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Carbon-Phosphorus Bond Cleavage in Triphenylphosphine Complexes. Reactions of η^5 -(Cyclopentadienyl)carbonyltriphenylphosphinerhodium and -iridium with Pentacarbonylmethylmanganese and -rhenium. Isolation of Bridged Diphenylphosphido-Heterodinuclear Metal Complexes¹

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Abstract: The reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]$, M = Rh or Ir, with $\text{CH}_3\text{M}'(\text{CO})_5$, M' = Mn or Re, have resulted in isolation of two types of heterodinuclear metal complexes, $(\eta^5\text{-C}_5\text{H}_5)\text{M}-\mu\text{-}[\text{C}(\text{C}_6\text{H}_5)\text{O}]-\mu\text{-}[\text{C}(\text{CH}_3)\text{O}]-\mu\text{-}[\text{P}(\text{C}_6\text{H}_5)_2]-\text{Mn}(\text{CO})_3$ (**1**) (M = Ir, **1a**; Rh, **1b**) and $(\eta^5\text{-C}_5\text{H}_5)\text{M}-\mu\text{-}[\text{P}(\text{C}_6\text{H}_5)_2]-\text{M}'(\text{CO})_4$ (**2**) (M-M' = Ir-Mn, **2a**; Rh-Mn, **2b**; Rh-Re, **2c**), both containing bridging diphenylphosphido ligands. The new complexes are characterized through infrared, ¹H NMR, and mass spectral data. The analogous reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]$ with $\text{CH}_3\text{Mn}(\text{CO})_5$ leads only to ligand interchange giving $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ and $\text{CH}_3\text{Mn}(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]$.

In view of the demonstrated donor properties of $(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]$ in forming adducts with HgCl_2 , ZnBr_2 , and TiCl_3 ² and our earlier interest in donor-acceptor complexes of transition metals,³ we combined the aforementioned iridium complex and the corresponding cyclopentadienylcobalt and -rhodium derivatives as potential donors with $\text{CH}_3\text{Mn}(\text{CO})_5$ and $\text{CH}_3\text{Re}(\text{CO})_5$ as potential acceptors.⁴ We found no evidence of simple adducts of these molecules when combined at ambient temperatures or slightly above. Instead, a number of other transformations were observed at elevated temperatures which experiments and results are set forth below.

Results and Discussion

The Systems Ir-Mn and Rh-Mn. Combination of $(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]$ and $\text{CH}_3\text{Mn}(\text{CO})_5$ in refluxing toluene resulted in gas evolution and preponderant production (80% yield) of a yellow, crystalline, air-stable substance, **1a**. In cyclohexane solution the compound exhibits three stretching absorptions of terminal carbonyl groups as listed in Table I.

Investigation of the analogous system $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]$ with $\text{CH}_3\text{Mn}(\text{CO})_5$ in refluxing benzene yielded a slightly different product mix from which only a small yield of an analog of **1a**, namely about 5.8% of a yellow compound, **1b**, was isolated. This compound

showed corresponding absorptions in the infrared analogous to **1a** (see Table I). Only one other product was isolated from the mixture and is discussed below.

Further characterization of products **1a** and **1b** provided the following data. The proton magnetic resonance (¹H NMR) spectra of these compounds are complicated by the presence of 0.5 mol of benzene of crystallization for each mole of molecular complex; the phenyl region indicates overlap of the resonances of these two. Accordingly, a sample of **1a** was recrystallized from a mixture of benzene-*d*₆ and pentane, and its ¹H NMR spectrum obtained in benzene-*d*₆ solution gave satisfactory integrals. The chemical shifts and relative areas, tabulated in Table I, are given as follows. For **1a**, four principal features are observed: a broad multiplet centered at τ 2.51 followed by three sharp singlets, one at τ 2.96, another at τ 5.26, and the third at τ 7.55. The total relative intensity under the first two peaks, which are in the phenyl region, is 15 while that of the third in the η^5 -cyclopentadienyl region is 5 and that of the highest resonance, 3. There was no evidence of any other signals from τ 1.80 to 35.0. The ¹H NMR spectrum for **1b** was almost identical with that of **1a** with corresponding resonances at τ 2.52 and 3.02, 5.30, and 7.55 in the same relative intensities as described for **1a**. The chemical shifts and relative areas of the resonances suggested complexes containing three phenyl groups, an η^5 -cyclopentadienyl group,

