

# Preparation, Properties, and Chemical Reactivity of Phospha- and Arsaacetylenedicobalt Hexacarbonyl Complexes, $(RCE)Co_2(CO)_6$ ( $E = P, As$ )<sup>1</sup>

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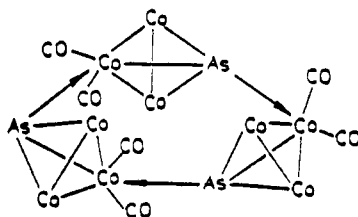
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Phosphaacetylenedicobalt hexacarbonyls,  $(RCP)Co_2(CO)_6$ , and arsaacetylenedicobalt hexacarbonyls,  $(RAs)Co_2(CO)_6$  ( $R = CH_3, Ph$ , and  $Me_3Si$  for the former;  $R = H, CH_3, Ph$ , and  $Me_3Si$  for the latter) have been prepared by the reaction of dicobalt octacarbonyl in THF with the respective  $RCCL_2ECl_2$  ( $E = P, As$ ) at low temperature. The  $RCCL_2ECl_2$  compounds were obtained by reaction of the respective  $RCCL_2Li$  with  $ECl_3$  at low temperature. The arsaacetylenedicobalt hexacarbonyl complexes were devoid of donor properties, but the phosphaacetylenedicobalt hexacarbonyl complexes formed adducts (via P) with  $Cr(CO)_5$ ,  $Mo(CO)_5$ , and  $W(CO)_5$  moieties. The  $(PhCE)Co_2(CO)_6$  ( $E = P, As$ ) complexes could be para-acetylated with  $CH_3COCl/AlCl_3$ . Ceric ion oxidation of  $(PhCAs)Co_2(CO)_6$  resulted in formation of  $PhCO_2CH_3$  and  $PhC(O)CO_2CH_3$  when the reaction was carried out in methanol. Thermolysis of  $(PhCAs)Co_2(CO)_6$  at 200 °C gave cobalt arsenide.

## Introduction

Cobalt carbonyl cluster complexes containing phosphorus<sup>2</sup> and arsenic<sup>2b,d,e,3</sup> have been the subject of research during the past dozen years. They are of particular interest because there are two cluster series (shown in Figure 1 for the one containing phosphorus) which include the tetrahedral homotetranuclear species and all possible heterotetranuclear species. Also known is a  $P_3Co$  cluster complex in which the three CO ligands on cobalt are replaced by the tripod phosphine  $CH_3C(CH_2PPh_2)_3$ .<sup>4</sup>

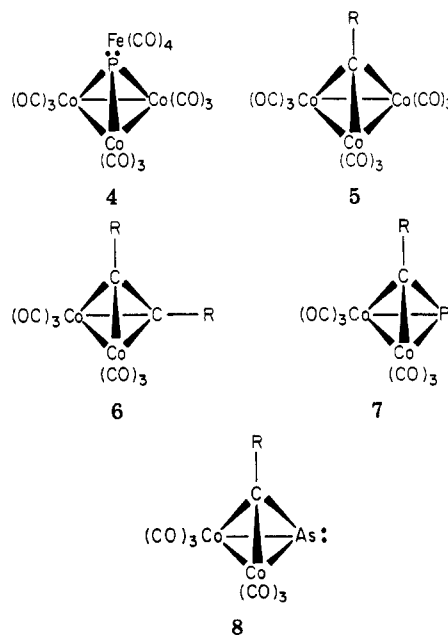
In this paper we shall focus on those complexes which contain one or two group 5 atoms,  $ECo_3(CO)_9$ , 1, and  $E_2Co_2(CO)_6$ , 2 ( $E = P, As$ ). The arsenic complex,  $AsCo_3(CO)_9$ , has been prepared by the reaction of arsenic triiodide with  $Na[Co(CO)_4]$  in hexane solution and isolated in the form of deep violet crystals. These are stable in the solid state under carbon monoxide, but in hexane solution under a nitrogen atmosphere intermolecular CO displacement results in formation of the green "trimer" 3.<sup>2b</sup>



3 (CO ligands of  $Co(CO)_3$  omitted for clarity)

The arsenic atom of  $AsCo_3(CO)_9$  is a donor site: the complexes  $(OC)_9Co_3AsFe(CO)_4$  and  $(OC)_9Co_3AsM(CO)_5$  ( $M =$

$Cr, Mo, W$ ) are readily formed.<sup>5</sup> The diarsenic complex  $As_2Co_2(CO)_6$ , a red oil, is produced in the reaction of arsenic trichloride with dicobalt octacarbonyl in tetrahydrofuran (THF) solution.<sup>3b</sup> The monophosphorus cluster  $PCo_3(CO)_9$ , obtained by the reaction of white phosphorus with  $Co_2(CO)_8$  in hexane or of a phosphorus trihalide with a salt of  $[Co(CO)_4]^-$  in THF, is much more reactive than its arsenic analogue, and, in fact, it undergoes "cyclootrimerization" to give the phosphorus analogue of 3 so readily that it cannot be isolated as the pure "monomer". A solution spectroscopic study showed that the lifetime of  $PCo_3(CO)_9$  was less than 10 min in hexane at room temperature.<sup>2c</sup> However, it could be trapped in the form of its  $Fe(CO)_4$  complex, 4. The reaction of  $PCl_3$  or  $PBr_3$  with  $Na[Co(CO)_4]$  in THF gave  $P_2Co_2(CO)_6$  as a red oil; this is the most stable member of the mixed P/Co( $CO$ )<sub>3</sub> clusters. The  $E_2Co_2(CO)_6$  complexes appear to be devoid of donor reactivity.



In previous research we have studied the preparation, the interconversions and other reactions of  $\mu_3$ -alkyli-

(1) (a) Part 34 of the series Organocobalt Cluster Complexes. Part 33 (mislabelled 23): Seyferth, D.; Nestle, M. O. *J. Am. Chem. Soc.* 1981, 103, 3320. (b) The current Chemical Abstracts index names for these complexes are hexacarbonyl[ $\mu$ - $\eta^2$ : $\eta^2$ -(alkylidene)phosphine]dicobalt( $Co-Co$ ) and hexacarbonyl[ $\mu$ - $\eta^2$ : $\eta^2$ -(alkylidene)arsine]dicobalt( $Co-Co$ ); the preferred names in line with the IUPAC rules of nomenclature are  $\mu$ -( $P$ - $\alpha$ - $\eta$ : $P$ - $\alpha$ - $\eta$ -alkylidene)phosphine-hexacarbonyldicobalt( $Co-Co$ ) and  $\mu$ -( $As$ - $\alpha$ - $\eta$ : $As$ - $\alpha$ - $\eta$ -alkylidene)arsine-hexacarbonyldicobalt( $Co-Co$ ). We thank Dr. K. L. Loening, Chemical Abstracts Service, for advice on nomenclature.

(2) (a) Vizi-Orosz, A.; Pályi, G.; Markó, L. *J. Organomet. Chem.* 1973, 60, C25. (b) Vizi-Orosz, A.; Galamb, V.; Pályi, G.; Markó, L. *Ibid.* 1976, 107, 235. (c) Vizi-Orosz, A. *Ibid.* 1976, 111, 61. (d) Vizi-Orosz, A.; Galamb, V.; Pályi, G.; Markó, L. *Ibid.* 1981, 216, 105. (e) Morrell, C. E.; Taranke, L. B. German Offen. 2 260 534, 1973; *Chem. Abstr.* 1973, 79, 125792.

(3) (a) Foust, A. S.; Foster, M. S.; Dahl, L. F. *J. Am. Chem. Soc.* 1969, 91, 5631. (b) Foust, A. S.; Foster, M. S.; Dahl, L. F. *Ibid.* 1969, 91, 5633.

(4) Di Vaira, M.; Ghilardi, C. A.; Midollini, S.; Sacconi, L. *J. Am. Chem. Soc.* 1978, 100, 2550.

