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Reactions of Poly(tertiary phosphines) with Dicobalt Octacarbonyl. Formation of Monocarbonyl Derivatives of Cobalt(I)

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Received November 15, 1972

The recent report by King and Saran[1] of tertiary phosphine and arsine derivatives of cobalt(I) isocyanides prompts us to communicate the synthesis of a very similar series of cobalt carbonyl complexes. Studies of the reactions of dicobalt octacarbonyl or its derivatives with poly(tertiary phosphines) have been reported in the literature. These include the reaction of the bis(norbornadiene) derivative of dicobalt octacarbonyl with both di- and tri(tertiary phosphines) to give neutral species of formula $Co_2(CO)_4L_2$[2] and the report by Sacco[3] of the reaction of 1,2-bis(diphenylphosphino)ethane with $Co_2(CO)_8$ to give cationic phosphine carbonyl species which have the general formula $[Co_2(CO)_4(\text{ligand})_3]^{2+}$. There was no observation of further substitution of carbonyl by phosphine in these thermal reactions. Interest in the capacity of polydentate ligands to give more highly substituted products in reactions with metal carbonyls and in the possible catalytic properties of new metal carbonyl phosphines so formed has led us to investigate both the thermal and photolytic reactions of dicobalt octacarbonyl with a series of poly(tertiary phosphine and arsine) ligands. These ligands, together with the abbreviations previously assigned them,[4] are as follows: 1,2-bis(diphenylphosphino)ethane, Pf-Pf; *cis*-1,2-bis(diphenylphosphino)ethylene, *cis*-Pf=Pf; 1-diphenylphosphino-2-diphenylarsinoethane, Asf-Pf; 1,2-bis(diphenylarsino)ethane, Asf-Asf; bis(2-diphenylphosphinoethyl)phenylphosphine, Pf-Pf-Pf; tris(2-diphenylphosphinoethyl)phosphine, P(-Pf)$_3$; 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane, Pf-Pf-Pf-Pf.

Experimental Section

Materials. Dicobalt octacarbonyl and the phosphine ligands were purchased from Pressure Chemical Co., Pittsburgh, Pa. The ligands were not further purified.

Thermal Reactions of $Co_2(CO)_8$ with Trivalent Phosphorus Ligands (Table I). The indicated quantities (Table I) of $Co_2(CO)_8$ and the trivalent phosphorus ligand were mixed in 50 ml of benzene. After gas evolution ceased, the solution was concentrated by partial evaporation of the solvent under vacuum, and the product was precipitated by addition of petroleum ether (bp 60–80°). The solid was redissolved in a minimum of acetone. A large excess of $NaB(C_6H_5)_4$ in acetone was added and the final product was precipitated by addition of a small amount of water. The solid which precipitated was washed with cold methanol. Recrystallization was effected from an acetone–water solution, and the resultant crystals were dried under vacuum to give the first three products of Table I. Solubility properties with the PF_6^- anion precluded isolation of analyzable salts of this anion.

Photolytic Reactions of $Co_2(CO)_8$ with Trivalent Phosphorus and Arsenic Ligands (Table I). The indicated quantities (Table I) of $Co_2(CO)_8$ and the phosphorus- or arsenic-containing ligands were irradiated in an acetone solution for 5–12 hr. The irradiation source was a low-pressure mercury quartz lamp. The solution was filtered and the solvent was removed under vacuum. The solid residue was washed repeatedly with petroleum ether (bp 60–80°). This solid was redissolved in acetone and treated with excess $NaB(C_6H_5)_4$. Air was bubbled through the solution for 12 hr and decomposition solids were filtered out. Addition of a few drops of water to the concentrated acetone solution initiated formation of the crystalline products of Table I.

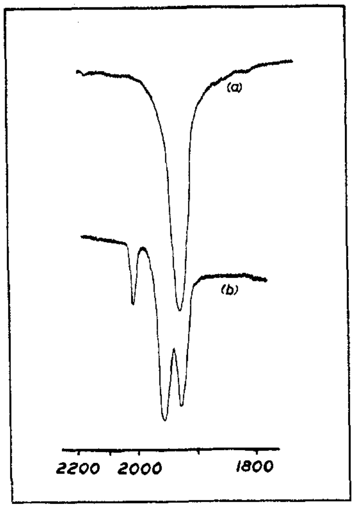

Figure 1. Infrared spectrum in the ν(CO) region for (a) pure $[Co(\text{Asf-Pf})_2(CO)][B(C_6H_5)_4]$ in $CHCl_3$ and (b) the products obtained after its exposure to an atmosphere of CO for 24 hr in $CHCl_3$. New bands at 2008 and 1953 cm^{-1} agree in frequency and relative intensities with those of the dinuclear species $[Co(\text{Asf-Pf})_3(CO)_4][B(C_6H_5)_4]_2$. Spectrum a is typical of all mononuclear monocarbonyl species isolated.