Table I

Complex	Infrared, $\nu_{C\equiv O}^a$ (cm ⁻¹)	¹ H NMR data ^b (τ)	Mass spectrum parent ion (<i>m/e</i>)	
			Obsd	Calcd
C ₃₂ H ₂₆ O ₅ PMnIr, 1a	2025 s, 1942 m, 1918 s	2.51 m, 2.96 s (15), 5.26 s (5), 7.55 s (3)	dec ^c	730 ^{d,e}
C ₃₂ H ₂₆ O ₅ PMnRh, 1b	2027 s, 1945 m, 1921 s	2.52 m, 3.02 s (15), 5.30 s (5), 7.55 s (3)	dec ^c	640 ^d
C ₂₂ H ₁₅ O ₅ PMnIr, 2a	2051 s, 1988 vs, 1977 m, 1951 s, 1935 s	2.38 m, 2.71 m (10), 4.66 s (5) ^f	638 ^e	638 ^e
C ₂₂ H ₁₅ O ₅ PMnRh, 2b	2052 s, 1998 s, 1980 m, 1956 s, 1939 s	2.32 m, 3.03 m (10), 5.02 s (5)	548	548
C ₂₂ H ₁₆ O ₅ PReRh, 2c	2073 m, 1998 s, 1982 m, 1966 s, 1937 s	2.34 m, 3.02 m (10), 5.07 s (5)	680 ^g	680 ^g

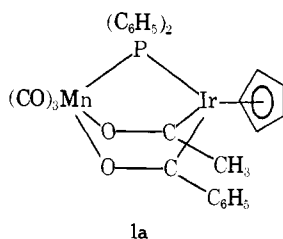
^aCyclohexane solution; relative intensities: vs = very strong, s = strong, m = medium. ^bBenzene-*d*₆ solution except as indicated under footnote ^f below; m = multiplet, s = singlet; relative intensities of signals are given in parentheses. ^cSee text for discussion. ^dFormula weight not including 0.5 mol C₆H₆ of crystallization. ^eCalculated for ¹⁹³Ir. ^fCDCl₃ solution. ^gCalculated for ¹⁸⁷Re.

and a methyl group, or a multiple of such a combination.

To obtain mass spectra of these two products it was required to heat **1a** to 180–200° and **1b** to 138–170° to observe any signals. The first observed peaks indicated apparent parent ions at *m/e* 1235 for **1a** and *m/e* 706 for **1b**. An osmometric molecular weight determination of **1a** in benzene, however, yielded a value of 772 g/mol. It was apparent that the high temperatures required to volatilize **1a** had caused extensive rearrangements. We confirmed this for compound **1a** by a separate pyrolysis described in the experimental section and assumed such rearrangements were also occurring in attempts to obtain the mass spectrum of the rhodium analog. Similar experiences in the mass spectra of organometallic compounds have been reported by others.⁵

Infrared spectrum in KBr pellet for **1a** is shown in supplemental Figure A,⁶ upper trace; the maxima for both compounds **1a** and **1b** which are closely analogous are listed in Table II.⁶ Features expected for phenyl and cyclopentadienyl groups were observed along with one additional strong absorption at 1508 cm⁻¹ for **1a** and 1529 cm⁻¹ for **1b**. Both from their position and intensity, these suggested the presence of acyl groups bonded to metal through oxygen. Such assignments have been previously proposed for a variety of complexes⁷ and confirmed in several structure determinations.⁸

The accumulated spectroscopic and analytical data (see experimental section below) for the two complexes did not lead to any familiar structure formulations, and a single-crystal X-ray study of **1a** was therefore undertaken. This is described in detail in the companion paper⁹ and the results are indicated by the figure shown here.

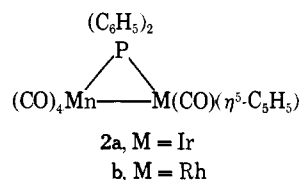


Both the infrared and ¹H NMR data mentioned above are satisfactorily accounted for. The close correlation between the data of **1a** and **1b** indicates the rhodium complex must have the same overall structural geometry.

Two other products also having analogous relation to each other were isolated, though in somewhat reduced yields, one each from the Ir–Mn and Rh–Mn systems described above. These were red and orange-red complexes, **2a** and **2b**, eluted prior to **1a** and **1b** in yields of <1 and 6.7%, respectively. These both have similar patterns for carbonyl stretching modes in the infrared region (see Table I).