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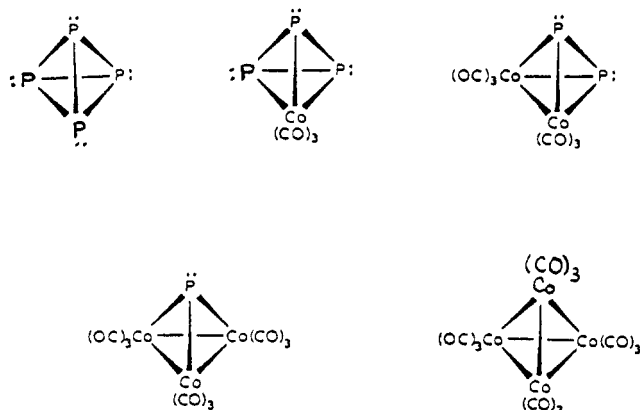


Figure 1. Cluster series containing P and  $\text{Co}(\text{CO})_3$  units.

dyne-tricobalt nonacarbonyl complexes,  $\text{RCCo}_3(\text{CO})_9$ , **5**,<sup>6,7</sup> as well as some reactions of acetylenedicobalt hexacarbonyl complexes, **6**.<sup>8,9</sup> In terms of structure and bonding, these classes of organocobalt carbonyls are closely related to the  $\text{ECo}_3(\text{CO})_9$  and  $\text{E}_2\text{Co}_2(\text{CO})_6$  ( $\text{E} = \text{P}, \text{As}$ ) complexes, respectively. For this reason we felt that it would be of interest from several standpoints to prepare hybrids of the  $\text{ECo}_3(\text{CO})_9$  and  $\text{RCCo}_3(\text{CO})_9$  clusters, i.e., complexes of type **7** and **8** in which an RC unit has replaced a  $\text{Co}(\text{CO})_3$  unit of  $\text{ECo}_3(\text{CO})_9$ . First, it might be expected that such a substitution to give **7** might well modify the donor reactivity of the phosphorus atom to an extent sufficient to allow the isolation of **7** as the "monomer". Furthermore, by varying the nature of the substituent R on the carbon atom in the cluster (from electron releasing to electron attracting), it might be possible to "fine tune" the donor reactivity of P and As in **7** and **8**, respectively. Finally, clusters of type **7** and **8** may be regarded as  $\text{Co}_2(\text{CO})_6$  complexes of phospho- and arsaacetylenes,  $\text{RC}\equiv\text{E}$  ( $\text{E} = \text{P}, \text{As}$ ), so they are also related to the acetylene complexes  $(\text{RC}_2\text{R})\text{Co}_2(\text{CO})_6$ , **6**. The latter are prepared by the reaction of dicobalt octacarbonyl with the respective acetylene, and on oxidation under appropriate conditions the acetylene is regenerated.<sup>9</sup> Thus one might hope that complexes of type **7** and **8**, however they may have been prepared, could, upon appropriate chemical or physical degradation, provide a source of the free ligands,  $\text{RC}\equiv\text{P}$  and  $\text{RC}\equiv\text{As}$ . With these ideas in mind, we commenced our investigations aimed at the preparation and study of complexes of type **7** and **8**.

## Results and Discussion

(1) **Syntheses of Phospha- and Arsaacetylenedicobalt Hexacarbonyl Complexes.** As noted in the introduction,  $\mu_3$ -phosphido- and  $\mu_3$ -arsenido-tricobalt nonacarbonyl complexes generally are prepared by the reaction of the respective phosphorus and arsenic trihalide with either dicobalt octacarbonyl or a salt of the  $[\text{Co}(\text{CO})_4]^-$  anion. A generally applicable preparation of  $\mu_3$ -alkyldyne-tricobalt nonacarbonyl complexes uses the reaction of an organic trihalide,  $\text{RCX}_3$ , or dihalide,  $\text{RCHX}_2$ , with dicobalt octacarbonyl.<sup>6</sup> A reasonable strategy for the synthesis of  $(\text{RCE})\text{Co}_2(\text{CO})_6$  ( $\text{E} = \text{P}, \text{As}$ ) complexes seemed to us to be one which combined both of these reactions in one synthetic step. To ensure the presence of a C-P (or

## Scheme I. Preparation of Phospha- and Arsaacetylenedicobalt Hexacarbonyl Complexes

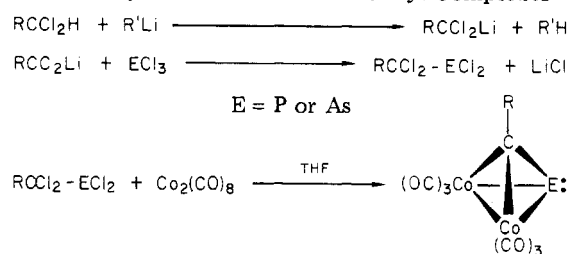


Table I. Preparation of Phospha- and Arsaacetylenedicobalt Hexacarbonyl Complexes

complex	% yield <sup>a</sup>
$(\text{HCAs})\text{Co}_2(\text{CO})_6$	9
$(\text{CH}_3\text{CAs})\text{Co}_2(\text{CO})_6$	27
$(\text{C}_6\text{H}_5\text{CAs})\text{Co}_2(\text{CO})_6$	28
$(\text{Me}_3\text{SiCAs})\text{Co}_2(\text{CO})_6$	25
$(\text{CH}_3\text{CP})\text{Co}_2(\text{CO})_6$	23
$(\text{C}_6\text{H}_5\text{CP})\text{Co}_2(\text{CO})_6$	18
$(\text{Me}_3\text{SiCP})\text{Co}_2(\text{CO})_6$	8

<sup>a</sup> Based on starting  $\text{RCCl}_2\text{H}$  (cf. Scheme I).

C-As) bond in the product complex, it was desirable to use a starting material in which such a bond was already present; i.e., the starting materials should be of the type  $\text{RCX}_2\text{EX}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ;  $\text{E} = \text{P}, \text{As}$ ). These then should react with dicobalt octacarbonyl to give the expected cluster complexes, **7** and **8**. This chemistry is outlined in Scheme I. The required ( $\alpha,\alpha$ -dihaloalkyl)dihalo-phosphines and -arsines were unknown at the time we began our study.

In earlier work we had occasion to use known<sup>10</sup> polyhaloalkyllithium reagents such as  $\text{PhCCl}_2\text{Li}$ ,  $\text{CCl}_3\text{Li}$ , and  $\text{CHCl}_2\text{Li}$  and to develop others such as  $\text{CH}_3\text{CCl}_2\text{Li}$ ,<sup>11</sup>  $\text{CF}_3\text{CCl}_2\text{Li}$ ,<sup>12</sup> and  $(\text{CH}_3)_3\text{SiCCl}_2\text{Li}$ .<sup>13</sup> Such reagents can be prepared by lithium/hydrogen or lithium/halogen exchange reactions. Due to the facility with which they undergo decomposition via an  $\alpha$ -elimination process, they must be prepared and used at low temperature ( $-78$  to  $-100$  °C, depending on R) and special solvent systems usually are used.<sup>10,12</sup>

Such reagents, we found, do react with phosphorus trichloride and arsenic trichloride at low temperature. In order to avoid di and trisubstitution, the  $\text{RCCl}_2\text{Li}$  which we used ( $\text{R} = \text{H}, \text{CH}_3, \text{C}_6\text{H}_5, (\text{CH}_3)_3\text{Si}$ ) were added, while maintained at low temperature, to a solution of the respective  $\text{ECl}_3$  at  $-100$  °C. The  $\text{RCCl}_2\text{PCL}_2$  and  $\text{RCCl}_2\text{AsCl}_2$  thus produced were not isolated, but the solutions containing them were added in turn to a cold ( $-78$  °C), dilute solution of dicobalt octacarbonyl in THF. As the reaction mixtures thus formed were allowed to warm slowly, moderate to brisk evolution of carbon monoxide commenced at around  $-10$  to  $0$  °C. This procedure, which requires three low-temperature reactions and two low-temperature transfers, is rather cumbersome, but it does give the desired products, mixed cluster complexes of type **7** and **8**. They were isolated by evaporation of the reaction mixture at reduced pressure, extraction of the residue with pentane, and purification of the material which had been extracted

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(7) Nicholas, K. M.; Nestle, M. O.; Seyferth, D. "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1978; Vol. II, pp 45-58.

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(11) (a) Seyferth, D.; Armbrecht, F. M., Jr. *J. Organomet. Chem.* **1969**, *16*, 249. (b) Seyferth, D.; Mueller, D. C. *J. Organomet. Chem.* **1971**, *28*, 325.

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(13) Seyferth, D.; Hanson, E. M.; Armbrecht, F. M., Jr. *J. Organomet. Chem.* **1970**, *23*, 361.

Table II. Nuclear Magnetic Resonance Spectra of Phospha- and Arsaacetylenedicobalt Hexacarbonyl Complexes and Their Derivatives

