

COORDINATION COMPLEXES OF ACETYLENIC PHOSPHINES AND DIPHOSPHINES

V. ACETYLENE BRIDGED DERIVATIVES OF DICOBALT OCTACARBONYL

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SUMMARY

Reactions of the phosphinoacetylenes $RR'PC\equiv CR''$ ($R=R'=Ph, R''=H, CF_3, Ph, Me, t-Bu$; $R=R'=C_6F_5, R''=Ph, Me$; $R=Ph, R'=Me, R''=Me$) with $Co_2(CO)_8$ have been studied. Complexes of four types have been characterised: (A) $(RR'PC_2R'')Co_2(CO)_6$ ($R=R'=C_6F_5, R''=Ph, Me$; $R=R'=Ph, R''=t-Bu$), (B) $(RR'PC_2R'')_2Co_4(CO)_{10}$ ($R=R'=Ph, R''=H, CF_3, Ph, Me$; $R=R'=C_6F_5, R''=Me$; $R=Ph, R'=Me, R''=Me$), (C) $(RR'PC_2R'')_2Co_2(CO)_6$ ($R=R'=Ph, R''=t-Bu$), (D) $(RR'P(O)C_2R'')Co_2(CO)_6$ ($R=R'=Ph, R''=t-Bu$; $R=R'=C_6F_5, R=Ph$). The complexes were characterised by microanalysis, IR, NMR and where possible mass spectra. Substitution reactions of the complexes with tertiary phosphites are described. In complexes of type (A) only the alkyne function is utilised whereas the tetranuclear compounds (B) have structures in which both alkyne and phosphorus moieties are coordinated. Compounds of type (C) are simple disubstituted phosphine complexes of $Co_2(CO)_8$ and those of type (D) are μ -alkyne derivatives of acetylenic phosphine oxides. The mechanism of formation of complexes of type (B) is discussed in the light of IR data.

INTRODUCTION

Extensive investigations of the reactions of tertiary phosphines and phosphites with $Co_2(CO)_8$ have been reported¹⁻⁷. Typical products include carbonyl bridged and non-bridged $Co_2(CO)_{8-n}L_n$ ($n=1, 2, 3$) (L =phosphine or phosphite)²⁻⁴ species, disproportionation products $[Co(CO)L_4][Co(CO)_4]^5$ and $[Co(CO)_3L_2][Co(CO)_4]^5$, diphosphine bridged binuclear complexes, for example $(f_4fos)Co_2(CO)_6$ [$f_4fos = Ph_2PC=CPPh_2(CF_2)_2$]⁶ and diphosphine bridged tetranuclear compounds $[Co_2(CO)_7]_2DPPA$ [$DPPA = bis(diphenylphosphino)acetylene$]⁷. A novel arsine complex $(ffars)Co_2(CO)_5$ [$ffars = Me_2AsC=CAsMe_2(CF_2)_2$] has also been characterised⁶. Green paramagnetic complexes $[Co(CO)_2PR_3]_3$ prepared from $HCo(CO)_3PR_3$ or $(\pi-C_4H_7)Co(CO)_2PR_3$ have recently been described⁸.

By way of contrast alkynes usually react with $\text{Co}_2(\text{CO})_8$ at room temperature forming alkyne bridged $(\text{RC}_2\text{R}')\text{Co}_2(\text{CO})_6$ complexes⁹, although a product with the composition $(\text{PhC}_2\text{H})_3\text{Co}_2(\text{CO})_6$ but of unknown structure is produced in the phenylacetylene reaction¹⁰. However, at higher temperatures, oligomerisation of the acetylenes and/or reaction with carbon monoxide may occur leading to cyclopentadienone, lactone and $(\text{RC}_2\text{R}')_3\text{Co}_2(\text{CO})_4$ complexes as well as a variety of organic derivatives⁹. Nonacarbonyltricobalt cluster compounds $(\text{RCH}_2\text{C})\text{Co}_3(\text{CO})_9$ may also be obtained at higher temperatures¹¹. The propensity of $\text{Co}_2(\text{CO})_8$ to oligomerise acetylenes and also form stable derivatives with phosphines prompted the present study of reactions with phosphinoacetylenes of the types $\text{RR}'\text{PC}\equiv\text{CR}''$ ($\text{R}=\text{R}'=\text{Ph}$, $\text{R}''=\text{H}$, CF_3 , Ph , Me , $t\text{-Bu}$; $\text{R}=\text{R}'=\text{C}_6\text{F}_5$, $\text{R}''=\text{Ph}$, Me ; $\text{R}=\text{Ph}$, $\text{R}'=\text{Me}$, $\text{R}''=\text{Me}$)¹². Surprisingly, although phosphine substituted metal carbonyl complexes are known to be active catalysts for acetylene oligomerisation reactions, with the exception of the bridging ligand DPPA¹³, the coordination behaviour of alkynylphosphines has not been extensively documented. A few derivatives of $\text{Ph}_2\text{PC}\equiv\text{CR}$ ($\text{R}=\text{Me}$, Ph)^{14,15} and $\text{Ph}_2\text{PCH}_2\text{C}\equiv\text{CCH}_2\text{PPh}_2$ ¹⁶ in which only phosphorus coordination occurs, have been described and a brief report on the complex $(\text{HC}_2)_3\text{As}[\text{Co}_2(\text{CO})_6]_3$ has appeared¹⁷. In a parallel study we have shown that the alkynylpnictogens $\text{Ph}_2\text{MC}\equiv\text{CCF}_3$ ($\text{M}=\text{P}$, As) with activated triple bonds yield trinuclear ferracyclopentadiene complexes of the type $[\text{Ph}_2\text{MC}_4(\text{CF}_3)_2]_2\text{MPh}_2\text{Fe}_3(\text{CO})_8$ with $\text{Fe}_3(\text{CO})_{12}$ ¹⁸. A brief report on the structure of $(\text{Ph}_2\text{PC}_2\text{CF}_3)_2\text{Co}_4(\text{CO})_{10}$ has been published¹⁹.

EXPERIMENTAL

The solvents benzene, petroleum ether (60–80° and 30–60°) n-heptane, and diethyl ether were dried over LiAlH_4 and distilled under a nitrogen atmosphere. All other solvents used were reagent grade and degassed prior to use. Dicobalt octacarbonyl from Strem Chemicals was sublimed before use. Methoxydiphenylphosphine was a gift from Arapahoe Chemicals. Triphenyl phosphite and trimethylphosphite were purchased from Aldrich Chemical Co. Inc.

All reactions and subsequent manipulations were carried out under nitrogen. Chromatography was generally performed with neutral alumina (Fisher, A-540).