The ¹H NMR spectrum of **2a** in CDCl₃ solution exhibited two broad multiplets at τ 2.38 and 2.71 (phenyl region, relative area 10) and a sharp singlet at τ 4.66 (η^5 -cyclopentadienyl region, relative area 5). The corresponding resonances for **2b** in benzene-*d*₆ solution, listed in Table I, are in the same ratio of relative intensity.

Contrary to our experiences with **1a** and **1b**, mass spectra for these compounds gave results consistent with other data. Parent ions at *m/e* 638 (¹⁹³Ir) and *m/e* 548 were obtained at 70 eV and 118–127° and 110–115° for **2a** and **2b**, respectively. Both derivatives show fragments separated by *m/e* 28 indicating loss, successively, of up to five carbonyl groups. This evidence taken together with analytical data and a high resolution mass spectrum scan of the parent peak for **2b** suggests the structure shown below.



The five maxima in the carbonyl region are accounted for by the presence of a cis tetracarbonyl group on manganese and a single carbonyl group on iridium or rhodium. The ¹H NMR spectrum clearly indicates cleavage of the triphenylphosphine group, analogous to that observation in the formation of **1a** and **1b**. No bridging acetyl or benzoyl groups are present in these derivatives and neither do the full range infrared spectra of these compounds contain the expected strong absorption for these in the range 1495–1550 cm⁻¹⁷ which were observed for **1a** and **1b**. A KBr pellet infrared spectrum of compound **2a** is shown in the lower trace of supplemental Figure A⁶ and the maxima for compounds **2a** and **2b** (and a third analogous derivative **2c**, discussed below) are given in Table III.⁶ The close correlation of data for **2a** and **2b** indicates similar structures for both complexes.

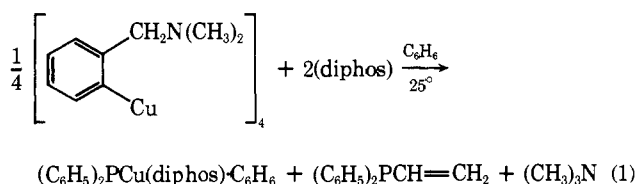
The Systems Co–Mn, Rh–Re, and Ir–Re. In view of the unusual results noted thus far, it was of interest to explore reactions of the complexes containing congeners of metals in the above mentioned starting materials. Reaction of (η^5 -C₅H₅)Co(CO)[P(C₆H₅)₃] with CH₃Mn(CO)₅ was attempted both at room temperature and at 80°. None of the products mentioned above for iridium and rhodium was observed. Instead, a simple ligand exchange occurred requiring 4 days for completion at room temperature or 1 hr at 80°. This led to isolation of (η^5 -C₅H₅)Co(CO)₂ and CH₃Mn(CO)₄[P(C₆H₅)₃]. This observation parallels report of the instability of the cobalt complex noted earlier by King.¹⁰

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]$ with $\text{CH}_3\text{Re}(\text{CO})_5$ in refluxing toluene resulted in isolation in 29% yield of a complex, **2c**, analogous to **2a** and **2b** discussed above. Infrared and ^1H NMR data parallel those of complexes **2a** and **2b** and are listed in Table I and Table III.⁶ Mass spectrum at 100–125° probe temperature and 70 eV ionizing voltage gave a parent ion at m/e 680 (^{187}Re) with successive loss of five carbonyl fragments. This evidence indicates the analogous molecular structure $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Rh}-\mu\text{-}[\text{P}(\text{C}_6\text{H}_5)_2]\text{-Re}(\text{CO})_4$, which formulation is confirmed by its high resolution mass spectrum. Acetophenone was identified as a by-product in this reaction; its significance is discussed below.

The reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]$ with $\text{CH}_3\text{Re}(\text{CO})_5$ showed great complexity. No significant quantities of any materials could be isolated by column chromatography or crystallization, nor, specifically, did we see evidence of derivatives analogous to complexes **1** or **2**. We did not examine this system any further.