complex	<sup>1</sup> H NMR <sup>a</sup>	<sup>13</sup> C NMR <sup>b</sup>	<sup>31</sup> P NMR <sup>c</sup>
(HCAs)Co <sub>2</sub> (CO) <sub>6</sub> (CH <sub>3</sub> CAs)Co <sub>2</sub> (CO) <sub>6</sub>	8.39 (s, CDCl <sub>3</sub> ) 3.13 (s, CCl <sub>4</sub> )	31.5 (CH <sub>3</sub> ), 170.4 (cluster C), 198.0 (CO, CDCl <sub>3</sub> )	
(CH <sub>3</sub> CAs)Co <sub>2</sub> (CO) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub>	1.62, 1.83 (s, CH <sub>3</sub> , 2 isomers), 7.40 (br s, Ph, CDCl <sub>3</sub> )		
(C <sub>6</sub> H <sub>5</sub> CAs)Co <sub>2</sub> (CO) <sub>6</sub>	7.17-7.70 (m, Ph, CDCl <sub>3</sub> )	127.7 (para-C), 128.8 (meta-C), 131.5 (ortho-C), 148.5 (ipso-C), 165.9 (cluster C), 200.1 (CO, CDCl <sub>3</sub> )	
(Me <sub>3</sub> SiCAs)Co <sub>2</sub> (CO) <sub>6</sub> (CH <sub>3</sub> CP)Co <sub>2</sub> (CO) <sub>6</sub>	0.37 (s, Me <sub>3</sub> Si, CDCl <sub>3</sub> ) 2.90 (d, J(P-H) = 8 Hz, CH <sub>3</sub> , CCl <sub>4</sub> )	26.43 (s, CH <sub>3</sub> ), 144.43 (d, J(P-C) = 129 Hz, cluster C-P), 199.87 (CO, CCl <sub>4</sub> )	-65.5 (s)
(CH <sub>3</sub> CP)Co <sub>2</sub> (CO) <sub>5</sub> PPh <sub>3</sub>	2.17 (d, J(P-H) = 8 Hz, CH <sub>3</sub> ), 7.03-7.65 (m, Ph, CDCl <sub>3</sub> )		
(Me <sub>3</sub> SiCP)Co <sub>2</sub> (CO) <sub>6</sub> (C <sub>6</sub> H <sub>5</sub> CP)Co <sub>2</sub> (CO) <sub>6</sub> (CH <sub>3</sub> CP)Co <sub>2</sub> (CO) <sub>6</sub>	0.40 (s, Me <sub>3</sub> Si, CDCl <sub>3</sub> ) 7.12-7.52 (m, Ph, CDCl <sub>3</sub> ) 3.04 (s, J(P-H) = 10 Hz, CH <sub>3</sub> , CCl <sub>4</sub> )		-69.5 (s) 24.2 (s)
↓ Cr(CO) <sub>5</sub>			
(CH <sub>3</sub> CP)Co <sub>2</sub> (CO) <sub>6</sub> ↓ W(CO) <sub>5</sub>	2.91 (d, J(P-H) = 11 Hz, CH <sub>3</sub> , CDCl <sub>3</sub> )		
(C <sub>6</sub> H <sub>5</sub> CP)Co <sub>2</sub> (CO) <sub>6</sub> ↓ Cr(CO) <sub>5</sub>	7.10-7.55 (m, Ph, CCl <sub>4</sub> )		23.5 (s)
(C <sub>6</sub> H <sub>5</sub> CP)Co <sub>2</sub> (CO) <sub>6</sub> ↓ Mo(CO) <sub>5</sub>	7.16-7.56 (m, Ph, CDCl <sub>3</sub> )		-21.0 (s)
(C <sub>6</sub> H <sub>5</sub> CP)Co <sub>2</sub> (CO) <sub>6</sub> ↓ W(CO) <sub>5</sub>	7.10-7.54 (m, Ph, CCl <sub>4</sub> )		-57.5 (s with W satellites, J(W-P) = 232 Hz)

<sup>a</sup> δ units, ppm downfield from internal tetramethylsilane.<sup>b</sup> δ<sub>C</sub> units, ppm downfield from internal tetramethylsilane.<sup>c</sup> δ<sub>P</sub> units, ppm downfield from external 85% aqueous H<sub>3</sub>PO<sub>4</sub>.

by column chromatography and short-path distillation. The overall yields of the (RCE)Co<sub>2</sub>(CO)<sub>6</sub> complexes, based on starting RCl<sub>2</sub>H or RCl<sub>3</sub>, i.e., for the three-step sequence, were satisfactory in most cases considering the synthetic procedure used. The cluster complexes prepared in this manner are listed in Table I.

The mechanism of formation of the (RCE)Co<sub>2</sub>(CO)<sub>6</sub> complexes is not known. One possibility is a sequence involving dehalogenation of RCl<sub>2</sub>ECl<sub>2</sub> by Co<sub>2</sub>(CO)<sub>8</sub><sup>14</sup> to give RC≡P or RC≡As, followed by reaction of the latter with dicobalt octacarbonyl to form 7 or 8. Phosphaacetylenes (or alkylidynephosphines), RC≡P, are a known class of, for the most part, rather unstable organophosphorus compounds. Only a few members have been reported to date;<sup>16</sup> only two are stable enough for chemical study.<sup>16d,e</sup> Their reactions with dicobalt octacarbonyl have not yet been reported, but they may be expected to give clusters of type 7. On the other hand, the 7 and 8 complexes may be formed by a mechanism involving electron-

and atom-transfer steps without the intermediacy of free RC≡P or RC≡As.

(2) **Characterization.** All of the cluster complexes in Table I were isolated in the form of oils which ranged from orange to red in color. The arsenido complexes, with the exception of (HCAs)Co<sub>2</sub>(CO)<sub>6</sub>, were air-stable, but the phosphido complexes were not. All appeared to be reasonably thermally stable and could be distilled at reduced pressure in a short-path distillation unit.

The infrared spectra of these complexes showed three strong bands in the terminal carbonyl region, e.g., 2100, 2060, and 2036 cm<sup>-1</sup> for (CH<sub>3</sub>CP)Co<sub>2</sub>(CO)<sub>6</sub>, which is consistent with the presence of the Co<sub>2</sub>(CO)<sub>6</sub> unit (localized C<sub>3v</sub> symmetry). Their mass spectra (70-eV electron impact) also were consistent with the indicated structures, showing, inter alia, the molecular ion as well as fragment ions corresponding to the stepwise loss of the six CO ligands and then of the R substituent on carbon.

The nuclear magnetic resonance spectra of these complexes are given in Table II. Of special interest are the <sup>13</sup>C NMR spectra. The <sup>13</sup>C resonances of the cluster carbon atoms in μ<sub>2</sub>-acetylene-dicobalt complexes are found in the region δ<sub>C</sub> 91-95,<sup>17</sup> while cluster carbon atom shieldings in the <sup>13</sup>C NMR spectra of RCCO<sub>3</sub>(CO)<sub>9</sub> complexes are found at approximately 300-ppm downfield from tetramethylsilane.<sup>18</sup> Thus δ<sub>C</sub> of the (RCE)Co<sub>2</sub>(CO)<sub>6</sub> complexes (E = P, As) is approximately halfway between those of (RC<sub>2</sub>R)Co<sub>2</sub>(CO)<sub>6</sub> and RCCO<sub>3</sub>(CO)<sub>9</sub>. This may provide some indication of the bonding in the (RCE)Co<sub>2</sub>(CO)<sub>6</sub> complexes.

(14) Dicobalt octacarbonyl has been demonstrated to be a reactive dehalogenating agent with halogenated organic compounds. In some cases an organocobalt compound is formed, as in the RCX<sub>3</sub> + Co<sub>2</sub>(CO)<sub>8</sub> reaction. In other cases, only dehalogenation takes place, e.g.: Seyferth, D.; Millar, M. D. *J. Organomet. Chem.* 1972, 38, 373.

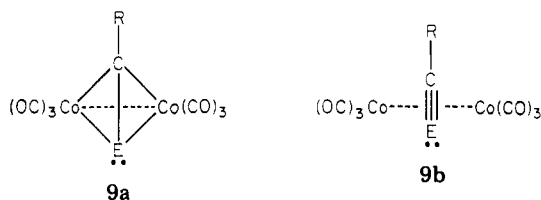
(15) Whether correct or not, this assumption provides the basis for our use of the 2Co<sub>2</sub>(CO)<sub>8</sub>/1RCCl<sub>2</sub>ECl<sub>2</sub> stoichiometry: dehalogenation will consume 1 equiv of Co<sub>2</sub>(CO)<sub>8</sub>, complexation the second.

(16) (a) Gier, T. E. *J. Am. Chem. Soc.* 1961, 83, 1769 (HC≡P). (b) Hopkinson, M. J.; Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C. *Chem. Phys. Lett.* 1976, 42, 460 (CH<sub>3</sub>C≡P). (c) Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C.; Westwood, N. P. C. *J. Am. Chem. Soc.* 1978, 100, 446 (FC≡P). (d) Cooper, T. A.; Kroto, H. W.; Nixon, J. F.; Ohashi, O. *J. J. Chem. Soc., Chem. Commun.* 1980, 333 (CF<sub>3</sub>C≡P). (e) Becker, G.; Gresser, G.; Uhl, W. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* 1981, 36B, 16 (Me<sub>3</sub>CC≡P); *J. Mol. Struct.* 1981, 75, 283. (f) Appel, R.; Westerhaus, A. *Tetrahedron Lett.* 1981, 22, 2159 (Me<sub>3</sub>SiC≡P).

(17) Aime, S.; Milone, L.; Rossetti, R.; Stanghellini, P. L. *Inorg. Chim. Acta* 1977, 22, 135.

(18) Seyferth, D.; Eschbach, C. S.; Nestle, M. O. *J. Organomet. Chem.* 1975, 97, C11. Also ref 1a.

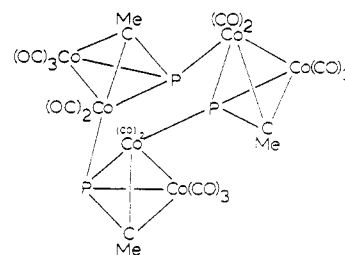
The  $(RC_2R)Co_2(CO)_6$  compounds have been described in terms of complexes of the first excited state of the acetylene with a  $Co_2(CO)_6$  unit.<sup>19</sup> IR,<sup>19</sup> <sup>1</sup>H, and <sup>13</sup>C NMR<sup>17,19c</sup> spectroscopic studies, as well as the X-ray crystal structures of some  $(RC_2R)Co_2(CO)_6$  complexes,<sup>20,21</sup> have all indicated that the bond between the two cluster carbon atoms is characterized by a high degree of double-bond character. Also, structural studies of  $E_2Co_2(CO)_5PPh_3$  complexes ( $E = P,^{22} As^{23}$ ) and calculations on  $P_2Co_2(CO)_6$ <sup>24</sup> have shown the E-E bond to closely approximate a double bond. Bonding in the  $\mu_3$ -alkylidyne-tricobalt nonacarbonyl complexes is best described in terms of the coordination of a carbyne, RC, with a *triangulo*-tricobalt species,<sup>25</sup> and, in fact,  $\delta_C$  for  $RCCo_3(CO)_9$  complexes are found in the same region in which the carbyne carbon atom shieldings of  $\mu$ -alkylidyne-metal complexes occur.<sup>26</sup> Caution must be exercised in the interpretation of carbon atom shieldings in organotransition-metal complexes, but on the basis of the available <sup>13</sup>C NMR data, we suggest a representation of the bonding in the  $(RCE)Co_2(CO)_6$  complexes in terms of resonance between the two extremes, **9a** and **9b**, with



both forms making approximately equal contributions. On this basis, it would appear that in the  $(RCE)Co_2(CO)_6$  complexes the ability of C and P or As to form a formal double bond is decreased in comparison with the homodiatom systems  $(RC_2R)Co_2(CO)_6$  and  $E_2Co_2(CO)_6$ .