IR spectra were run on Beckman IR-9 and Perkin-Elmer 457 spectrometers using where possible, n-hexane as the solvent for solution work and nujol mulls for solids. Matched silver chloride solution cells of path length 0.5 mm were used when the course of a reaction was followed by IR spectroscopy. ¹H NMR spectra were recorded on Varian T-60 and HA-100 spectrometers using TMS as an internal standard. Mass spectra were obtained on a Perkin-Elmer Hitachi RMU-6E instrument at 70 eV. Microanalyses were performed by Alfred Bernhard, Fritz Pregl Strasse, Elbach über Engelskirchen, Germany. Microanalytical data are given in Table 1.

With the exception of methylphenylpropynylphosphine the phosphinoacetylenes were prepared as previously described¹².

Preparation of methylphenylpropynylphosphine

Methylphenylchlorophosphine (4.0 g) in ether (10 ml) was added to a cooled (–78°) stirred solution of lithium propynylide [prepared from $\text{CH}_3\text{C}\equiv\text{CH}$ (1.0 g)

TABLE I

ANALYTICAL DATA FOR COBALT COMPLEXES

Compound	No.	%C		%H	
		Found	Calcd.	Found	Calcd.
$[(C_6F_5)_2PC_2Me]Co_2(CO)_6$	(I)	37.07	36.55	0.21	0.43
$[(C_6F_5)_2PC_2Me]_2Co_2(CO)_{10}$	(II)	35.74	36.28	0.78	0.45
$[(C_6F_5)_2PC_2Ph]Co_2(CO)_6$	(III)	41.42	41.51	0.66	0.66
$[Ph_2PC_2CF_3]_2Co_4(CO)_{10}^a$	(V)	45.09	44.80	2.33	1.87
$[Ph_2AsC_2CF_3]_2Co_4(CO)_{10}^b$	(VI)	41.29	41.40	1.85	1.75
$[Ph_2PC_2Me]_2Co_4(CO)_{10}$	(VII)	49.58	49.81	2.82	2.69
$[Ph_2PC_2Ph]_2Co_4(CO)_{10}$	(VIII)	55.03	55.18	2.66	2.77
$[Ph_2PC_2H]_2Co_4(CO)_{10}$	(IX)	48.50	48.75	2.30	2.36
$[PhMePC_2Me]_2Co_4(CO)_{10}$	(X)	42.62	42.89	2.77	2.63
$[Ph_2PC_2C(Me)_3]Co_2(CO)_6$	(XI)	51.98	52.22	3.31	3.46
$[Ph_2PC_2C(Me)_3]_2Co_2(CO)_6$	(XIII)	62.01	61.64	4.83	4.67
$[Ph_2P(O)C_2C(Me)_3]Co_2(CO)_6$	(XIV)	50.85	50.14	3.41	3.36
$[Ph_2PC_2CF_3]_2Co_4(CO)_8[(MeO)Ph_2P]_2$	(XV)	52.85	53.06	2.80	3.19
$[Ph_2AsC_2CF_3]_2Co_4(CO)_8[(PhO)_3P]_2$	(XVI)	51.21	51.53	2.79	2.91
$[Ph_2AsC_2CF_3]_2Co_4(CO)_8[(MeO)Ph_2P]_2$	(XVII)	50.05	50.03	3.01	2.99
$[Ph_2PC_2Me]_2Co_4(CO)_8[(PhO)_3P]_2$	(XVIII)	57.91	58.14	3.69	3.55
$[Ph_2PC_2Me]_2Co_4(CO)_8[(MeO)_3P]_2$	(XIX)	45.96	45.70	3.67	3.83
$[Ph_2PC_2Me]_2Co_4(CO)_8[(MeO)Ph_2P]_2$	(XX)	56.85	57.33	3.77	3.90
$[Ph_2PC_2Ph]_2Co_4(CO)_8[(MeO)_3P]_2$	(XXI)	50.27	50.65	4.32	3.77
$[Ph_2PC_2Ph]_2Co_4(CO)_8[(MeO)Ph_2P]_2$	(XXII)	60.79	60.68	4.15	3.82
$[(C_6F_5)_2PC_2Ph]Co_2(CO)_4[(PhO)_3P]_2$	(XXIII)	55.39	54.73	2.78	2.67
$[(C_6F_5)_2P(O)C_2Ph]Co_2(CO)_6$	(XXIV)	41.09	40.65	0.77	0.65
$[Ph_2PC_2Me]_2Co_2(CO)_4(PhC_2Ph)$	(XXV)	67.81	67.30	4.24	4.24

^a Found: P, 5.35; F, 10.35. Calcd.: P, 5.78; F, 10.63%. ^b Found: As, 12.20; F, 9.49. Calcd.: As, 12.92; F, 9.82%.

and *n*-BuLi in ether]. The solution was stirred for 2 h after allowing to warm to room temperature. The solution was filtered under nitrogen, to remove precipitated lithium chloride and distilled under reduced pressure. A colourless liquid (b.p. 110°, 0.4 mm) in 78% yield was obtained. The liquid goes dark on standing at room temperature *in vacuo* and is best stored at -10°. (Found: C, 73.96; H, 6.94. $C_{10}H_{11}P$ calcd.: C, 74.07; H, 6.79%.)

The IR spectrum of $MePhPC_2Me$ showed a medium intensity band at 2192 cm^{-1} due to $\nu(C\equiv C)$, similar to the values found for analogous acetylenic phosphines¹². The NMR spectrum {100 MHz, δ scale, $CDCl_3$: 1.43(d) [$^2J(P-H)$ 4.2 Hz], 1.90(d) [$^4J(P-H)$ 1.2 Hz], 7.26(m), 7.55(m)} shows a complex phenyl proton region and doublets due to the P-Me and C-Me groups coupled to ^{31}P . The mass spectrum at 70 eV exhibited the following ions in major abundance (intensities in brackets refer to the ion of m/e 147 = 100%) m/e 162(81), 147(100), 145(41), 132(12), 127(6), 121(15), 115(24), 108(12), 104(31), 77(29), 69(14), 63(5), 57(8), 51(20), 50(6), 39(20). The major fragmentation pathway for this phosphine is via successive loss of two CH_3 groups from the parent ion giving ions $C_6H_5PC_2CH_3^+$ and $C_6H_5PC_2^+$ of m/e 147 and 132 respectively. Similar processes are operative for other acetylenic phosphines¹².

Preparation of complexes

$[(C_6F_5)_2PC_2Me]Co_2(CO)_6$ (I). Bis(pentafluorophenyl)propynylphosphine (0.7 g) in petroleum ether (10 ml) was added dropwise to a stirred solution of dicobalt octacarbonyl (0.6 g) in the same solvent (50 ml). The mixture was refluxed for 2 h after which a small amount of precipitate (decomposition products) was filtered off. The filtrate was chromatographed on alumina and developed with petroleum ether. A bright red band was eluted first yielding a red solution. The solution was concentrated and yielded on prolonged cooling at 0° red, flaky crystals (m.p. 62°). The same product was obtained from the room temperature reaction with dicobalt octacarbonyl.