The Asf-Pf product was purified by chromatography on an alumina column eluted with warm methanol followed by acetone.

The Pf-Pf-Pf-Pf product could also be prepared by refluxing of the reaction solution.

Vibrational Spectra (Table II). The infrared and Raman spectra of all of the cobalt carbonyl phosphine complexes in the 2300–1700-cm^{-1} region (Table II) were measured. The solution infrared spectra were recorded using a Beckman Model IR-9 spectrophotometer with resolution and accuracy of about 1 cm^{-1} and were calibrated using deuterium chloride vapor frequencies in the 2000-cm^{-1} region. Raman spectra, obtained with a Spex Ramalog 1401 spectrophotometer and excited by the 5682-A Kr line of an Ar-Kr mixed-gas laser, have a resolution of about 5 cm^{-1} and an accuracy of at least ±5 cm^{-1}. Calibration was with the known laser emission frequencies.

Results and Discussion

We find that dicobalt octacarbonyl, in solution, readily undergoes disproportionation reactions with poly(tertiary arsine and phosphine) ligands to yield cationic, phosphine-substituted products and the tetracarbonylcobaltate anion. The cations appear to be dinuclear species of general formula $[Co_2(CO)_4(\text{ligand})_3]^{2+}$ (**1**) and mononuclear species of formula $[Co(CO)(\text{ligand})_n]^+$ (**2**). The complexes can be prepared by both thermal and photolytic activation with thermal reactions favoring the formation of type **1** and photolytic reactions favoring type **2** cations. The products obtained are summarized in Table I while Table II lists the vibrational spectrum in the ν(CO) frequency region for each product. Fluorescence and/or absorption problems precluded obtaining Raman spectra for any of the dinuclear products except $[Co_2(\text{Pf-Pf-Pf})_3(CO)_4]^{2+}$. For this ion the two Raman bands observed at $\Delta\nu = 1984$ and 2021 cm^{-1} in the solid material are approximately coincident with those in the infrared solution spectrum. The coincidence of two bands in the infrared and Raman spectra would be consistent with an approximate C_{2v} symmetry about each cobalt atom in a structure like **1**.

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(1) R. B. King and M. S. Saran, *Inorg. Chem.*, **11**, 2112 (1972).

(2) H. Behrens and W. Aquila, *Z. Anorg. Allg. Chem.*, **355**, 356 (1967).

(3) A. Sacco, *Gazz. Chim. Ital.*, **93**, 698 (1963).

(4) R. B. King, P. N. Kapoor, and R. N. Kapoor, *Inorg. Chem.*, **10**, 1841 (1971).

Table I. Preparations and Properties of Cobalt(I) Derivatives of Poly(tertiary phosphines) and Phosphino arsines

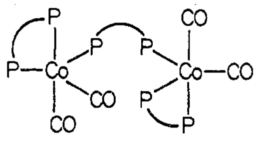
Compd[a]	Prepn,[b] mmol		Color	Mp,[d] °C	Anal,[e] %			
	Ligand[c]	$Co_2(CO)_8$			C	H	P	Co
[Co$_2$(Pf-Pf)$_3$(CO)$_4$][B(C$_6$H$_5$)$_4$]$_2$	Pf-Pf (2.0)	1.33	Yellow	150-157 (155)[f]				
[Co(*cis*-Pf=Pf)$_3$(CO)$_4$][B(C$_6$H$_5$)$_4$]$_2$	*cis*-Pf=Pf (1.0)	0.67	Orange		75.5 (75.9)	5.6 (5.2)	9.6 (9.0)	
[Co$_2$(Pf-Pf-Pf)$_3$(CO)$_4$][B(C$_6$H$_5$)$_4$]$_2$	Pf-Pf-Pf (1.0)	0.67	Yellow-orange	228-230	74.9 (74.8)	5.5 (5.6)	11.6 (11.3)	5.0 (4.8)
[Co(P[-Pf]$_3$)(CO)][B(C$_6$H$_5$)$_4$]	P(-Pf)$_3$ (0.77)	0.77	Orange	234-236	74.0 (74.7)	5.8 (5.8)	11.2 (11.5)	
[Co(Pf-Pf-Pf-Pf)(CO)][B(C$_6$H$_5$)$_4$]	Pf-Pf-Pf-Pf (0.38)	0.38	Orange	257-260	73.9 (74.7)	5.7 (5.8)	11.0 (11.5)	
[Co(Asf-Pf)$_2$(CO)][B(C$_6$H$_5$)$_4$]	Asf-Pf (2.0)	1.0	Red	212-215	71.8 (71.4)	5.6 (5.3)	5.0 (4.9)	