**(3) Chemical Reactivity.** As indicated above, the  $(RCE)Co_2(CO)_6$  complexes were isolated as oils. They could not be crystallized, but they could be converted to solid derivatives by displacement of one or two CO ligands by triphenylphosphine. All of the arsenic complexes, **8**, were converted to bis(triphenylphosphine) derivatives by heating them in benzene with a slight excess of triphenylphosphine. Bis(triphenylphosphine) derivatives also were prepared of the phosphorus-containing clusters  $(PhCP)Co_2(CO)_6$  and  $(Me_3SiCP)Co_2(CO)_6$ . The methyl-substituted complex  $(CH_3CP)Co_2(CO)_6$  was converted to its monosubstitution product  $(CH_3CP)Co_2(CO)_5(PPh_3)$ . The methyl proton resonance in the NMR spectrum of this derivative showed an upfield shift (2.17 vs. 2.90 ppm) compared with the hexacarbonyl compound, in line with an increase in the cluster electron density on phosphine-for-carbon monoxide substitution.

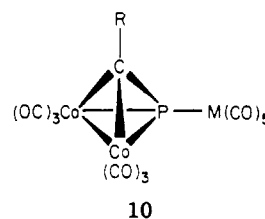
Of great interest with respect to one of the stated objectives of this study was the reactivity of the phosphorus and arsenic atoms in **7** and **8** toward transition-metal



**Figure 2.** A proposed structure of  $(CH_3CP)_3Co_6(CO)_{15}$ .

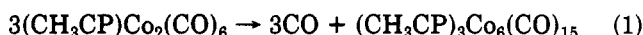
complexes. The  $(RCAs)Co_2(CO)_6$  complexes, **8**, appear to be devoid of donor activity toward transition-metal centers. Neither the  $R =$  methyl nor the  $R =$  phenyl compounds reacted with  $Cr(CO)_5(THF)$  or  $W(CO)_5(THF)$ .  $(PhCAs)Co_2(CO)_6$  did not react with methyl fluorosulfonate,  $CH_3OSO_2F$ , a powerful alkylating agent.

In contrast to the lack of reactivity displayed by **8**, the corresponding  $(RCP)Co_2(CO)_6$  complexes proved to be quite reactive in the Lewis base sense.  $(CH_3CP)Co_2(CO)_6$  and  $(PhCP)Co_2(CO)_6$  reacted readily with  $M(CO)_5(THF)$  ( $M = Cr, Mo, W$ ) species to give purple, crystalline adducts of type **10**. That the phosphorus atom in **7** is the site of



the  $M(CO)_5$  coordination was demonstrated by the <sup>31</sup>P NMR spectrum of  $(PhCP-W(CO)_5)Co_2(CO)_6$ . A singlet was observed at  $\delta_P - 57.5$  with tungsten satellites with  $J(P-W) = 232$  Hz. This coupling constant is in agreement with those found for other phosphine complexes of tungsten(0).<sup>27</sup> As expected,<sup>27</sup> downfield <sup>31</sup>P shifts occurred when  $M(CO)_5$  complexes of the cluster ligands were formed. For  $(PhCP)Co_2(CO)_6$  the coordination chemical shifts were 93.0, 48.5, and 12.0 ppm for the  $Cr(CO)_5$ ,  $Mo(CO)_5$ , and  $W(CO)_5$  complexes, respectively. For the formation of  $(CH_3CP-Cr(CO)_5)Co_2(CO)_6$  from the  $(CH_3CP)Co_2(CO)_6$  ligand, the coordination chemical shift was 89.7 ppm.

Another indication of the Lewis basicity of the  $(RCP)Co_2(CO)_6$  complexes is given by the formation of the "cyclotrimerization" product of  $(CH_3CP)Co_2(CO)_6$  (eq 1).



This complex was formed in 28% yield when a solution of  $(CH_3CP)Co_2(CO)_6$  was stirred at room temperature for 8.5 days. Its <sup>31</sup>P NMR spectrum showed two phosphorus resonances in 2:1 relative intensity and its <sup>1</sup>H NMR spectrum two  $CH_3$  resonances in 2:1 integrated ratio, which suggests a static structure, either the chair form shown in Figure 2 or the corresponding boat form. The trend in donor activity,  $(RCP)Co_2(CO)_6 > (RCAs)Co_2(CO)_6$ , thus parallels that observed with  $PCO_3(CO)_9$  and  $AsCO_3(CO)_9$ . However, as expected, substitution of the RC unit for one  $Co(CO)_3$  group in  $ECO_3(CO)_9$  has resulted in a very substantial decrease in the ability of the P and As centers to function as ligands in transition-metal complexes. In terms of lone-pair donor ability, one might expect the  $(RCE)Co_2(CO)_6$  complexes to be more reactive than  $MCO_3(CO)_9$ . However, in terms of  $\pi$ -back-bonding ability, one might expect the *triangulo*- $Co_3(CO)_9$  unit to be more effective

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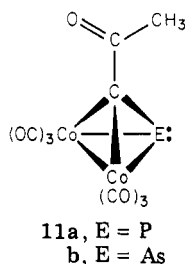
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than the  $\text{RCCo}_2(\text{CO})_6$  unit. From the observed results, it would appear that the latter factor dominates, making  $\text{ECO}_3(\text{CO})_9$  better ligands than  $(\text{RCE})\text{Co}_2(\text{CO})_6$  in transition-metal complexes.

One characteristic reaction of benzylidynetricobalt nonacarbonyl and diarylacetylenedicobalt hexacarbonyl complexes is their facile Friedel-Crafts acylation in the para position.<sup>28,29</sup> We find that  $(\text{PhCP})\text{Co}_2(\text{CO})_6$  and  $(\text{PhCAs})\text{Co}_2(\text{CO})_6$  also can be acylated in high yield by the acetyl chloride/aluminum chloride reagent to give products of type 11. The phosphorus-containing acetylated cluster



was obtained as a red oil in 43% yield. The arsenic analogue, also a red oil, could be prepared in 95% yield. Both products were converted to crystalline 1,2-bis(triphenylphosphine) derivatives.

That the  $(\text{RCE})\text{Co}_2(\text{CO})_6$  complexes may be considered as  $\text{Co}_2(\text{CO})_6$  complexes of phospha- and arsaacetylenes has been mentioned in a previous section. Since acetylenes may be released from their  $(\text{RC}_2\text{R})\text{Co}_2(\text{CO})_6$  complexes by oxidative degradation,<sup>7</sup> with ceric ammonium nitrate in aqueous acetone being very effective,<sup>29</sup> it was of some interest to see if  $\text{RC}\equiv\text{P}$  and  $\text{RC}\equiv\text{As}$  could be released from their  $\text{Co}_2(\text{CO})_6$  complexes. These species would not be stable to oxidative conditions, but one might hope to isolate an oxidation product derived from them. However, treatment of  $(\text{PhCAs})\text{Co}_2(\text{CO})_6$  with ceric ammonium nitrate in methanol gave only arsenic-free organic products:  $\text{PhCO}_2\text{CH}_3$  and  $\text{PhC}(\text{O})\text{CO}_2\text{CH}_3$ . The former is also obtained in the oxidation of  $\text{PhCCO}_3(\text{CO})_9$ , so its formation in this reaction is not surprising. However,  $\text{PhC}(\text{O})\text{CO}_2\text{CH}_3$  is an unexpected carbonylation product. We have no basis for speculation on the mechanism of formation of these products.

Thermal decomposition of  $(\text{PhCAs})\text{Co}_2(\text{CO})_6$  at 200 °C in the presence of tetraphenylcyclopentadienone, a potential "trap" for  $\text{PhC}\equiv\text{As}$ , gave no organoarsenic products. The complex decomposed, and a shiny black mirror, metallic in appearance, was deposited on the walls of the hot tube. Analysis indicated that this material contained 33% by weight of arsenic, so that a cobalt arsenide or a mixture of cobalt arsenide and metallic cobalt had been formed.