$[(C_6F_5)_2PC_2Me]_2Co_4(CO)_{10}$ (II). After elution of the red band in (I) above, a 1/1 mixture of benzene/petroleum ether eluted a dark brown solution. On reducing the volume brown crystals were obtained which were recrystallised from dichloromethane/ethanol (m.p. 191°).

The same compound can be prepared from $[(C_6F_5)_2PC_2Me]Co_2(CO)_6$ by refluxing in petroleum ether for 2–3 h.

$[(C_6F_5)_2PC_2Ph]Co_2(CO)_6$ (III). Dicobalt octacarbonyl (1.0 g) and bis(pentafluorophenyl)(phenylethynyl)phosphine (1.4 g) were stirred in benzene (30 ml) for 4 h. After filtration and evaporation to dryness the remaining solid was dissolved in a few ml of benzene and introduced on to an alumina column made up in petroleum ether. Elution with 10/1 petroleum ether/benzene yielded a violet solution which afforded violet crystals (m.p. 115°) on concentration.

$[(C_6F_5)_2PC_2Ph]_2Co_4(CO)_{10}$ (IV). This complex was obtained from (III) by refluxing in petroleum ether for 4–6 h. Extensive decomposition occurred on attempted recrystallisation and the product was therefore identified by its IR spectrum.

$[Ph_2PC_2CF_3]_2Co_4(CO)_{10}$ (V). Freshly distilled diphenyl(3,3,3-trifluoropropynyl)phosphine (1.0 g) in benzene (20 ml) was added dropwise to dicobalt octacarbonyl (1.2 g) in benzene (40 ml). After stirring for 3 h the solution was filtered leaving an unidentified brown solid then reduced in volume and chromatographed on an alumina column made up in n-heptane. Elution with 5/1 heptane/benzene mixtures gave a dark red band from which dark purple crystals were obtained on cooling. The complex was recrystallised from benzene/n-heptane (m.p. ~400°).

$[Ph_2AsC_2CF_3]_2Co_4(CO)_{10}$ (VI). This compound was prepared in a manner analogous to (V) above from diphenyl(3,3,3-trifluoropropynyl)arsine and dicobalt octacarbonyl in benzene. Violet-red crystals were obtained (m.p. 210°).

$[Ph_2PC_2Me]_2Co_4(CO)_{10}$ (VII). The procedure was similar to that for compound (V). The dark brown microcrystals were recrystallised from dichloromethane/ethanol (m.p. 208°).

$[Ph_2PC_2Ph]_2Co_4(CO)_{10}$ (VIII). Dicobalt octacarbonyl (0.8 g) and diphenyl(phenylethynyl)phosphine (0.7 g) were refluxed overnight in benzene (60 ml). Chromatography of the solution remaining after filtration of the reaction mixture and subsequent work up afforded dark brown crystals of (VIII) (m.p. 268–272°).

$[Ph_2PC_2H]_2Co_4(CO)_{10}$ (IX). The reaction between dicobalt octacarbonyl and freshly sublimed ethynyl-diphenylphosphine in benzene gave a red solution which yielded after chromatography violet-red flaky microcrystals, which were recrystallised from benzene/heptane (m.p. 290° d).

$[PhMePC_2Me]_2Co_4(CO)_{10}$ (X). The procedure was analogous to that for compound (V). The product is however quite air sensitive particularly in solution.

All manipulations of the compound were carried out either *in vacuo* or with the rigorous exclusion of oxygen using Schlenk tubes. Red-brown crystals were obtained from benzene/heptane (m.p. 165° decomp.).

$[(Ph_2PC_2C(Me)_3)Co_2(CO)_6]$ (XI). To dicobalt octacarbonyl (1.0 g) in benzene (20 ml) was added (3,3-dimethylbutynyl)diphenylphosphine (0.8 g). The reaction was monitored at regular intervals by recording solution spectra in the $\nu(CO)$ region. After 8 h the solution was taken to dryness. The solid was added to an alumina column as a slurry in heptane. The column was developed in heptane to give a fast moving pale brown band. Slow elution separated this band pure. Evaporation of the solution afforded dark cubes (m.p. 98°).

$[(Ph_2PC_2C(Me)_3)_2Co_4(CO)_{10}]$ (XII). After elution of (XI) a slow moving violet band was eluted with heptane. This constituted a major fraction. However, subsequent work up failed to give an analytically pure sample. The material was identified as (XII) by the characteristic IR spectrum.

$[Ph_2PC_2C(Me)_3]_2Co_2(CO)_6$ (XIII). Two bands remained on the column after removal of (XI) and (XII) above. An orange band eluted with 5/1 heptane/benzene afforded orange-brown needles on cooling (m.p. 118°). Better yields of (XIII) were obtained by a sealed Carius tube reaction of $Co_2(CO)_8$ (1 g) and $Ph_2PC_2C(Me)_3$ (0.6 g) in benzene (15 ml). After 3 days, chromatography revealed only traces of (XI) and (XII), the major product being (XIII).

$[Ph_2P(O)C_2C(Me)_3]Co_2(CO)_6$ (XIV). The last band on the column after removal of (XI), (XII), and (XIII) above was eluted with diethyl ether. Evaporation to small volume gave flaky red crystals of the phosphine oxide complex (m.p. 150–152°).

Substitution reactions with phosphites. A typical procedure for the synthesis of substitution products is given for the complex $[Ph_2PC_2CF_3]_2Co_4(CO)_8[(MeO)Ph_2P]_2$ (XV): The complex (V) (0.5 g) was refluxed with excess (MeO)Ph₂P (1 ml) in benzene for 3 h. Chromatography of the reaction mixture in 1/1 benzene/heptane gave a dark brown band which yielded a dark purple solid. Recrystallisation was achieved from benzene/heptane (m.p. 173°).

Similarly obtained were the derivatives: $(Ph_2AsC_2CF_3)_2Co_4(CO)_8[(PhO)_3P]_2$ (XVI), $(Ph_2AsC_2CF_3)_2Co_4(CO)_8[(MeO)Ph_2P]_2$ (XVII), $(Ph_2PC_2Me)_2Co_4(CO)_8[(PhO)_3P]_2$ (XVIII), $(Ph_2PC_2Me)_2Co_4(CO)_8[(MeO)_3P]_2$ (XIX), $(Ph_2PC_2Me)_2Co_4(CO)_8[(MeO)Ph_2P]_2$ (XX), $(Ph_2PC_2Ph)_2Co_4(CO)_8[(MeO)_3P]_2$ (XXI), $(Ph_2PC_2Ph)_2Co_4(CO)_8[(MeO)Ph_2P]_2$ (XXII), $[(C_6F_5)_2PC_2Ph]Co_2(CO)_4[(PhO)_3P]_2$ (XXIII).