Summary and Conclusions

A number of R_2P -bridged *homo*- and *hetero*bimetallic compounds have been obtained in the cleavage of R_4P_2 or R_2PH by a variety of metal carbonyls^{11a} or in the reaction of $\text{R}_2\text{PCl}^{11b,12}$ or its complexes¹² with carbonyl metalates. For cleavage of coordinated R_3P we may cite several precedents. Bradford et al.¹³ have observed cleavage of PPh_3 by $\text{Os}_3(\text{CO})_{12}$ in xylene at 150° yielding $\text{Os}_3(\text{CO})_8\text{-}(\text{PPh}_2)(\text{Ph})(\text{PPhC}_6\text{H}_4)$ among a variety of other similar products. The complex $[\text{Ir}(\text{CO})(\text{PPh}_3)(\mu\text{-PPh}_2)]_2$ has now been reported by two groups¹⁴ obtained in the reflux either of a decalin^{14a} or a dimethylformamide^{14b} solution of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ or the dimethylformamide solution of $\text{IrH}_3(\text{PPh}_3)_3$,^{14b} and Van Koten and Noltes¹⁵ have observed cleavage of $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ (diphos), shown in eq 1.



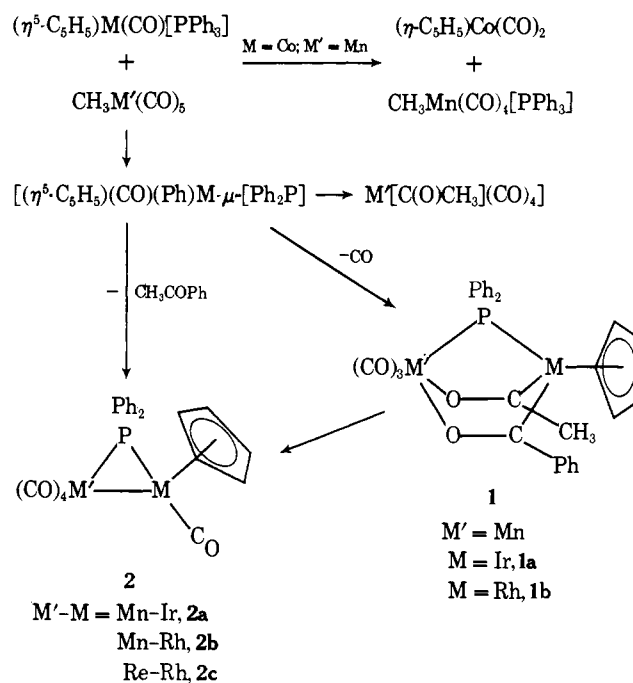
The present work bears resemblance to some of these reactions in the cleavage of PPh_3 and elimination of component parts of the reacting species but also shows an alternate pathway involving retention and rearrangement of those component parts. Without prejudice to the reaction sequences from which **1** and **2** are produced, it may be profitable to summarize these transformations and to indicate parallels in known organometallic reactions.

Formation of the acetyl and benzoyl groups must involve respectively migration of methyl or phenyl groups on metal to coordinated carbonyls.¹⁶ The presence of a phenyl group on iridium or rhodium may arise from cleavage of coordinated triphenylphosphine, for instance by internal oxidative addition in $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]$ ($\text{M} = \text{Rh}$ or Ir) to give a six-coordinate intermediate $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{-M}(\text{C}_6\text{H}_5)[\text{P}(\text{C}_6\text{H}_5)_2]$.

At some point, the complex of Ir or Rh must combine with the methylmanganese or -rhenium complexes. As indicated earlier, simple donor-acceptor interactions between complexes of the former two with the latter two were not observed. However, the phosphorus atom of the $\text{P}(\text{C}_6\text{H}_5)_2$ group in the six-coordinate intermediate of Rh or Ir postulated above would possess a free pair of electrons. This could coordinate to $\text{CH}_3\text{M}'(\text{CO})_5$ ($\text{M}' = \text{Mn}$ or Re) to give an intermediate adduct such as $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{M}'\text{-}\mu\text{-}(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_5)]$.