## Experimental Section

**General Comments.** All reactions were carried out under an atmosphere of prepurified tank nitrogen unless otherwise stated. Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl, and diethyl ether was distilled from lithium aluminum hydride. Reagent-grade pentane, dichloromethane, and carbon disulfide were deoxygenated by bubbling nitrogen through them for 15 min, prior to use. (Dichloromethyl)trimethylsilane (Petrarch),  $\alpha,\alpha$ -dichlorotoluene (Eastman Chemicals), and 1,1-dichloroethane (Eastman Chemicals) were distilled from  $\text{P}_2\text{O}_5$  prior to use. Dicobalt octacarbonyl (Strem Chemicals) was used as received without further purification unless otherwise stated.

Arsenic trichloride and phosphorus trichloride were obtained from Alfa-Ventron.

The progress of the reactions was monitored by thin-layer chromatography (TLC) (J. T. Baker Silica Gel 1B). Since these reactions yielded products which could be separated easily, full-scale chromatography was not required. Instead, filtration chromatography, in which the reaction products were dissolved in a suitable solvent and poured on top of a bed of Mallinckrodt 100 mesh silicic acid (ca. 200 mL) in a 350-mL glass-frit filter funnel, was used in most cases. The eluting solvent then was passed through with suction filtration.

Infrared spectra were obtained by using a Perkin-Elmer Model 457A double-beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either a Varian Associates T60 or a Hitachi-Perkin-Elmer R-20B spectrometer, both operating at 60 MHz. Chemical shifts are reported in  $\delta$  units, ppm downfield from internal tetramethylsilane. Chloroform or dichloromethane generally was used as an internal standard. The carbon-13 NMR spectra were recorded on a JEOL FX-60Q spectrometer operating at 15 MHz in the Fourier transform mode. Pulse width of 9  $\mu\text{s}$  was used. The samples were prepared by placing the oils in a 5-mm o.d. NMR tube along with approximately 20% chloroform-*d*. The spectrometer was locked on the deuterium signal of chloroform-*d* and 2000–3000 pulses were required to obtain spectra in which the cluster carbon atoms could be seen.

The phosphorus-31 NMR spectra were recorded on a JEOL FX-90Q spectrometer operating at 36.2 MHz in the Fourier transform mode. The spectrometer was locked externally on the deuterium signal of  $\text{D}_2\text{O}$ . The values are reported in  $\delta_p$  units, ppm downfield from 85% aqueous  $\text{H}_3\text{PO}_4$  using external  $\text{Ph}_3\text{P}$  (in the same solvent as the sample) as reference at -6.0 ppm. Mass spectra were obtained with a Varian MAT-44 instrument operating at 70 eV. Molecular ions were assigned on the basis of the most abundant natural isotope. Melting points were determined on analytically pure samples using a Büchi capillary melting point apparatus and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark.

Temperatures are reported in degrees centigrade (°C) and are uncorrected. Low temperatures were measured by using pentane thermometers (W. H. Kessler Co., Inc., +30 to -200 °C) with only the bulb immersed in the solution. However, these thermometers are total immersion thermometers and read -70 °C (bulb immersed) vs. -78 °C (total immersion) in a dry ice/acetone bath, so the temperatures reported are probably 8–10° high for the low-temperature reactions.

A considerable amount of attention is required in the preparation of the low-temperature lithium reagents  $\text{RCCl}_2\text{Li}$ . The temperatures must not be allowed to exceed -90 °C, and care must be taken not to allow the reaction mixture to freeze. This is best done by intermittent application of a liquid nitrogen bath with continuous monitoring of the temperature.

**Preparation of Phospha- and Arsaacetylenedicobalt Hexacarbonyl Complexes.** Essentially the same procedure was used in all preparations. That used in the synthesis of  $(\text{CH}_3\text{C-P})\text{Co}_2(\text{CO})_6$  is described in detail below. Table I summarizes the other preparations. The yields are not optimized and improvement should be possible. Spectroscopic and analytical data for all new products are given in Table III.

**Reaction between Dicobalt Octacarbonyl and (1,1-Dichloroethyl)phosphorus Dichloride. Step 1.**<sup>11</sup> A 300-mL three-necked Morton flask equipped with a mechanical stirrer, a serum cap, and a Claisen adapter fitted with a low-temperature thermometer and a nitrogen inlet tube was flushed with nitrogen. THF (90 mL), diethyl ether (45 mL), pentane (35 mL), and 2.1 mL (25 mmol) of  $\text{CH}_3\text{CCl}_2\text{H}$  (Eastman) were added by syringe. The resulting solution then was cooled to -100 °C by the intermittent application of a liquid nitrogen bath while stirring vigorously. By syringe, 10.8 mL (26 mmol) of 2.4 M *n*-BuLi in hexane was added over a 30-min period. The reaction mixture remained colorless. The mixture was stirred for an additional 1.5 h at -100 °C after the addition was completed.

**Step 2.** A 300-mL three-necked, round-bottomed flask equipped with a mechanical stirrer, a serum cap, and a Claisen adapter fitted with a low-temperature thermometer and a nitrogen inlet tube was flushed with nitrogen. THF (50 mL) and 2.2 mL (25 mmol) of  $\text{PCl}_3$  were added by syringe. This solution was cooled

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Table III. Phospha- and Arsaacetylenedicobalt Hexacarbonyl Complexes and Their Derivatives

complex	mp or bp, °C	anal. calcd (found), %		IR, terminal CO region, cm <sup>-1</sup>
		carbon	hydrogen	
(HCAs)Co <sub>2</sub> (CO) <sub>6</sub>	red oil	(partial dec on distillation)		2100 (s), 2065 (vs), 2040 (vs) (CCl <sub>4</sub> )
(HCAs)Co <sub>2</sub> (CO) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub>	dec without melting	58.46 (58.23)	3.71 (3.75)	
(CH <sub>3</sub> CAs)Co <sub>2</sub> (CO) <sub>6</sub>	40 (0.02 torr)	24.77 (24.97)	0.78 (0.89)	2100 (s), 2060 (vs), 2030 (vs) (CCl <sub>4</sub> )
		As, 19.32 (20.39)		
(CH <sub>3</sub> CAs)Co <sub>2</sub> (CO) <sub>5</sub> PPh <sub>3</sub>		48.26 (48.25)	2.92 (3.00)	
(CH <sub>3</sub> CAs)Co <sub>2</sub> (CO) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub>	dec without melting	58.90 (57.99)	3.88 (3.90)	2020 (s), 1945 (s) (CHCl <sub>3</sub> )
(C <sub>6</sub> H <sub>5</sub> CAs)Co <sub>2</sub> (CO) <sub>5</sub>	red oil	34.70 (35.32)	1.12 (1.35)	2090 (m), 2060 (s), 2035 (s) (CHCl <sub>3</sub> )
(C <sub>6</sub> H <sub>5</sub> CAs)Co <sub>2</sub> (CO) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub>	dec without melting	61.45 (61.13)	3.84 (3.96)	2025 (s), 1940 (s) (CHCl <sub>3</sub> )
(Me <sub>3</sub> SiCAs)Co <sub>2</sub> (CO) <sub>6</sub>	55 (0.1 torr)	26.63 (25.63)	2.03 (2.03)	2100 (s), 2062 (vs), 2039 (vs) (CDCl <sub>3</sub> )
(CH <sub>3</sub> CP)Co <sub>2</sub> (CO) <sub>6</sub>	45 (0.2 torr)	27.94 (27.74)	0.88 (0.99)	2100 (s), 2060 (vs), 2036 (vs) (CCl <sub>4</sub> )
(CH <sub>3</sub> CP)Co <sub>2</sub> (CO) <sub>5</sub> PPh <sub>3</sub>	108-110	51.93 (51.58)	3.14 (3.26)	2075 (s), 2010 (s), 1968 (m), (CH <sub>2</sub> Cl <sub>2</sub> )
(CH <sub>3</sub> CP)Co <sub>2</sub> (CO) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub>	235-238			2030 (s), 1968 (m) (CH <sub>2</sub> Cl <sub>2</sub> )
(Me <sub>3</sub> SiCP)Co <sub>2</sub> (CO) <sub>6</sub>	55 (0.7 torr)	(partial dec on distillation)		2107 (s), 2070 (vs), 2040 (vs) (CCl <sub>4</sub> )
(Me <sub>3</sub> SiCP)Co <sub>2</sub> (CO) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub>	172-174	60.70 (60.38)	4.51 (4.62)	
(C <sub>6</sub> H <sub>5</sub> CP)Co <sub>2</sub> (CO) <sub>6</sub>	65 (0.07 torr)			2100 (s), 2070 (vs), 2045 (vs) (CCl <sub>4</sub> )
(C <sub>6</sub> H <sub>5</sub> CP)Co <sub>2</sub> (CO) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub>	203-206	64.55 (64.45)	4.03 (4.13)	2030 (s), 1973 (s) (CH <sub>2</sub> Cl <sub>2</sub> )
(CH <sub>3</sub> CP)Co <sub>2</sub> (CO) <sub>6</sub>	65-66.5	29.13 (29.09)	0.56 (0.69)	2111 (m), 2079 (vs), 2055 (s), 2050 (sh), 1996 (w), 1992 (w), 1963 (vs) (CCl <sub>4</sub> )
↓ Cr(CO) <sub>5</sub>				
(CH <sub>3</sub> CP)Co <sub>2</sub> (CO) <sub>6</sub>	77-79	23.38 (23.44)	0.45 (0.57)	2112 (m), 2080 (vs), 2055 (vs), 1996 (w), 1992 (w), 1960 (vs) (CHCl <sub>3</sub> )
↓ W(CO) <sub>5</sub>				
(C <sub>6</sub> H <sub>5</sub> CP)Co <sub>2</sub> (CO) <sub>6</sub>	86-88	36.15 (36.29)	0.84 (0.90)	2107 (m), 2072 (vs), 2050 (s), 1995 (w), 1990 (w), 1962 (vs) (CCl <sub>4</sub> )
↓ Cr(CO) <sub>5</sub>				
(C <sub>6</sub> H <sub>5</sub> CP)Co <sub>2</sub> (CO) <sub>6</sub>	69-71	33.68 (34.03)	0.78 (1.00)	2105 (m), 2070 (vs), 2046 (s), 2032 (sh), 2015 (w), 1967 (vs) (CCl <sub>4</sub> )
↓ Mo(CO) <sub>5</sub>				
(C <sub>6</sub> H <sub>5</sub> CP)Co <sub>2</sub> (CO) <sub>6</sub>	98-99	29.62 (29.59)	0.69 (0.77)	2110 (m), 2076 (vs), 2051 (s), 1993 (w), 1989 (w), 1960 (vs) (CCl <sub>4</sub> )
↓ W(CO) <sub>5</sub>				