[a] The ligand abbreviations are listed in the introduction of this note. [b] The general preparations for the mononuclear and dinuclear complexes are given in the Experimental Section. [c] The numbers of millimoles of ligand used in these reactions are indicated in parentheses. [d] Melting points were taken in open capillaries and are uncorrected. In each case melting took place with decomposition. [e] Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Calculated values are given in parentheses. [f] Reported value. See ref 3.

Table II. Carbonyl Stretching Frequencies (cm^{-1})

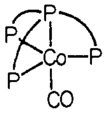
Compd[a]	Ir spectra in $CHCl_3$	Raman spectra of solids
[Co(Pf-Pf)$_3$(CO)$_4$][B(C$_6$H$_5$)$_4$]$_2$	1964, 2012	
[Co$_2$(*cis*-Pf=Pf)$_3$(CO)$_4$][B(C$_6$H$_5$)$_4$]$_2$	1969, 2022	
[Co$_2$(Asf-Pf)$_3$(CO)$_4$][B(C$_6$H$_5$)$_4$]$_2$	1953, 2008	
[Co$_2$(Asf-Asf)$_3$(CO)$_4$][B(C$_6$H$_5$)$_4$]$_2$	1959, 2008	
[Co$_2$(Pf-Pf-Pf)$_3$(CO)$_4$][B(C$_6$H$_5$)$_4$]$_2$	1986, 2033	1984, 2021
[Co$_2$(P[-Pf]$_3$)$_3$(CO)$_4$][B(C$_6$H$_5$)$_4$]$_2$	1985, 2032	
[Co$_2$(Pf-Pf-Pf-Pf)$_3$(CO)$_4$][B(C$_6$H$_5$)$_4$]$_2$	1985, 2030	
[Co(P[-Pf]$_3$)(CO)][B(C$_6$H$_5$)$_4$]	1958	1952
[Co(Pf-Pf-Pf-Pf)(CO)][B(C$_6$H$_5$)$_4$]	1948	
[Co(Asf-Pf)$_2$(CO)][B(C$_6$H$_5$)$_4$]	1939	

[a] The ligand abbreviations are listed in the introduction of this note.



1

Photolysis of $Co_2(CO)_8$ with the two tetra(tertiary phosphines) and with the mixed di(tertiary arsine-phosphine) ligand $(C_6H_5)_2AsCH_2CH_2P(C_6H_5)_2$ gave cationic products which differ from the thermal product as shown by their ν(CO) spectra (Table II, Figure 1a). The presence of one band in this region, at the same frequency in both the infrared and Raman spectra, points to a monocarbonyl species of structure 2. Elemental analyses and conductance measurements in nitrobenzene confirm this conclusion. This tendency toward higher substitution *via* photolysis of metal carbonyls has been recently demonstrated and discussed.[5] Elemental analyses and infrared spectra indicate the formation of only the dinuclear species with the tritertiary ligand Pf-Pf-Pf. Although an expected mononuclear species of formula $[Co(Pf\text{-}Pf\text{-}Pf)(CO)_2]^+$ could have an infrared spectrum essentially identical with that of the dimer, it was not indicated by elemental analysis.



2

Several observations point to the formation of complexes of type 1 enroute to the type 2 mononuclear monocarbonyl species and also indicate reversibility of the reaction which converts 1 to 2. The dinuclear cations 1 can be converted to the mononuclear species by uv irradiation under the same conditions used to generate type 2 species directly from $Co_2(CO)_8$ and ligand. In addition, the thermal reaction of $Co_2(CO)_8$ with Pf-Pf-Pf-Pf produces a mixture of 1 and 2 type products in proportions which appear to depend upon such factors as temperature and time of reaction. Finally, carbonylation of the $[Co(Asf\text{-}Pf)_2CO]^+$ cation at atmospheric pressure produced some of the dinuclear cation $[Co_2(Asf\text{-}Pf)_3(CO)_4]^{2+}$ as shown by the infrared spectrum before and after carbonylation (Figure 1). This indicates that the reaction

$$2[Co(Asf\text{-}Pf)_2CO]^+ + 2CO \rightarrow [Co_2(Asf\text{-}Pf)_3(CO)_4]^{2+} + Asf\text{-}Pf$$

occurs readily in solution.

