored using symmetry coordinates generated from the in-

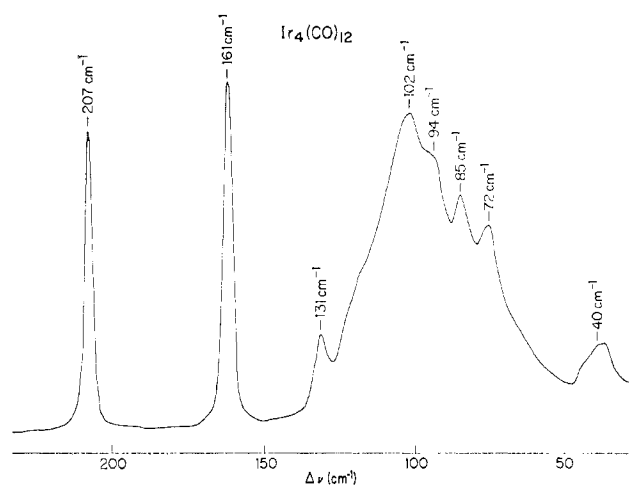


Figure 2.—Low-frequency Raman spectrum for $\text{Ir}_4(\text{CO})_{12}$. Conditions: He-Ne 6328-\AA laser excitation; spectral slit width 2 cm^{-1} ; time constant 3 sec. ; scan rate $12 \text{ cm}^{-1}/\text{min.}$

ternal coordinates by standard group theoretical techniques.⁸ Although the Ir-Ir-C angles are sufficient to define the metal-carbon deformation modes, C-Ir-C angles were also included for consistency with related calculations on $\text{Os}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$.² These two-angle coordinate sets contain six redundancies between them.

The matrices were set up for calculation of all of the fundamental frequencies. Since our interest here is restricted to frequencies below 250 cm^{-1} , however, only metal-metal stretching and metal-carbon deformation force constants were varied to obtain a least-squares fit to the low-frequency Raman spectrum, using Schachtschneider's program FPERT.⁷ Force constants for C-O and M-C stretching and for M-C-O bending were chosen to calculate approximately the higher frequencies and were held fixed. Previous experience² has indicated that small changes in these values have no significant influence on the low-frequency fit. The initial metal-metal force constant was estimated from the A_1 cluster frequency. The bending constants were expected to fall in the range $0.1\text{--}0.6 \text{ m dyn}\cdot\text{\AA}$ with $K_{\text{C-M-C}} > K_{\text{M-M-C}}$.

Attempts to fit the spectrum with the E cluster mode assigned to 102 cm^{-1} were unsuccessful. This assignment perforce requires that the lone sharp band at 131 cm^{-1} be assigned to M-C deformation. However, the six bending modes are always calculated as three closely spaced pairs unless very large interaction constants are introduced. On the other hand, if the E cluster mode is reassigned to 131 cm^{-1} , then the two bands at 102 and 94 cm^{-1} are readily assigned as one of the bending pairs. A second pair can be assigned to the bands at 85 and 72 cm^{-1} and the third pair to the broad band at 40 cm^{-1} . With these assignments, the six bending frequencies can be calculated to within experimental error (see Table II) using only the two primary bending force constants and a single interaction constant. The slight discrepancies could be eliminated with addition of further interaction constants. An adequate fit of the

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TABLE II
NORMAL-COORDINATE ANALYSIS RESULTS FOR $\text{Ir}_4(\text{CO})_{12}$

Obsd	Raman freq, cm^{-1}	Calcd	$V_{\text{M-M}}^a$
207		206.9 (A_1)	90.8
161		161.2 (T_2)	88.2
131		130.9 (E)	83.5
102		99.6 (T_2)	1.5
94		96.5 (E)	5.4
85		79.7 (T_2)	6.0
72		76.4 (A_1)	5.6
40		40.8 (T_2)	0.9
40		39.0 (E)	7.0

$$K_{\text{M-M}} = 1.69 \text{ mdyne/\AA} \quad K_{\text{M-M-C}} = 0.12 \text{ mydn-\AA}$$

$$k'_{\text{M-M}} = -0.13 \text{ mydn/\AA} \quad K_{\text{C-M-C}} = 0.19 \text{ mdyne-\AA}$$

$$k''_{\text{M-M}} = 0.13 \text{ mdyne/\AA} \quad k'_{\text{C-M-C}} = 0.10 \text{ mdyne-\AA}$$

^a Percentage contribution to the potential energy from the metal-metal coordinate. ^b Interaction constants: $k'_{\text{M-M}}$, between adjacent metal-metal bonds; $k''_{\text{M-M}}$, between opposite metal-metal bonds; $k'_{\text{C-M-C}}$, between adjacent C-M-C angles.

cluster frequencies requires, in addition to the primary metal-metal stretching constant, both interaction constants (for adjacent and nonadjacent bonds).