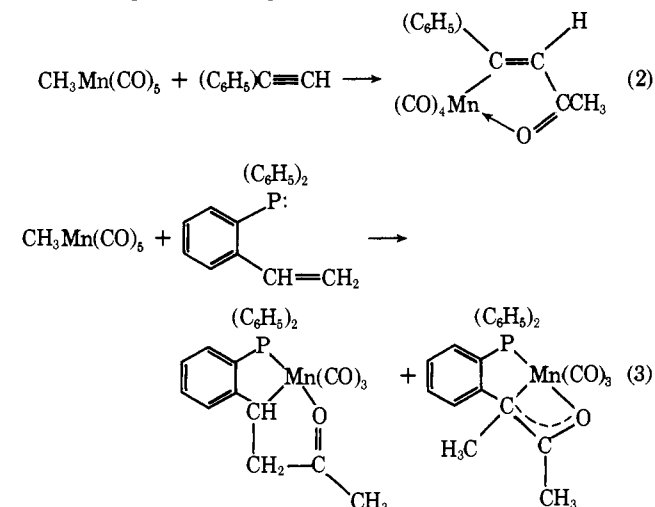
$(\text{C}_6\text{H}_5)[(\text{C}_6\text{H}_5)_2\text{P}] \rightarrow \text{M}'(\text{C}(\text{O})\text{CH}_3)(\text{CO})_4$. Such a species would lead to product **2** by loss of acetophenone, as shown in Scheme I in which this and the other transforma-

Scheme I



tions observed in this study are summarized. Indeed, acetophenone is observed in the Rh–Re system in which the product is obtained in yields sufficiently high for detection of this by-product. Presumably acetophenone is also formed in the Ir–Mn and Rh–Mn systems, but the yields were too small to permit detection of the by-product.

Alternatively, the intermediate adduct may be converted to **1** through a number of additional steps, possibly competing with or preceding formation of **2**, about which there are some further comments below. Presence of the benzoyl group on M may be accounted for by migration of a phenyl group to CO coordinated to this metal. At some point, the acetyl group coordinated to M' must be transferred to M. This transformation is accompanied by coordination of the oxygen atom of this group back to M' from which it migrated. Two examples of the transfer of an acetyl group may be cited in which the oxygen of the transferred group is coordinated in the final product to the metal from which it migrated. This is observed in the reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ with acetylenes¹⁷ or with *o*-styryl(diphenyl)phosphine,^{8d} shown in eq 2 and 3, respectively.



Finally, reaction to form **1** is completed when the benzoyl group coordinates to M' with expulsion of one molecule of CO from that metal. It is remarkable that, given the complexity of possibilities indicated by these reactions, an 80% yield of complex **1a** is attained in the Ir-Mn system.

We also investigated potential interconversions between products **1** and **2** either directly or through some common intermediate. Accordingly pyrolyses of **1a** and **1b** resulted in complexes **2a** and **2b**, respectively, but in low yields. Therefore, we believe that the transformations to obtain complex **2** indicated in Scheme I must occur more in parallel than in sequence. It also seemed possible that complex **1a** might be converted to **2a** in the presence of excess CO through some common intermediate at the same temperatures at which these two complexes are formed from the starting material. This proved unsuccessful as was also an attempt to form **1a** from the reaction of **2a** with excess acetophenone. These negative results do not exclude the possibility of a common intermediate but indicate if such exists, it is not readily re-formed from the products under the conditions attempted.

Experimental Section

General Procedures and Physical Measurements. All reactions were performed in standard Schlenk-type tubes and flasks under an inert atmosphere of nitrogen or argon. The infrared spectra in the 1800–2100-cm⁻¹ region were recorded on a Beckman IR-4 spectrophotometer equipped with a LiF prism. A Perkin-Elmer 421 grating spectrophotometer was used for higher and lower infrared regions. Solution spectra were calibrated to the 2138.6-cm⁻¹ absorption of cyclohexane. Proton magnetic resonance spectra were obtained on a Varian A-60D spectrometer using tetramethylsilane as internal reference. A Mechrolab vapor phase osmometer (Model 301A) was used to obtain the one solution molecular weight. Mass spectra of gases were taken on a Consolidated Engineering Corp. (E. I. du Pont de Nemours and Co.) Model 21-620 mass spectrometer with an ionizing current of 20 μ A. Mass spectra of solids were obtained on an AEI-MS9 spectrometer, operated by Ms. Beth Irwin of the UCLA Chemistry Department. Carbon and hydrogen elemental analyses were performed by Miss Heather King of the UCLA Chemistry Department; Ir, P, and Mn elemental analyses were obtained from Schwartzkopf Microanalytical Laboratory, Woodside, N.Y. A Varian Aerograph Series 1400 analytical gas chromatograph was used for gas chromatographic analysis.