to -100 °C by the intermittent application of a liquid nitrogen bath with vigorous stirring. A cannula wrapped in a paper towel was soaked with acetone, and the acetone was frozen with liquid nitrogen. In this manner, the temperature of the cannula was regulated at -78 °C, and the cannula was used to transfer the solution generated in step 1 into the reaction flask in step 2. (The reaction solution remained colorless.) When the addition was complete, the reaction mixture was stirred for an additional 2 h at -100 °C.

**Step 3.** A 3-L three-necked, round-bottomed flask equipped with a mechanical stirrer, a serum cap, and a Claisen adapter fitted with a low-temperature thermometer and a nitrogen inlet tube was flushed with nitrogen and then charged with 18.1 g (53 mmol) of Co<sub>2</sub>(CO)<sub>8</sub> (Strem) and 1 L of THF. The dark brown solution was cooled to -78 °C (dry ice/acetone bath), and the solution generated in step 2 was cannulated into the reaction vessel. The cooling bath was removed, and the reaction mixture was allowed to warm slowly to room temperature. No color changes were observed. At ca. -5 °C moderate gas evolution ensued. The reaction mixture was stirred at room temperature overnight.

The solution was filtered to remove the blue CoCl<sub>2</sub>. Solvent was removed on a rotary evaporator under nitrogen, leaving a brown-black, oily residue. This residue was extracted with hot pentane until the extracts were colorless. The combined extracts were concentrated on a rotary evaporator under nitrogen to yield a red-brown oil. Chromatography (silicic acid/pentane) yielded a red band which, upon removal of solvent, gave 1.978 g (5.75 mmol, 23% yield) of (MeCP)Co<sub>2</sub>(CO)<sub>6</sub> as a slightly air-sensitive, red oil. This material was short-path distilled at 45 °C (0.2 mm) to yield an analytically pure sample.

A solid triphenylphosphine derivative was prepared by the addition (over 15 min) of 0.63 g (2.40 mmol) of PPh<sub>3</sub> to a refluxing solution of 1.00 g (2.91 mmol) of (MeCP)Co<sub>2</sub>(CO)<sub>6</sub> in 100 mL of benzene. This procedure gave 0.971 g (1.68 mmol, 58% yield based on the cluster) of (MeCP)Co<sub>2</sub>(CO)<sub>5</sub>(PPh<sub>3</sub>) as an air-stable, orange solid (recrystallization from pentane), mp 108-110 °C. The second product isolated was 0.305 g (0.374 mmol, 13% yield based on the cluster) of (MeCP)Co<sub>2</sub>(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> as an air-stable, dark-purple solid (recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane), mp 235-238 °C.

**Reaction between (2-Methyl-1-phosphaacetylene)dicobalt Hexacarbonyl and Pentacarbonyl(tetrahydrofuran)tung-**

**sten.** A 300-mL three-necked, round-bottomed flask equipped with a magnetic stir-bar, two serum caps, a reflux condenser, a nitrogen inlet needle, and a gas outlet was flushed with nitrogen and charged with 1.02 g (2.91 mmol) of W(CO)<sub>6</sub> (Pressure Chemical) and 200 mL of THF. Nitrogen was bubbled through the solution as it was irradiated by a Hanovia high-pressure mercury lamp. After a few minutes, all of the W(CO)<sub>6</sub> had dissolved and the solution became yellow. After 3.5 h the irradiation was stopped, and the solution was yellow-orange.

A solution of 1.00 g (2.91 mmol) of (MeCP)Co<sub>2</sub>(CO)<sub>6</sub> in 25 mL of THF was cannulated into the reaction vessel. Immediately, the reaction mixture became deep ruby red. TLC showed the disappearance of all starting material after addition was complete. Solvent was removed on a rotary evaporator, leaving a dark red solid which was chromatographed (silicic acid/pentane). Elution with 10% CH<sub>2</sub>Cl<sub>2</sub>/pentane yielded a deep red band which, upon removal of solvent, gave 1.407 g (2.11 mmol, 72% yield) of [MeCPW(CO)<sub>5</sub>]Co<sub>2</sub>(CO)<sub>6</sub> as air-stable, red-purple crystals, mp 77-79 °C (from pentane). The mass spectrum showed the molecular ion and fragment ions corresponding to the successive loss of the 11 CO ligands.

The W(CO)<sub>5</sub> adduct of (PhCP)Co<sub>2</sub>(CO)<sub>6</sub>, purple crystals, mp 98-99 °C (from pentane), was prepared in 71% yield in similar fashion. Its mass spectrum also showed the molecular ion and [M<sup>+</sup> - nCO] fragment ions (n = 1-11).

**Reaction between (2-Methyl-1-phosphaacetylene)dicobalt Hexacarbonyl and Pentacarbonyl(tetrahydrofuran)chromium.** The standard apparatus was assembled, flushed with nitrogen, and charged with 0.64 g (2.91 mmol) of Cr(CO)<sub>6</sub> (Strem) and 200 mL of THF. After the solution had been irradiated for 2.5 h, it was yellow-orange. A solution of 1.00 g (2.91 mmol) of (MeCP)Co<sub>2</sub>(CO)<sub>6</sub> in 25 mL of THF was cannulated into the reaction vessel. Immediately, the solution became a deep red. Solvent was removed on a rotary evaporator, leaving a red solid which was chromatographed (silicic acid/pentane). First, pentane eluted a red band which gave 0.266 g (0.77 mmol) of (MeCP)Co<sub>2</sub>(CO)<sub>6</sub>. Continued elution with pentane then yielded a deep red band which, upon removal of solvent, gave 0.688 g (1.28 mmol, 60% yield based on recovered starting material) of [MeCPCr(CO)<sub>5</sub>]Co<sub>2</sub>(CO)<sub>6</sub> as an air-stable, red-purple solid, mp 65-66.5 °C (from pentane). The mass spectrum showed the molecular ion and fragment ions corresponding to successive loss of the 11 CO



ligands.

**Reaction between (2-Phenyl-1-phosphaacetylene)dicobalt Hexacarbonyl and Pentacarbonyl(tetrahydrofuran)molybdenum.** The standard apparatus was assembled, flushed with nitrogen, and charged with 1.32 g (5 mmol) of  $\text{Mo}(\text{CO})_5$  (Strem) and 100 mL of THF. After the solution had been irradiated for 2.5 h, it was yellow-orange. Next, 0.80 g (1.97 mmol) of  $(\text{PhCP})\text{Co}_2(\text{CO})_6$  in 30 mL of THF was cannulated into the reaction flask. After the reaction mixture had been stirred for 1 h, solvent was removed on a rotary evaporator, leaving a red solid which was chromatographed (silicic acid/pentane). First, pentane eluted a red band which gave 0.124 g (0.31 mmol) of  $(\text{PhCP})\text{Co}_2(\text{CO})_6$ . Continued elution with pentane yielded a deep red band which, upon removal of solvent, gave 0.490 g (0.763 mmol, 46% yield based on recovered starting material) of  $[(\text{PhCPMo}(\text{CO})_5)_3\text{Co}_2(\text{CO})_6]$  as an air-stable, purple-red solid, mp 69–71 °C (from pentane). The mass spectrum showed the molecular ion and fragment ions corresponding to the successive loss of the 11 CO ligands.

A similar reaction of  $(\text{PhCP})\text{Co}_2(\text{CO})_6$  (2.96 mmol) with  $\text{Cr}(\text{CO})_5(\text{THF})$  (3.5 mmol) in THF gave  $[(\text{PhCP-Cr}(\text{CO})_5)_3\text{Co}_2(\text{CO})_6]$ , air-stable purple-black crystals, mp 86–88 °C (from pentane), in 76% yield. The mass spectrum was characterized by  $\text{M}^+$  and  $[\text{M}^+ - n\text{CO}]$  ( $n = 1-11$ ).