Reaction of $[(C_6F_5)_2PC_2Ph]Co_2(CO)_6$ with bromine. Complex (iii) (1.0 g) dissolved in benzene (25 ml) was stirred and bromine (0.2 g) in benzene added dropwise. There was no apparent colour change. The reaction mixture was refluxed for 1 h. On filtration a few mg of $CoBr_2$ were obtained. Comparative thin layer chromatography on the solid remaining after evaporation and complex (III) indicated the presence of a new complex which moved only slowly compared to (III). The product was separated on a column using chloroform as eluant. Red-purple crystals of $[(C_6F_5)_2P(O)C_2Ph]Co_2(CO)_6$ (XXIV) were obtained (m.p. 146–147°).

$(Ph_2PC\equiv CMe)_2Co_2(CO)_4(PhC_2Ph)$ (XXV). This complex was prepared by the reaction of $(PhC_2Ph)Co_2(CO)_6$ ²⁰ (0.5 g) with excess propynyldiphenylphosphine in boiling benzene. Dark brown plates crystallised on cooling (m.p. 234°).

RESULTS AND DISCUSSION

A. Complexes of the type $LCo_2(CO)_6$

The acetylenic phosphines $(C_6F_5)_2PC_2R$ ($R=Me, Ph$) reacted with dicobalt octacarbonyl in hydrocarbon solvents at room temperature, affording as the major products complexes for which microanalytical data indicated the stoichiometry $LCo_2(CO)_6$. The mass spectra of these derivatives (Fig. 1) did not exhibit parent ions but showed successive loss of five carbonyl groups from $LCo_2(CO)_6^+$ to yield the ions LCo_2^+ in high abundance for $R=Ph$ and medium abundance for $R=Me$. There was no evidence for Co_3^+ or Co_4^+ fragments. For compound (III) the highest m/e fragment ion in the spectrum corresponded to $[LCo_2(CO)_6-F]^+$. Initial loss of a fluorine atom from the parent ion also occurs in the mass spectra of other fluorinated organometallic complexes²¹. This latter process does not however compete effectively with loss of CO from $LCo_2(CO)_6^+$ since the series of ions corresponding to $[(C_6F_4)-(C_6F_5)PC_2Ph]Co_2(CO)_{6-x}$ ($x=1-6$) were of very low abundance. Previous investigators^{21,22} have found that fragmentation of the major ions LCo_2^+ (L =fluorinated acetylene) in the mass spectra of $LCo_2(CO)_6$ complexes, proceeds largely by elimination of CoF_2 . For compounds (I) and (III) however ions in major abundance below LCo_2^+ correspond to L^+ , $C_6F_5C_2R^+$ ($R=Me, Ph$) and $C_6F_5H^+$. Loss of two

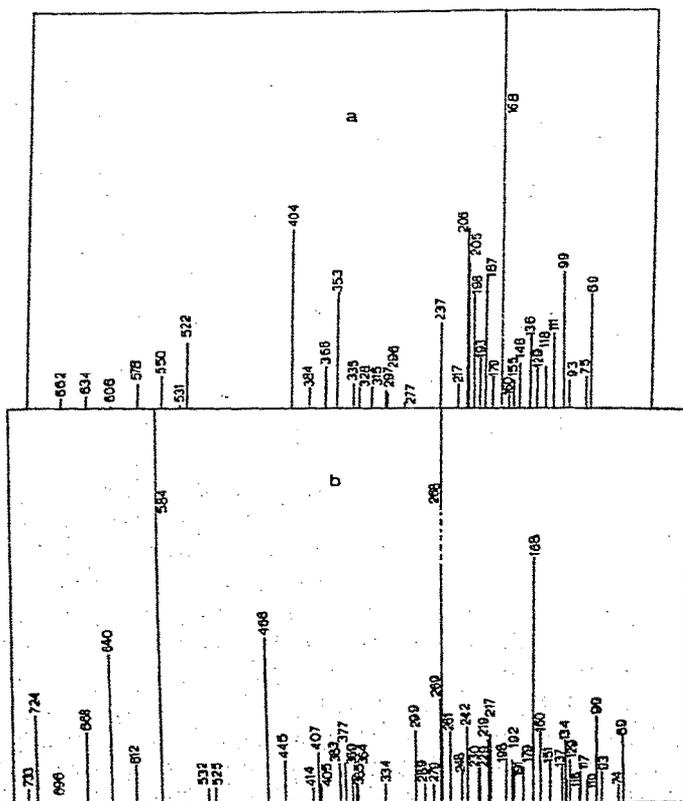


Fig. 1. Mass spectra at 70 eV for: (a) $[(C_6F_5)_2PC_2Me]Co_2(CO)_6$ (I); (b) $[(C_6F_5)_2PC_2Ph]Co_2(CO)_6$ (III).

TABLE 2

INFRARED SPECTRA IN THE $\nu(\text{CO})$ (2300–1800 cm^{-1}) AND $\nu(\text{C}=\text{C})$ (1600–1500 cm^{-1}) REGIONS FOR COBALT CARBONYL COMPLEXES