To our knowledge, this constitutes the first example of formation of a monocarbonyl complex of cobalt(I) by direct substitution for CO under atmospheric conditions. The ready formation of such highly substituted metal carbonyl complexes is not generally observed due to the increasing M- -CO bond strength as weaker π acids such as phosphine are substituted for the carbonyl. However, the recent report of the direct formation of penta- and hexasubstituted $M(CO)_6$ species by irradiation[5] indicates that irradiation, perhaps in combination with the chelate effect, can promote more extensive substitution in metal carbonyls than is otherwise obtained. Our results substantiate this observation while at the same time providing further illustration of the close parallel between metal carbonyl and isocyanide chemistry.

The failure to isolate a monocarbonyl complex using the ligand $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ is perplexing in view of the close similarity between arsines and phosphines as ligands. Irradiation of this ligand with $Co_2(CO)_8$ produced only a bright green complex with a ν(CO) spectrum entirely different from that of either type 1 or 2 species. This product has not yet been characterized.

Acknowledgment. This study was partially supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. [Co$_2$(Pf-Pf)$_3$(CO)$_4$][B(C$_6$H$_5$)$_4$]$_2$, 39394-78-0; [Co$_2$(*cis*-Pf=Pf)$_3$(CO)$_4$][B(C$_6$H$_5$)$_4$]$_2$, 39394-75-7; [Co$_2$(Asf-Pf)$_3$(CO)$_4$][B(C$_6$H$_5$)$_4$]$_2$, 39394-76-8; [Co$_2$(Asf-Asf)$_3$(CO)$_4$][B(C$_6$H$_5$)$_4$]$_2$, 39394-77-9; [Co$_2$(Pf-Pf-Pf)$_3$(CO)$_4$][B(C$_6$H$_5$)$_4$]$_2$, 39394-79-1; [Co$_2$(P[-Pf]$_3$)$_3$(CO)$_4$][B(C$_6$H$_5$)$_4$]$_2$, 39394-80-4; [Co$_2$(Pf-Pf-Pf-Pf)$_3$(CO)$_4$][B(C$_6$H$_5$)$_4$]$_2$,

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(5) R. Mathieu and R. Poilblanc, *Inorg. Chem.*, 11, 1858 (1972).

39394-81-5; [Co(P[-Pf]$_3$)(CO)][B(C_6H_5)$_4$], 41777-22-4; [Co(Pf-Pf-Pf-Pf)(CO)][B(C_6H_5)$_4$], 41777-23-5; [Co(Asf-Pf)$_2$(CO)][B(C_6H_5)$_4$], 41777-24-6; $Co_2(CO)_8$, 10210-68-1.

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Infrared Spectrum of Matrix-Isolated Nickel Carbonyl

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Received April 5, 1973

The infrared and Raman spectra and normal-coordinate analysis of $Ni(CO)_4$ have been reported by many investigators.[1] However, its matrix-isolated spectrum has not been previously reported. Although DeKock[2] obtained the infrared spectra of the $Ni(CO)_{1-4}$ series in an Ar matrix, his measurements were limited to the CO stretching region. No information has been available on matrix-isolation spectra of $Ni(CO)_4$ and other metal carbonyls in the low-frequency region. This paper reports the matrix-isolation and gaseous-phase infrared spectra of $Ni(CO)_4$ in the CO stretching (2300-2000 cm^{-1}) and Ni-C-O bending and Ni-C stretching (500-400 cm^{-1}) regions.

Experimental Section

$Ni(CO)_4$ was purchased from Strem Chemical Co., Danvers, Mass., and purified by vacuum distillation. A mixture of $Ni(CO)_4$ with argon at *ca.* a 1/1000 ratio was deposited on a CsI window at *ca.* 14 K which was cooled by a Cryogenic Technology Model 20 closed-cycle refrigerator. The matrix-isolated spectra were measured on a Beckman IR-12 infrared spectrophotometer with an expanded frequency scale. The spectrum of $Ni(CO)_4$ in the gaseous phase was obtained by using a 10-cm gas cell with CsBr windows. Calibration of the frequency reading was made by measuring the spectra of water vapor and carbon dioxide. The accuracy of the frequency reading was ±0.2 cm^{-1}.