**Trimerization of (2-Methyl-1-phosphaacetylene)dicobalt Hexacarbonyl in Tetrahydrofuran.** A 200-mL round-bottomed flask fitted with a stir bar and a serum cap was flushed with nitrogen and charged with 1.00 g (2.91 mmol) of  $(\text{MeCP})\text{Co}_2(\text{CO})_6$  in 50 mL of THF. The reaction mixture was stirred for 8.5 days while it was monitored by TLC. Solvent was removed from the dark, brown-red solution on a rotary evaporator, leaving a black, oily solid which was chromatographed (silicic acid/pentane). Pentane eluted a red band which, upon removal of solvent, gave 0.327 g (0.951 mmol) of  $(\text{MeCP})\text{Co}_2(\text{CO})_6$ . Elution with 10%  $\text{CH}_2\text{Cl}_2$ /pentane yielded a black-red band which, upon removal of solvent, gave 0.170 g [0.179 mmol, 27.5% conversion based on recovered  $(\text{MeCP})\text{Co}_2(\text{CO})_6$ ] of  $[(\text{MeCP})\text{Co}_2(\text{CO})_5]_3$  as an air-stable, brown-black solid. After recrystallization from pentane, mp 107–109 °C, it was identified on the basis of the following data: IR ( $\text{CH}_2\text{Cl}_2$ ) 2960 (w), 2910 (w), 1010 (w)  $\text{cm}^{-1}$ , terminal carbonyl region, 2097 (w), 2070 (vs), 2040 (s)  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  2.71 [d,  $J(\text{P-H}) = 6$  Hz,  $\text{CH}_3$ ] and 2.79 [d,  $J(\text{P-H}) = 6$  Hz,  $\text{CH}_3$ ] in a 1:2 ratio;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{P}}$  16.08 (s, 2 P) and 28.39 (s, 1 P) (see Figure 2); mass spectrum,  $m/e$  (relative intensity) 948 ( $\text{M}^+$ , 14%), 920 ( $\text{M}^+ - \text{CO}$ , 0.7%), 892 ( $\text{M}^+ - 2\text{CO}$ , 42%), 864 ( $\text{M}^+ - 3\text{CO}$ , 0.7%), 836 ( $\text{M}^+ - 4\text{CO}$ , 2%), 808 ( $\text{M}^+ - 5\text{CO}$ , 10%), 780 ( $\text{M}^+ - 6\text{CO}$ , 22%), 752 ( $\text{M}^+ - 7\text{CO}$ , 6%), 724 ( $\text{M}^+ - 8\text{CO}$ , 23%), 696 ( $\text{M}^+ - 9\text{CO}$ , 80%), 668 ( $\text{M}^+ - 10\text{CO}$ , 67%), 640 ( $\text{M}^+ - 11\text{CO}$ , 64%), 612 ( $\text{M}^+ - 12\text{CO}$ , 61%), 584 ( $\text{M}^+ - 13\text{CO}$ , 73%), 556 ( $\text{M}^+ - 14\text{CO}$ , 94%), 528 ( $\text{M}^+ - 15\text{CO}$ , 100%).

Anal. Calcd for  $\text{C}_7\text{H}_3\text{Co}_2\text{O}_5\text{P}$ : C, 26.61; H, 0.96. Found: C, 26.23; H, 1.02.

When 1.00 g (2.91 mmol) of  $(\text{MeCP})\text{Co}_2(\text{CO})_6$  in 75 mL of benzene was refluxed for 1 h, 0.109 g (0.115 mmol, a 12% yield) of  $[(\text{MeCP})\text{Co}_2(\text{CO})_5]_3$  was obtained. It was identified by comparison of its mass spectrum with that of an authentic sample. Further,  $(\text{MeCP})\text{Co}_2(\text{CO})_6$  was found to decompose (on storage at  $-30$  °C under nitrogen) to  $[(\text{MeCP})\text{Co}_2(\text{CO})_5]_3$  after prolonged periods of time.

**Reaction between (2-Phenyl-1-arsaacetylene)dicobalt Hexacarbonyl and Acetyl Chloride in the Presence of Aluminum Chloride.** A 300-mL three-necked round-bottomed flask equipped with a nitrogen inlet, a pressure-equalizing addition funnel, and a magnetic stir bar was flushed with nitrogen and charged with 0.35 g (4 mmol) of acetyl chloride in 50 mL of dichloromethane. Then, 0.59 g (4 mmol) of aluminum chloride was added with stirring to the solution, and the reaction mixture was stirred for 30 min. Meanwhile, the addition funnel was charged with 1.00 g (2.2 mmol) of (2-phenyl-1-arsaacetylene)dicobalt hexacarbonyl in 50 mL of dichloromethane. Then, the solution of this complex was added to the stirred acetyl chloride/aluminum chloride solution over a period of 5 min. TLC showed that the reaction was complete upon addition.

The reaction mixture was poured into 100 mL of water, the organic layer was separated and dried over  $\text{MgSO}_4$ , and the solvent was removed on a rotary evaporator to yield a red oil. The oil

was chromatographed on a silicic acid column. Benzene eluted a single fraction which yielded 1.05 g (2.1 mmol, 95% yield) of (2-(*p*-acetylphenyl)-1-arsaacetylene)dicobalt hexacarbonyl as a red oil, 11b: NMR ( $\text{CCl}_4$ )  $\delta$  2.48 (s, 3 H,  $\text{CH}_3$ ), 7.4–7.95 (m, AA'BB' pattern, 4 H, phenyl).

11b could not be distilled without decomposition, and a satisfactory combustion analysis could not be obtained. However, it could be converted to a bis(triphenylphosphine) derivative. Treatment with 2 equiv of triphenylphosphine in refluxing benzene yielded the 1,2-bis(triphenylphosphine) derivative, (2-(*p*-acetylphenyl)-1-arsaacetylene)dicobalt bis(triphenylphosphine) tetracarbonyl, which decomposed without melting at 145 °C: IR ( $\text{CHCl}_3$ ) 3060 (w), 3005 (w), 2080 (sh), 1665 (s), 1582 (s), 1480 (m), 1432 (m), 1400 (w), 1368 (w), 1300 (w), 1270 (w), 1175 (w), 1090 (s), 1025 (vw), 1000 (vw), 955 (vw), 935 (vw)  $\text{cm}^{-1}$ , terminal carbonyl region, 2030 (s), 1950 (vs)  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  2.56 (s, 3 H,  $\text{CH}_3$ ) and 6.67–7.56 (m, 34 H, phenyl).

Anal. Calcd for  $\text{C}_{49}\text{H}_{37}\text{AsCo}_2\text{O}_5\text{P}_2$ : C, 61.27; H, 3.88. Found: C, 61.46; H, 4.30.

**Reaction between (2-Phenyl-1-phosphaacetylene)dicobalt Hexacarbonyl and Acetyl Chloride in the Presence of Aluminum Chloride.** With use of the procedure described above, 5 mmol each of acetyl chloride and aluminum chloride in 50 mL of dichloromethane was treated with a solution of 2.46 mmol of  $(\text{PhCP})\text{Co}_2(\text{CO})_6$  in 50 mL of dichloromethane. TLC showed the reactants had been consumed during the course of the 10-min addition period. Workup as above gave a red oil which was chromatographed (silicic acid/ $\text{CH}_2\text{Cl}_2$ ) to give 0.471 g (1.05 mmol, 43% yield) of (2-(*p*-acetylphenyl)-1-phosphaacetylene)dicobalt hexacarbonyl as a red, air-sensitive oil which was identified on the basis of the following data: IR ( $\text{CCl}_4$ ) 3060 (w), 3030 (w), 2960 (m), 2935 (m), 2860 (m), 1715 (m), 1680 (s) (C=O), 1592 (m), 1400 (m), 1360 (m), 1302 (m), 1265 (s), 1180 (m), 1110 (w), 1075 (w), 1015 (w), 955 (m), 913 (m), 840 (w), 650 (m), 630 (m), 595 (w)  $\text{cm}^{-1}$ , terminal carbonyl region, 2100 (s), 2065 (vs), 2040 (vs)  $\text{cm}^{-1}$ ; NMR ( $\text{CCl}_4$ )  $\delta$  2.45 (s, 3 H,  $\text{CH}_3$ ) and 7.05–7.85 (m, 4 H, phenyl).

A bis(triphenylphosphine) derivative was prepared by heating (2-(*p*-acetylphenyl)-1-phosphaacetylene)dicobalt hexacarbonyl with 2 equiv of triphenylphosphine in 60 mL of refluxing benzene for 6 h. After recrystallization from  $\text{CH}_2\text{Cl}_2$ /pentane, the red-purple crystals, mp 115–116.5 °C, were identified as (2-(*p*-acetylphenyl)-1-phosphaacetylene)dicobalt bis(triphenylphosphine) tetracarbonyl: IR ( $\text{CH}_2\text{Cl}_2$ ) terminal carbonyl region, 2035 (s), 1975 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{49}\text{H}_{37}\text{Co}_2\text{O}_5\text{P}_3$ : C, 64.21; H, 4.07. Found: C, 64.17; H, 4.50.