Compound	$\nu(\text{CO})$ (cm^{-1})	$\nu(\text{C}=\text{C})^a$ (cm^{-1})
(I)	Nujol 2097 s, 2062 vs, 2038 (sh), 2032 vs, 2020 s, 2086 m C ₆ H ₁₂ 2098 s, 2064 vs, 2034 vs, 1995 (sh)	1560 m
(II)	Nujol 2074 vs, 2038 vs, 1986 m CHCl ₃ 2074 vs, 2040 s, 2030 (sh), 1986 m	1555 m
(III)	Nujol 2096, 2066, 2042 (sh), 2032 s, 2019 s, 1984 m C ₆ H ₁₂ 2100 m, 2068 vs, 2042 s, 2038 s, 2018 w	1555 m
(IV)	CHCl ₃ 2072 w, 2050 s, 2040 s, 2029 s, 1986 (sh)	Not identified
(V)	Nujol 2085 (sh), 2078 s, 2034 s, 1993 m, 1987 m CHCl ₃ 2080 s, 2044 vs, 1998 m C ₆ H ₁₂ 2080 s, 2044 s, 1997 m	1535 m
(VI)	CHCl ₃ 2080 s, 2042 vs, 1998 m	1540 w, 1525 w
(VII)	CHCl ₃ 2058 s, 2017 vs, 1995 (sh), 1972 m	1525 m
(VIII)	CHCl ₃ 2058 s, 2020 s, 1995 (sh), 1972 m	1540 m
(IX)	CHCl ₃ 2064 s, 2028 vs, 1997 (sh), 1973 m	1502 m
(X)	CHCl ₃ 2057 s, 2012 s, 1998 (sh), 1964 m C ₆ H ₁₂ 2058 s, 2018 vs, 2012 (sh), 1992 (sh), 1974 m	1528 m
(XI)	2088 s, 2081 s, 2030 vs, 2010 (sh), 1973 vw	1524
(XII)	C ₆ H ₁₂ 2060 s, 2019 vs, 1998 s, 1970 m	Not identified
(XIII)	CHCl ₃ 2043 w, 2014 w, 1984 (sh), 1960 vs, 1933 (sh)	2220 m, 2171 s (uncoordinated)
(XIV)	C ₆ H ₁₂ 2096 s, 2066 s, 2037 vs, 2022 (sh)	1535 m
(XV)	CHCl ₃ 2033 s, 2016 vs, 1986 s, 1970 (sh)	Not identified
(XVI)	CHCl ₃ 2055 (sh), 2045 s, 2026 vs, 2002 m, 1984 w	1515, 1525
(XVII)	CHCl ₃ 2040 (sh), 2033 s, 2016 vs, 1986 s, 1971 (sh)	Not identified
(XVIII)	CHCl ₃ 2028 (sh), 2018 s, 1993 s, 1970 s, 1952 (sh)	1540 vw
(XIX)	CHCl ₃ 2029 (sh), 2018 vs, 1993 s, 1969 s, 1947 (sh)	1530 m
(XX)	CHCl ₃ 2023 (sh), 2012 s, 1990 s, 1963 vs, 1945 (sh)	1520 m
(XXI)	CHCl ₃ 2031 (sh), 2019 s, 1993 s, 1965 s, 1948 (sh)	1540 m
(XXII)	CHCl ₃ 2028 (sh), 2014 s, 1989 vs, 1964 s, 1948 (sh)	1520 m
(XXIII)	C ₆ H ₁₂ 2048 s, 2020 m, 1996 vs	1590 m
(XXIV)	C ₆ H ₁₂ 2105 m, 2080 s, 2053 s, 2046 s, 2022 (sh)	1555 m
(XXV)	CHCl ₃ 2022 s, 1996 s (bd)	1630 m (uncoordinated)

^a Bands due to coordinated $-\text{C}=\text{C}-$ of acetylene (Nujol mull spectra).

cobalt atoms from LCo_2^+ leaving L^+ is therefore a preferred mechanism. In agreement with this, the lower regions of the spectra display a marked similarity to the spectra of the free ligands and an ion at m/e 525 for (III) corresponds to LCo^+ . Attempts to obtain meaningful mass spectra of complexes (XI) and (XIV), which have (*vide infra*) simple (μ -alkyne) $\text{Co}_2(\text{CO})_6$ structures were unsuccessful.

IR spectra in the $\nu(\text{CO})$ and $\nu(\text{C}=\text{C})$ (coordinated acetylene) regions (Table 2) are notable for the absence of bands near 2200 cm^{-1} due to $\nu(\text{C}\equiv\text{C})$ of the free ligands [*cf.* complex (XXV)]. New medium-weak bands, absent in the ligands occur between $1500\text{--}1600\text{ cm}^{-1}$. We assign these bands to $\nu(\text{C}=\text{C})$ of the coordinated acetylenes, the large frequency shift ($\Delta\nu \approx 650\text{ cm}^{-1}$) being consistent with a significant decrease in $-\text{C}\equiv\text{C}-$ bond order on complexing. X-ray structure analyses of $(\text{PhC}_2\text{Ph})\text{Co}_2(\text{CO})_6$ ²³ and $(\text{Ph}_2\text{PC}_2\text{CF}_3)_2\text{Co}_4(\text{CO})_{10}$ ¹⁹ have revealed C-C distances of 1.46 \AA and 1.349 \AA (*av*) for the coordinated acetylenes, a considerable lengthening when compared to the normal value of ca 1.20 \AA for $-\text{C}\equiv\text{C}-$ in acetylenes. From detailed spectroscopic studies of $(\text{HC}\equiv\text{CH})\text{Co}_2(\text{CO})_6$ and deuterated analogues, Iwashita *et al.*²⁴ assigned $\nu(\text{C}\equiv\text{C})$ at 1402.5 cm^{-1} , a lowering of 571.3 cm^{-1} when compared to the free acetylene value.

The $\nu(\text{CO})$ spectra of complexes (I), (III), (XI), (XIV) and (XXIV), (Table 2) provide compelling evidence that these have the (μ -alkyne) $\text{Co}_2(\text{CO})_6$ structure (i) similar to $(\text{PhC}_2\text{Ph})\text{Co}_2(\text{CO})_6$ ²³. Typical spectra are shown in Fig. 2. The similarity of band contours, intensities and positions is striking, and strongly reminiscent of the $(\text{PhC}_2\text{Ph})\text{Co}_2(\text{CO})_6$ spectrum²⁵. Bor²⁵ has investigated the $\nu(\text{CO})$ spectra of (μ -alkyne) $\text{Co}_2(\text{CO})_6$ complexes using $\text{Co}_2(\text{CO})_8$ as a reference, basing his assignments on the similarity of the $\text{Co}_2(\text{CO})_6\text{C}_2\text{C}_{2v}$ skeleton of the latter to that of the alkyne