Reagents. The following materials were obtained from the indicated sources: Mn₂(CO)₁₀, Re₂(CO)₁₀, and Co₂(CO)₈, Pressure Chemical Co. Pittsburgh, Pa; IrCl₃·3H₂O and RhCl₃·3H₂O, Strem Chemicals, Inc., Danvers, Mass. All other reagents and solvents were obtained from the UCLA Chemistry storeroom and are available from most chemical vendors. (η^5 -C₅H₅)M(CO)₂[P(C₆H₅)₃], M = Ir or Rh, was synthesized by the procedure described by Oliver and Graham.² (η^5 -C₅H₅)Co(CO)[P(C₆H₅)₃] was prepared from (η^5 -C₅H₅)Co(CO)₂ by the method of King.¹⁰ CH₃M'(CO)₅, M' = Mn or Re, was synthesized as described by King¹⁸ but modified to employ a 0.4% sodium amalgam in place of a methanolic solution of sodium hydroxide or metallic sodium as reducing agent.

Iridium. Reaction of (η^5 -C₅H₅)Ir(CO)[P(C₆H₅)₃] with CH₃Mn(CO)₅. (η^5 -C₅H₅)Ir(CO)[P(C₆H₅)₃] (0.244 g, 0.446 mmol) and CH₃Mn(CO)₅ (0.200 g, 0.955 mmol) were dissolved in 40 ml of toluene under argon in a Schlenk flask. The solution was brought to reflux after which the initial canary yellow color turned dark yellow in 1.25 hr. A sample of the gas evolved up to this point was collected and subjected to mass spectrometric analysis; the gas consisted principally of CO with a trace (<10%) of CH₄. The solution was next cooled under a stream of argon and solvent removed under vacuum (20 mm, 40°). The product mixture was placed on a column (34 × 2 cm) of alumina (neutral, activity III) or silica gel and was eluted first with pure hexane and then with hexane containing increasing proportions of benzene. The first band, containing Mn₂(CO)₁₀, was followed by bands containing small amounts of (η^5 -C₅H₅)Mn(CO)₃, CH₃Mn(CO)₅, CH₃Mn(CO)₄-

[P(C₆H₅)₃], and unreacted (η^5 -C₅H₅)Ir(CO)[P(C₆H₅)₃]. With 10% benzene in hexane a bright yellow band was eluted containing **2a**. It was isolated as 2 mg of red crystals (mp 173.0–174.7°, sealed tube) from hexane solution at room temperature in 0.7% yield (based on iridium) calculated from molecular formula analogous to those of **2b** and **2c** deduced below. The above yellow band was followed by several bands containing materials which were difficult to separate from one another and as a consequence have not as yet been characterized. With 70% benzene in hexane 0.275 g of complex **1a** (80% yield based on Ir from formula established by analysis and structure determination described in the companion paper⁹) was eluted. Crystallization from a benzene-pentane mixture gave yellow crystals (mp 190.0–191.5°, sealed tube) which proved to contain benzene of solvation from ¹H NMR evidence. The compound is air stable in solution and in the crystalline state.

Anal. Calcd for C₃₂H₂₆O₅PMnIr: C, 50.01; H, 3.41; P, 4.03; Mn, 7.15; Ir, 25.00. Found: C, 50.60; H, 3.50; P, 3.95; Mn, 6.53; Ir, 24.05.

A sample submitted for mass spectrum required unusually elevated temperatures (180–200°) to produce any signal; at that point, an apparent parent ion was obtained at *m/e* 1235. An osmometric molecular weight determination in benzene solution indicated a value of 772 g/mol compared to 720 g/mol calculated for the molecular complex without the benzene of solvation.

Pyrolysis of 1a. In view of the discrepancy between the mass spectral and osmometric molecular weight data, it was suspected that the heating required to observe a signal in **1a** was bringing about significant rearrangement. Accordingly, **1a** (99.6 mg, 0.130 mmol) was heated in a sealed tube under vacuum at 190° for 2.5 hr, giving a red oil. Infrared spectrum in cyclohexane solution revealed terminal carbonyl absorptions due to **1a** and **2a**, exclusively. A series of mass spectral scans of the red oil subjected to temperatures in the range of 72–186° revealed the *m/e* peak at 1235 at approximately 140°. The spectrum was identical with that earlier obtained for **1a** at higher temperatures except that background noise was reduced. These data confirmed that the compounds responsible for the mass spectrum obtained from **1a** were the result of pyrolysis of that substance in the probe. A ¹H NMR spectrum in CDCl₃ of the volatile materials obtained from the pyrolysis of **1a** revealed only the presence of benzene. The pyrolysis residue was placed on a column (26 × 1.3 cm) of alumina (neutral, activity III). Pure hexane eluted trace amounts of (η^5 -C₅H₅)Ir(CO)₂ and (η^5 -C₅H₅)Mn(CO)₃ followed by **2a** (13.6 mg, 16.4%). Benzene (50%) in hexane as eluent brought down **1a** (7.4 mg, 7.4%). No other carbonyl-containing materials were eluted with up to 100% benzene; a brown solid remained at the top of the column.