**Oxidation of (2-Phenyl-1-arsaacetylene)dicobalt Hexacarbonyl with Ceric Ammonium Nitrate in Methanol.** A 250 mL one-necked round-bottomed flask equipped with a magnetic stir bar was charged with 1.00 g (2.2 mmol) of  $(\text{PhCAs})\text{Co}_2(\text{CO})_6$  in 100 mL of absolute methanol. Then, the red solution was stirred, and 3.62 g (6.6 mmol) of ceric ammonium nitrate was added in small portions over a 30-min period. As the ceric ammonium nitrate was added, gas was evolved and the solution became a pale orange in color when the addition was complete. The methanol was removed at reduced pressure, and the residue was treated with 100 mL of water and 100 mL of dichloromethane. The organic layer was separated, and the aqueous layer was extracted with an additional 100 mL of dichloromethane. The combined extracts were dried over  $\text{MgSO}_4$ , and the solvent was removed on a rotary evaporator to yield 0.28 g of a pale yellow oil. GLC analysis of this oil (2 ft SE-30 column, 147°) showed the presence of two major products. The first was identified as methyl benzoate,  $\text{PhC}(\text{O})\text{OCH}_3$ , by comparison of its GLC retention time and IR spectrum with those of authentic material (Aldrich Chemicals). The second product was identified as methyl benzoylformate,  $\text{PhC}(\text{O})\text{C}(\text{O})\text{OCH}_3$ , by comparison of its GLC retention time and IR spectrum with those of authentic material (Aldrich Chemicals).

The aqueous layer from the oxidation was acidified with hydrochloric acid, and hydrogen sulfide was bubbled through the solution resulting in the formation of a yellow precipitate. The precipitate was filtered, washed with ethanol and carbon disulfide, and dried to yield 0.15 g (0.97 mmol of As, 44%) of  $\text{As}_2\text{S}_5$ .

**Thermolysis of (2-Phenyl-1-arsaacetylene)dicobalt Hexacarbonyl in the Presence of Tetraphenylcyclopentadienone.** A thick-walled Pyrex tube was charged with 1.00 g (2.2 mmol)

of  $(\text{PhCAs})\text{Co}_2(\text{CO})_6$  and 0.84 g (2.2 mmol) of tetraphenylcyclopentadienone in 20 mL of benzene. The solution was freeze-thaw degassed, and the tube was sealed under vacuum. The tube then was placed in an oven at 200 °C for 10 h. At the end of 10 h, the tube was removed from the oven and allowed to cool to room temperature. It was noted that the tube was coated with a shiny metallic mirror. The tube was opened, the contents were filtered, and the tube and the residue were washed with benzene until the washings were clear. The filtrate was reduced in volume and chromatographed on a silicic acid column using benzene as eluent. Benzene eluted a red-purple band which yielded 0.6 g (74% recovery) of tetraphenylcyclopentadienone. Several other bands were noted on the column, but none were in sufficient quantity to isolate.

The shiny black coating which had formed on the walls of the tube was shown to be nonmagnetic and therefore was not cobalt metal. The substance was then tested for arsenic by the method reported in "Comprehensive Analytical Chemistry" for the determination of arsenic by conversion to arsenic trichloride, distilling the arsenic trichloride, and precipitating it as  $\text{As}_2\text{S}_3$ .<sup>30</sup>

(30) Morries, P. In "Comprehensive Analytical Chemistry"; Wilson, C. L., Wilson, D. W. Eds.; Elsevier: New York, 1962; Vol. 1c, p 237.

(31) Notes added in proof (May 14, 1982). (a) Since this paper was written, the reaction of a stable phosphacetylene,  $(\text{CH}_3)_3\text{CC}\equiv\text{P}$ , with dicobalt octacarbonyl to give the complex  $[(\text{CH}_3)_3\text{CCP}(\text{CO})_2(\text{CO})_6]$  has been reported: Burkett-St. Laurent, J. C. T. R.; Hitchcock, P. T.; Kroto, H. W.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* 1981, 1141. (b) An X-ray crystallographic study which has not yet been completed has confirmed the structure of  $[\text{PhCPW}(\text{CO})_2(\text{CO})_2(\text{CO})_6]$  (CPCo<sub>2</sub> core cluster with P-W(CO)<sub>6</sub> coordination): Fackler, J. P., Jr., private communication.

Following the literature procedure, 0.387 g of the material was shown to contain 0.127 g (33% by weight) of arsenic. This roughly corresponds to the composition  $\text{Co}_2\text{As}$  (38% As by weight) assuming the remainder of the residue was entirely cobalt. The total yield of the black substance was 0.4 g. Therefore, if the composition were indeed  $\text{Co}_2\text{As}$ , 0.4 g represents 2.07 mmol, or a 94% yield of cobalt and arsenic.

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**Registry No.** 7, R = Me, 69138-19-8; 7, R = Ph, 69138-20-1; 7, R = Me<sub>3</sub>Si, 69138-21-2; 8, R = Ph, 68417-27-6; 8, R = H, 81476-20-2; 8, R = Me, 68417-26-5; 8, R = Me<sub>3</sub>Si, 81476-21-3; 10, R = Me, M = W, 69138-17-6; 10, R = Ph, M = W, 81496-88-0; 10, R = Me, M = Cr, 69138-16-5; 10, R = Ph, M = Mo, 81476-22-4; 10, R = Ph, M = Cr, 81476-23-5; 11a, 69138-18-7; 11b, 68417-28-7;  $(\text{MeCP})\text{Co}_2(\text{CO})_5(\text{PPh}_3)$ , 81476-24-6;  $(\text{MeCP})\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2$ , 81476-25-7;  $[(\text{MeCP})\text{Co}_2(\text{CO})_5]_3$ , 81476-26-8;  $(p\text{-CH}_3\text{COC}_6\text{H}_4\text{CAs})\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2$ , 81476-27-9;  $(p\text{-CH}_3\text{COC}_6\text{H}_4\text{CP})\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2$ , 81476-28-0;  $(\text{MeCAs})\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2$ , 81476-29-1;  $(\text{HCAs})\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2$ , 81476-30-4;  $(\text{MeCAs})\text{Co}_2(\text{CO})_5(\text{PPh}_3)$ , 81476-31-5;  $(\text{PhCAs})\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2$ , 81476-32-6;  $(\text{Me}_3\text{SiC})\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2$ , 81476-33-7;  $(\text{PhCp})\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2$ , 81476-34-8;  $\text{Co}_2(\text{CO})_8$ , 10210-68-1;  $\text{W}(\text{CO})_5$ , 14040-11-0;  $\text{Cr}(\text{CO})_6$ , 13007-92-6;  $\text{Mo}(\text{CO})_6$ , 13939-06-5;  $\text{Cr}(\text{CO})_5(\text{THF})$ , 15038-41-2;  $\text{PhC}(\text{O})\text{OCH}_3$ , 93-58-3;  $\text{PhC}(\text{O})\text{C}(\text{O})\text{OCH}_3$ , 15206-55-0;  $\text{Co}_2\text{As}$ , 12254-83-0;  $\text{As}_2\text{S}_6$ , 1303-34-0;  $\text{CH}_2\text{Cl}_2\text{H}$ , 1300-21-6;  $\text{PCl}_3$ , 7719-12-2; acetyl chloride, 75-36-5.

## Communications

### Synthesis of Diastereoisomeric Transition-Metal Complexes with Five Different and Independent Ligands. Resolution through an Optically Active Germanium

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**Summary:** Optically active germeryl ligands are easily introduced in transition-metal complexes. Reaction of optically active  $\text{MePh}(1\text{-C}_{10}\text{H}_7)\text{GeLi}$  with  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{NO}$  ( $\text{M} = \text{Mo}, \text{W}$ ) results in replacement of CO and formation of anionic species which can be alkylated with  $\text{CH}_3\text{I}$  to afford mixtures of diastereoisomeric complexes,  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})(\text{NO})(\text{GeR}_3)\text{CH}_3]$  ( $\text{R}_3 = \text{MePh}(1\text{-C}_{10}\text{H}_7)$ ,  $\text{M} = \text{Mo}, \text{W}$ ).

Optically active transition-metal complexes in which the metal is chiral are of current interest<sup>1,2</sup> and a few have been obtained with a square-pyramidal geometry. However, up

to the present, all complexes of this type obtained have two identical ligands; this is the result of one of the constraints applied to such systems in order to restrict the number of the possible isomers.<sup>2</sup>

In previous work we have described the synthesis of square-pyramidal complexes having five different and independent ligands and have provided evidence for their configurational stability.<sup>3</sup> These complexes can be prepared as a result of the ease of replacement of carbonyl ligands by  $\text{R}_3\text{Ge}^-$  in transition-metal complexes.<sup>4,5</sup>

We report here the synthesis, characterization, and resolution of diastereoisomeric complexes which have a square-pyramidal geometry by means of an optically active germanium substituent. The preparation of the complex (eq 1,  $\text{M} = \text{Mo}, \text{W}$ ) involves nucleophilic displacement of a carbonyl ligand and methylation of the anion obtained.

Slow addition of 10 mmol of (methylphenyl-1-naphthylgermyl)lithium<sup>6</sup> (prepared by stirring at room temperature for 1 h 2.92 g (10 mmol) of  $\text{MePh}(1\text{-C}_{10}\text{H}_7)\text{-GeH}$  ( $[\alpha]_D^{25} \pm 26^\circ$ ) and 10 mmol of *n*-butyllithium in 20 mL of ether) to a solution of 2.5 g (10 mmol) of  $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{NO}$ <sup>7</sup> in 50 mL of ether at room temperature resulted in smooth evolution of carbon monoxide as the

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