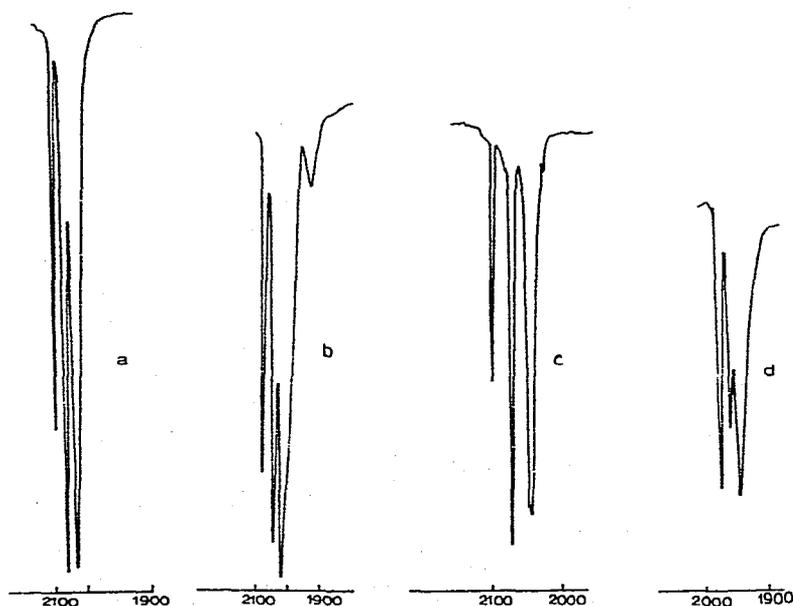
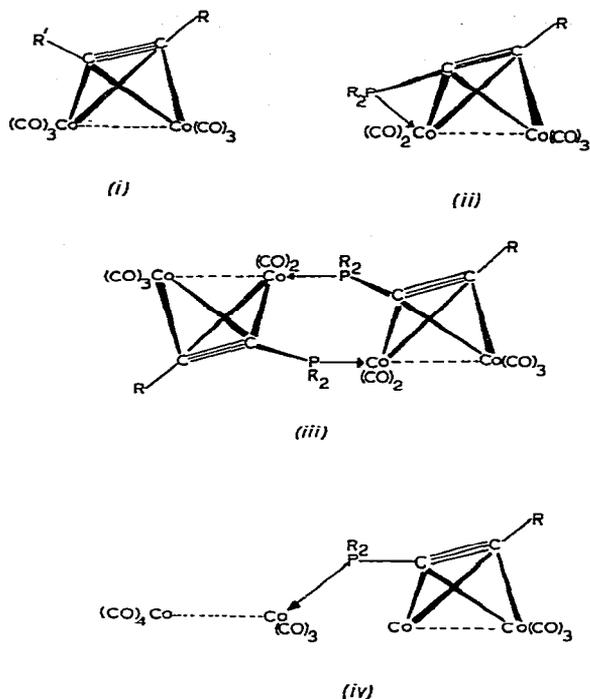


Fig. 2 $\nu(\text{CO})$ IR spectra in cyclohexane of: (a) $[(\text{C}_6\text{F}_5)_2\text{PC}_2\text{Me}]\text{Co}_2(\text{CO})_6$ (I); (b) $[\text{Ph}_2\text{PC}_2\text{C}(\text{Me})_2]\text{Co}_2(\text{CO})_6$ (XI); (c) $[(\text{C}_6\text{F}_5)_2\text{PC}_2\text{Ph}]\text{Co}_2(\text{CO})_6$ (III); (d) $[(\text{C}_6\text{F}_5)_2\text{PC}_2\text{Ph}]\text{Co}_2(\text{CO})_4[(\text{PhO})_3\text{P}]_2$ (XXIII).



bridged complexes. The highest frequency band in the spectra of complexes (I), (III), (XI), (XIV), and (XXIV) corresponds to the weak totally symmetric A_1 $\nu(\text{CO})$ band of $\text{Co}_2(\text{CO})_8$. The higher intensity of this band in the complexes is presumably an indication of somewhat lower overall symmetry²⁴. The presence of this medium-strong band near 2100 cm^{-1} [*cf.* $(\text{HC}\equiv\text{CH})\text{Co}_2(\text{CO})_6$ 2097.8 cm^{-1} ²⁴, $(\text{PhC}_2\text{Ph})\text{Co}_2(\text{CO})_6$ 2090.6 cm^{-1} ²⁵, $(\text{PhC}_2\text{H})\text{Co}_2(\text{CO})_6$ 2094.5 cm^{-1} ^{25,33}] is characteristic of complexes with structure (i) and readily distinguishes these from the $\text{L}_2\text{Co}_4(\text{CO})_{10}$ or $\text{L}_2\text{Co}_2(\text{CO})_6$ types. Additional evidence for the $(\mu\text{-alkyne})\text{Co}_2(\text{CO})_6$ formulation was provided by the synthesis of the disubstitution product (XXIII) from (III). The spectrum of (XXIII) exhibits the expected lowering of $\nu(\text{CO})$ on substitution of CO by $(\text{PhO})_3\text{P}$ (Fig. 2) and resembles the spectra of $(\text{PhC}_2\text{Ph})\text{Co}_2(\text{CO})_4(\text{Ph}_3\text{P})_2$ ¹⁰ and $(\text{PhC}_2\text{Ph})\text{Co}_2(\text{CO})_4(\text{Ph}_2\text{PC}_2\text{Me})$ (XXV).

It is of interest to note that the $\nu_1(\text{CO})$ frequencies of $\text{Co}_2(\text{CO})_8$ and the complexes described herein decrease in the order: $\text{Co}_2(\text{CO})_8 > (\text{C}_6\text{F}_5)_2\text{P}(\text{O})\text{C}_2\text{Ph} > (\text{C}_6\text{F}_5)_2\text{PC}_2\text{Ph} > (\text{C}_6\text{F}_5)_2\text{PC}_2\text{Me} > \text{Ph}_2\text{P}(\text{O})\text{C}_2\text{C}(\text{Me})_3 > \text{Ph}_2\text{PC}_2\text{C}(\text{Me})_3$. This is exactly the order predictable on the basis of the relative π -acceptor properties of the acetylenes assuming that the π -acid character of the alkynes is determined by the electron withdrawing power of the substituents. An analogous relationship between $\nu(\text{CO})$ and substituent electronegativity has been found by Cetini and coworkers²⁷ for a series of $(\text{RC}\equiv\text{CR}')\text{Co}_2(\text{CO})_6$ complexes. Furthermore the $\nu_1(\text{CO})$ frequencies apparently correlate well with rate constants for alkyne exchange²⁷, the more stable complexes having the highest $\nu(\text{CO})$ frequencies.

The formulation of complexes (I), (III), and (XI) as $(\mu\text{-alkyne})\text{Co}_2(\text{CO})_6$ species implies the presence of an uncoordinated phosphorus atom. These are there-

fore the first reported examples where $-C\equiv C-$ coordination competes effectively with phosphorus coordination in reactions of acetylenic phosphines*. The presence of a "free" phosphine in (III) was unexpectedly confirmed in attempts to liberate the free acetylene from (III) by treatment with bromine. Although partial decomposition to $CoBr_2$ occurred the major product was complex (XXIV) with a typical alkyne bridged $Co_2(CO)_6$ spectrum but exhibiting an intense band at 1222 cm^{-1} absent in (III). Oxidation of (III) with bromine presumably occurs with the intermediate formation of a dibromophosphorane complex of cobalt carbonyl $[(C_6F_5)_2Br_2PC_2Ph]Co_2(CO)_6$ which is hydrolysed on work up to the phosphine oxide complex. The final proof of the structures of complexes (XIV) and (XXIV) came from direct synthesis from the phosphine oxides and $Co_2(CO)_8$ in non-polar solvents. Both compounds were obtained in high yield via this route. The uncoordinated phosphorus atom of compound (XI) is considerably more sensitive to oxidation than that in (III). Indeed (XI) converts slowly to the oxide complex (XIV) on an alumina column, hence only small yields of (XI) were obtainable from the reaction of $Ph_2PC_2C(Me)_3$ with $Co_2(CO)_8$. We had previously noted from related studies with $(\pi-C_5H_5)_2Ni_2(CO)_2$ that coordination of the alkyne moiety of $Ph_2PC_2C(Me)_3$ to nickel facilitates phosphorus oxidation²⁸.