Attempted Reaction of 1a with CO. **1a** (91.1 mg, 0.118 mmol) and CO (6.38 mmol, 4.4 atm) in 18 ml of benzene were sealed in a Carius tube and heated for 4 hr at 110°. After cooling, the tube was opened, and CO and solvent were removed under vacuum (1 mm, 40°). Infrared and ¹H NMR spectra indicated the presence only of starting material **1a**.

Attempted Reaction of 2a with Acetophenone. Infrared-scale combination of **2a** (2.0 mg, 0.0031 mmol) and acetophenone (19.0 mg, 0.158 mmol) in a sealed capillary at 110° revealed no reaction after a period of 4 hr.

Reaction of (η^5 -C₅H₅)Ir(CO)[P(C₆H₅)₃] with CH₃Re(CO)₅. A 40-ml toluene solution of (η^5 -C₅H₅)Ir(CO)[P(C₆H₅)₃] (0.246 g, 0.450 mmol) and CH₃Re(CO)₅ (0.310 g, 0.910 mmol) was refluxed under N₂ for 5 hr. The initial yellow color of the solution became dark red-amber. After cooling the solution to room temperature under a stream of N₂, the solvent was removed under vacuum (20 mm, 45°). The red oil obtained was placed on a 38 × 2 cm column of alumina (neutral, activity III) or silica gel and eluted first with hexane and then with increasing proportions of benzene. The first materials down the column, eluted with pure hexane, were Re₂(CO)₁₀ and (η^5 -C₅H₅)Re(CO)₃. With increasing amounts of benzene in hexane up to 100% benzene a number of compounds were eluted in varying quantities and not well-separated from each other. While most of these showed complex absorptions in the carbonyl stretching region of the infrared, none exhibited maxima analogous to those of complexes **1** or **2**.

Rhodium. Reaction of (η^5 -C₅H₅)Rh(CO)[P(C₆H₅)₃] with CH₃Mn(CO)₅. A mixture of (η^5 -C₅H₅)Rh(CO)[P(C₆H₅)₃] (0.602 g, 1.31 mmol) and CH₃Mn(CO)₅ (0.545 g, 2.59 mmol) in 90 ml of

benzene was refluxed under N_2 for 7 hr. The solution was cooled under a stream of N_2 gas, and solvent and excess $CH_3Mn(CO)_5$ were removed under vacuum (20 mm, 40°). The dark red-brown oily reaction mixture was placed on a column (46×3 cm) packed with silica gel and hexane. Using at first pure hexane, $Mn_2(CO)_{10}$ was eluted, followed by $(\eta^5-C_5H_5)Rh(CO)_2$ and $(\eta^5-C_5H_5)Mn(CO)_3$, identified by their carbonyl stretching absorptions in the infrared region. Elution next with increasing amounts of benzene (10–17%) in hexane brought down an orange band containing a product, **2b**, analogous to **2a** observed in the reaction mixture in the iridium–manganese system. It was isolated as orange-red crystals (48.1 mg, 6.7% yield, based on rhodium; mp 131.5 – 132.5° , sealed tube) from hexane solution at room temperature: high resolution mass spectrometry: calcd for $^{12}C_{22}H_{15}^{16}O_5^{31}P^{55}Mn^{103}Rh$, 547.9085; found: 547.9091 ± 0.0011 .

Anal. Calcd for $C_{22}H_{15}O_5PMnRh$: C, 48.20; H, 2.76. Found: C, 47.83; H, 2.92.

Compound **1b** was eluted with a 75% benzene in hexane mixture. Crystallization from a benzene–pentane mixture yielded 0.049 g of a gold-yellow product (5.8% yield based on rhodium, mp 177 – 179° (sealed tube)).