Table II lists the adjusted force constants, compares observed and calculated frequencies, and gives the contribution of the metal-metal coordinate to the potential energy of each of the low-frequency normal modes. Mixing of cluster modes with M-C deformation modes is quite limited, less than was observed for $\text{Os}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$.² On the other hand, with the reassignment of the E cluster mode, the cluster frequency ratios, $\nu_{A_1}:\nu_{T_2}:\nu_E = 2:1.56:1.27$, are further from the simple cluster prediction than was thought,³ reflecting the requirement for substantial metal-metal interaction constants. It is evident that simple cluster predictions must be treated with some caution in making band assignments.

The value of the primary metal-metal force constant is much higher for $\text{Ir}_4(\text{CO})_{12}$ (1.69 mdyne/\AA) than for $\text{Os}_3(\text{CO})_{12}$ ² (0.91 mdyne/\AA). While the direction of the difference is consistent with the increase in metal-metal distance (2.68 \AA for $\text{Ir}_4(\text{CO})_{12}$,⁴ 2.89 \AA for $\text{Os}_3(\text{CO})_{12}$ ⁸), its size is disproportionate and no doubt reflects the greater complexity of the $\text{Ir}_4(\text{CO})_{12}$ force field. Indeed the symmetry force constants for the A_1 breathing modes, 1.30 and 0.91 mdyne/\AA, respectively, for $\text{Ir}_4(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$, seem to provide a more reasonable basis for comparison. The force constants for metal-carbon deformation are substantially lower for $\text{Ir}_4(\text{CO})_{12}$ than for $\text{Os}_3(\text{CO})_{12}$, although they are not directly comparable in view of the different forms of the redundancies in the two calculations.

Experimental Section

$\text{Ir}_4(\text{CO})_{12}$ was obtained from Alfa Inorganics, Inc., and was purified by sublimation in a stream of CO. Infrared spectra were recorded on a Beckman IR12 spectrometer using Nujol mulls. Raman spectra were obtained with microcrystalline samples using a spectrometer⁹ equipped with an He-Ne laser

source. The instrument was calibrated using helium and argon discharge lines. Attempts to grow single crystals of sufficient size and quality for polarization studies were unsuccessful.

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Nickel(II) Complexes of Some Tetradentate Salicylaldimine Ligands¹

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The relationships between spectral and magnetic properties and stereochemistry of four-coordinate Ni(II) and Co(II) complexes of salicylaldimine ligands are well established.² Monomeric bis complexes occur in either the planar (low-spin) or the pseudotetrahedral (high-spin) configuration in the solid state. In solutions of noncoordinating solvents some Ni(II) complexes become involved in a rapid equilibrium between the two limiting configurations. Presumably the planar \rightarrow tetrahedral configurational change involves a rotation of the two chelate ring planes with respect to one another such that the dihedral angle between them changes from $\sim 0^\circ$ (planar) to $\sim 90^\circ$ (tetrahedral). This is accompanied by a change in spin state.

We are interested in designing ligands which force an intermediate stereochemistry on four-coordinate complexes of Ni(II) and Co(II) in hopes of obtaining some complexes at the point of spin-multiplicity change. It appeared that tetradentate complexes of I offer a reasonable chance of success for $M = \text{Ni(II)}$. Cu(II) complexes of structure I become increasingly distorted from planarity as n is increased.³ The Co(II) complexes of I where $n = 4-10$ are tetrahedral,⁴ the $n = 3$ complex is high spin and is believed to have a flattened tetrahedral structure,^{4b} and the $n = 2$ complex is planar.⁵ Ni(II) complexes of Schiff bases derived from pyrrole-2-carboxaldehyde and diamines having two to five carbons are diamagnetic and monomeric.⁶ Ni(II) complexes of structure I with $n = 2-4$ are diamagnetic and presumably planar or nearly planar.⁷ This note

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