B. Complexes of the type $L_2Co_4(CO)_{10}$

The room temperature reaction of $Ph_2MC_2CF_3$ ($M=P, As$) with dicobalt octacarbonyl in benzene gave crystalline complexes (V) and (VI) of empirical formulae $LCo_2(CO)_x$ ($x=5$ or 6). In contrast to the compounds of type (A) however (V) and (VI) are sparingly soluble in saturated hydrocarbon solvents and have $\nu(CO)$ spectra (Table 2) lacking the band near 2100 cm^{-1} characteristic of the $LCo_2(CO)_6$ species. Some typical spectra for these and related complexes are shown in Fig. 3. The major differences between the IR spectra of (A) and (B) type complexes (compare Figs. 2 and 3) are in the shift of all $\nu(CO)$ bands to lower frequency in the (B) class spectra and the dissimilarity of the intensity patterns. Analogous shifts to lower frequency occur on formation of $(PhC_2Ph)Co_2(CO)_5(PPh_3)$ from $(PhC_2Ph)Co_2(CO)_6$ ¹⁰ and $(HC_2H)Co_2(CO)_5(PPh_3)$ from $(HC_2H)Co_2(CO)_6$ ²⁴. Coordination of $-C\equiv C-$ was indicated by the absence of $\nu(C\equiv C)$ of the free ligands and the appearance of bands between $1500-1600\text{ cm}^{-1}$ due to $\nu(C\equiv C)$ coordinated. Products of the same stoichiometry, with similar spectral features (Table 2) were obtained from the reactions of Ph_2PC_2R ($R=H, Me, Ph$) and $PhMePC_2Me$ with $Co_2(CO)_8$. A more detailed analysis of the $\nu(CO)$ spectra of these compounds provided good evidence for a structure based on an $[(RC_2R')Co_2(CO)_5P]$ skeleton. Thus, for example the spectrum of $(Ph_2PC_2H)_2Co_4(CO)_{10}$ (IX) (Table 2) compares favourably with that of $(PhC_2Ph)Co_2(CO)_5(PPh_3)[\nu(CO) 2066, 2028, 2004, 1968\text{ cm}^{-1}]$ ¹⁰. In an attempt to confirm this basic stereochemistry substitution reactions with phosphites were carried out under reflux conditions. Products of empirical formulae $LCo_2(CO)_4P(OR)_3$ [compounds (XV)–(XXII)] were obtained. Since simple $(\mu\text{-alkyne})Co_2(CO)_6$ species readily afford disubstitution products $(\mu\text{-alkyne})Co_2(CO)_4L_2$ (L' = phosphine)¹⁰ under identical conditions, the isolation of complexes (XV)–(XXII) clearly confirmed the intra or

* One example has been reported where $-C\equiv C-$ coordination occurs in preference to arsenic; see ref. 17.

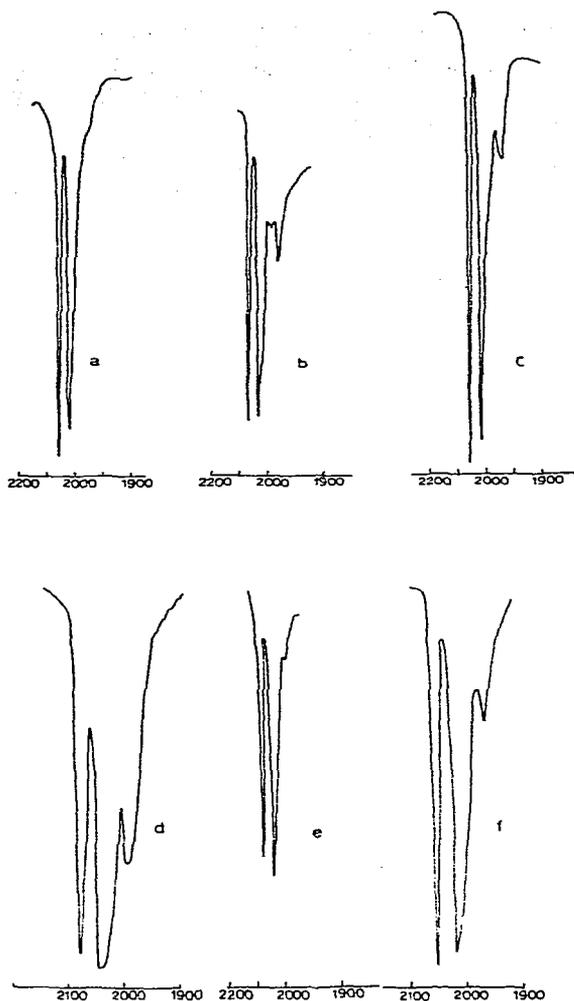


Fig. 3. $\nu(\text{CO})$ IR spectra in chloroform of: (a) $(\text{Ph}_2\text{PC}_2\text{H})_2\text{Co}_4(\text{CO})_{10}$ (IX); (b) $[(\text{C}_6\text{F}_5)_2\text{PC}_2\text{Me}]_2\text{Co}_4(\text{CO})_{10}$ (II); (c) $(\text{Ph}_2\text{PC}_2\text{Ph})_2\text{Co}_4(\text{CO})_{10}$ (VIII); (d) $(\text{Ph}_2\text{AsC}_2\text{CF}_3)_2\text{Co}_4(\text{CO})_{10}$ (VI); (e) $(\text{Ph}_2\text{PC}_2\text{CF}_3)_2\text{Co}_4(\text{CO})_{10}$ (V); (f) $(\text{Ph}_2\text{PC}_2\text{Me})_2\text{Co}_4(\text{CO})_{10}$ (VI).

intermolecular coordination of the phosphorus atoms in the initial compounds. Synthesis of complex (XXV) in which the phosphinoacetylene ligands are coordinated via the phosphorus atom only, as a model complex and further comparison of the $\nu(\text{CO})$ spectra of compounds (XV)–(XXII) with (XXV) (Table 2) validates this conclusion.