Anal. Calcd for $C_{32}H_{26}O_5PMnRh$: C, 56.58; H, 3.86. Found: C, 56.75; H, 4.38.

Pyrolysis of 1b. Approximately 5 mg of **1b** was heated for 1 hr at 190° in a sealed capillary. The dark red oil obtained exhibited terminal carbonyl stretch absorptions characteristic of **1b** and **2b**.

Reaction of $(\eta^5-C_5H_5)Rh(CO)[P(C_6H_5)_3]$ with $CH_3Re(CO)_5$. A mixture of $(\eta^5-C_5H_5)Rh(CO)[P(C_6H_5)_3]$ (0.140 g, 0.305 mmol) and $CH_3Re(CO)_5$ (0.143 g, 0.418 mmol) in 25 ml of toluene was refluxed under N_2 for 4.5 hr. The resulting dark red-brown solution was cooled under N_2 and solvent removed under vacuum (1 mm, 20°). The dark red tar was placed on a 34×2 cm column of alumina (neutral, activity III) or silica gel in hexane. Elution with pure hexane brought down first $Re_2(CO)_{10}$ followed by $CH_3Re(CO)_5$ and small amounts of $(\eta^5-C_5H_5)Rh(CO)_2$ and $(\eta^5-C_5H_5)Re(CO)_3$. A yellow band followed containing a new product, **2c**, analogous to **2a** and **2b**. **2c** (60.4 mg, 28.9% yield based on Rh) was isolated as yellow needles (mp 149.0 – 150.5° , sealed tube): high resolution mass spectrometry calcd for $^{12}C_{22}H_{15}^{16}O_5^{31}P^{187}Re^{103}Rh$, 679.9265; found, 679.9263 ± 0.0007 .

Anal. Calcd for $C_{22}H_{15}O_5PRh$: C, 38.89; H, 2.23. Found: C, 39.32; H, 2.54.

Further elution of the column with up to 100% benzene brought down small amounts of inseparable materials, none of which exhibited terminal carbonyl stretching absorptions similar to those of complexes **1a** and **1b**.

Before chromatography, the reaction mixture had an odor characteristic of an organic ketone. Therefore, a hexane solution of crude reaction mixture was subjected to gas chromatographic analysis on a column packed with 10% SE 30 Chromosorb G, 60–80 mesh. Peak enhancement studies using pure samples of acetophenone and benzophenone preliminarily identified the organic material as acetophenone. This was confirmed by observation of the characteristic methyl resonance of acetophenone in the benzene- d_6 solution 1H NMR of the reaction mixture and by observation of its keto stretch in the cyclohexane solution infrared spectrum.

Cobalt. Reaction of $(\eta^5-C_5H_5)Co(CO)[P(C_6H_5)_3]$ with $CH_3Mn(CO)_5$. $(\eta^5-C_5H_5)Co(CO)[P(C_6H_5)_3]$ (0.447 g, 1.08 mmol) and $CH_3Mn(CO)_5$ (0.313 g, 1.49 mmol) were dissolved in 80 ml of benzene and refluxed under N_2 . After 1 hr, infrared spectrum indicated the presence of some new bands which underwent

no further change under reflux for another 6.5 hr; no color change was observed. The solution was cooled under a slow stream of N_2 and solvent removed under vacuum (20 mm, 20°). The residue was placed on a column (45×3 cm) of deoxygenated alumina (neutral, activity III) and hexane. Elution with pure hexane produced first an orange band of $(\eta^5-C_5H_5)Co(CO)_2$ (0.146 g, 0.811 mmol, 75% based on Co) followed by a yellow band, $CH_3Mn(CO)_4[P(C_6H_5)_3]$ (0.144 g, 0.325 mmol). A small amount of $Mn_2(CO)_{10}$ was found to contaminate the first band; no further materials were eluted with up to 100% benzene.

Reaction of $(\eta^5-C_5H_5)Co(CO)[P(C_6H_5)_3]$ (0.195 g, 0.472 mmol) and $CH_3Mn(CO)_5$ (0.150 g, 0.715 mmol) in 80 ml of hexane at room temperature also resulted in near quantitative conversion to $(\eta^5-C_5H_5)Co(CO)_2$ and $CH_3Mn(CO)_4[P(C_6H_5)_3]$ after 4 days.

Supplementary Material Available. Infrared data in Tables II and III and Figure A will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105×148 mm, $24\times$ reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-2681.

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