Results and Discussion

The gaseous infrared spectrum of $Ni(CO)_4$ has been reported by Jones.[3] It exhibits four fundamentals at 2057 (ν_5), 459 (ν_6), 422 (ν_7), and 79 cm^{-1} (ν_8). Our frequencies shown in Tables I and II are in good agreement with those of Jones. ν_5 and ν_8 are definitely due to the CO stretching and C-Ni-C bending modes, respectively. However, the nature of the remaining two bands was not certain.[3] As is seen in Figure 1, ν_6 is weaker than ν_7. In general, the M-C-O bending mode is stronger than the M-C stretching mode in the infrared spectrum (for example, compare $Fe(CO)_5$[4] and $Mo(CO)_6$[5]). This tends to suggest that the stronger band (ν_7) is the Ni-C-O bending and the weaker band (ν_6) is the Ni-C stretching. On the other hand, the M-C-O bending frequency is generally higher than the M-C stretching frequency.[4,5] According to this trend, the 459-cm^{-1} band (ν_6) is the Ni-C-O bending and the 422-cm^{-1} band (ν_7) is the Ni-C stretching. Furthermore, the fact that these two bands are close in frequency suggests a possibility of vibrational coupling between these two modes in the F_2 species. The latter assignment was supported by recent normal-coordinate analyses[6,7] combined with the ^{13}C and/or ^{18}O substitutions. However, the preparation of these isotopically pure compounds involves technical inconveniences as well as financial burdens.

Table I. Infrared Spectra of $Ni(CO)_4$ in the 500-400-cm^{-1} Region

Gas	Ar matrix	Assignment[a]
	469.0	δ(NiCO)
458.5	464.0	
	454.4	
	433.4	$\nu(^{58}Ni\text{-}C)$
422.0	430.5	$\nu(^{60}Ni\text{-}C)$
	428.3	$\nu(^{62}Ni\text{-}C)$
	425.0	$\nu(^{64}Ni\text{-}C)$

[a] Key: ν, stretching; δ, bending.

Table II. Infrared Spectra of $Ni(CO)_4$ in the 2200-2000-cm^{-1} Region

Gas	Hexane soln[a]	Ar matrix	Assignment
		2150.0	
		2139.0	Free ^{12}CO
2121.0	2117.8	2125.0	A_1, $Ni(^{13}CO)(^{12}CO)_3$
2059.0	2045.7	2052.7	F_2, $Ni(^{12}CO)_4$
	2045.7	2048.2	E, $Ni(^{13}CO)(^{12}CO)_3$
		2045.7	
		2041.0	
2018.6	2007.5	2013.0	A_1, $Ni(^{13}CO)(^{12}CO)_3$
		2011.8	
		2007.0	

[a] Reference 8.

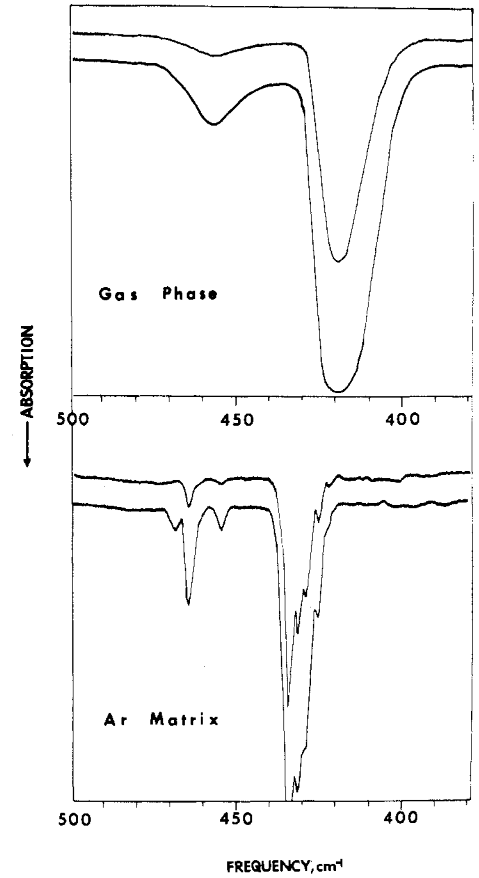

Figure 1. Infrared spectra of $Ni(CO)_4$ in the 500-400-cm^{-1} region.

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[7] L. H. Jones, R. S. McDowell, and M. Goldblatt, *J. Chem. Phys.*, 48, 2663 (1968).