Although the detailed synthetic and spectroscopic studies described above unequivocally favoured coordination of both the $-\text{C}\equiv\text{C}-$ and phosphorus sites in the complexes no distinction could be made between intramolecular phosphorus coordination as in (ii) or intermolecular interaction as in (iii). The low solubility of the complexes in suitable solvents precluded molecular weight measurements in solution. However molecular models suggested that structure (ii) was unfavourable

on geometric grounds since (ii) incorporates a highly strained $\overline{\text{C-Co-P}}$ ring. The ^1H NMR spectra of the ethynyl-diphenylphosphine and phenylmethylpropynylphosphine complexes (IX) and (X) shed further, though in retrospect somewhat unexpected light on the structures (ii) and (iii). The acetylenic proton of $\text{Ph}_2\text{PC}\equiv\text{CH}$ appears as a doublet at 100 MHz in CDCl_3 [$\delta = 2.03(\text{d})$, $^3J(\text{P-H}) 0.3 \text{ Hz}$]. In $(\text{Ph}_2\text{PC}_2\text{H})\text{Co}_4(\text{CO})_{10}$ however the resonance due to $\equiv\text{C-H}$ is a triplet [$\delta = 6.4(\text{t})$] with peak separations of 0.7 Hz. This spectrum can be compared with that of $(\text{HC}_2\text{H})\text{Co}_2(\text{CO})_5(\text{Ph}_3\text{P})$ where a doublet appears due to coupling of the acetylenic proton with phosphorus through the P-Co-C-H system²⁴. The marked downfield shift of the acetylenic protons in both $(\text{Ph}_2\text{PC}_2\text{H})_2\text{Co}_4(\text{CO})_{10}$ and $(\text{HC}_2\text{H})\text{Co}_2(\text{CO})_6$ ²⁴ is notable. This indicates a marked change in hybridisation for the acetylenic carbon atoms ($sp \rightarrow sp^2$) and suggests the interesting possibility of a marked increase in acidity of the acetylenic proton in (IX). We are currently exploring the synthetic implications of this idea. The triplet found in (IX) suggests coupling between two phosphorus atoms*. Clearly this would be impossible for a structure of type (ii). Thus the NMR data favour structure (iii) (or a higher polymer) for (IX) and by inference all other complexes discussed in this section. The NMR spectrum of (X) elicited similar conclusions. The P-Me resonance of (X) [CDCl_3 , 60 MHz $\delta = 2.45(\text{t})$] appeared as a 1/1/1 triplet with the central line broader than the two outer lines. Some care is necessary in interpretation here however since the complexed ligand $\text{PhMePC}\equiv\text{CMe}$ contains an optically active centre. Furthermore as can be seen from Fig. 4 *cis* and *trans* geometric isomers are also possible for a structure of the type $(\text{RR}'\text{PC}_2\text{R}'')_2\text{Co}_4(\text{CO})_{10}$ when R and R' differ. Thus the observed deceptively simple triplet could possibly arise from the superposition of two more chemically shifted resonances due to different

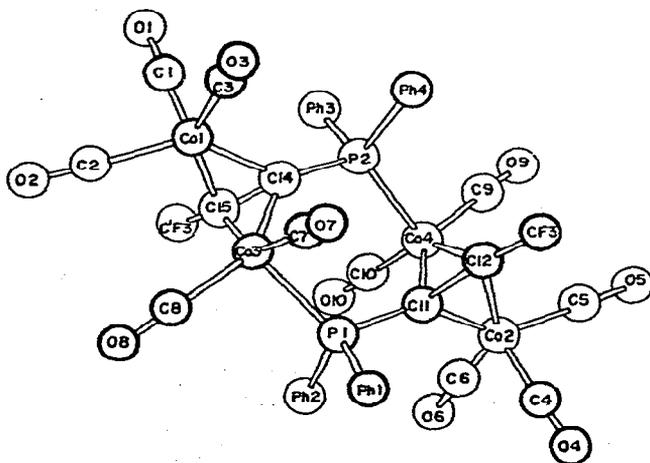


Fig. 4. Molecular structure of $(\text{Ph}_2\text{PC}_2\text{CF}_3)_2\text{Co}_4(\text{CO})_{10}$ showing the atomic numbering. Pertinent interatomic distances are Co1-Co3 (2.482 Å), Co2-Co4 (2.464 Å), Co3-P1 (2.236 Å), Co4-P2 (2.229 Å), C11-C12 (1.377 Å) and C14-C15 (1.320 Å).

* This resonance and the P-Me resonance of complex (X) are deceptively simple. The general analysis of $X_n\text{AA}'X'_n$ systems has been given by Harris²⁹. Deceptively simple triplets arising from so called "virtual coupling" between phosphorus atoms appear when $J(\text{AA}') \gg [J(\text{AX}) - J(\text{AX}')]]$. Such spectra are difficult to analyse completely and in general provide only an estimate of $J(\text{AA}')$ ³⁹.

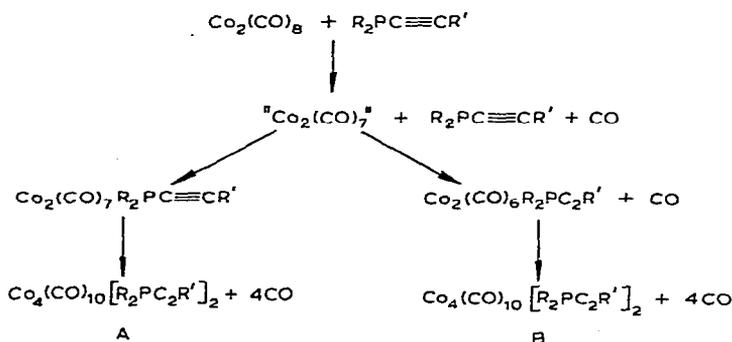
molecular stereochemistries. The similarity with other "virtually coupled" spectra in the literature^{30,31} is striking however and in view of the results for (IX) we prefer this explanation.

Final confirmation of the structure of the (B) type complexes was forthcoming from a single crystal X-ray structure determination of $(\text{Ph}_2\text{PC}_2\text{CF}_3)_2\text{Co}_4(\text{CO})_{10}$ ¹⁹. The molecular structure is shown in Fig. 4 from which it is evident that the alkyne function of the ligand is coordinated to two cobalt atoms of a $\text{Co}_2(\text{CO})_5$ fragment in μ -fashion, with the phosphorus atom of the same ligand attached to a cobalt atom of an adjacent $\text{Co}_2(\text{CO})_5$ unit. The formation of the complex can be envisaged in terms of intermolecular substitution of two CO ligands by the uncoordinated phosphorus atoms of the alkyne species $(\text{Ph}_2\text{PC}_2\text{CF}_3)\text{Co}_2(\text{CO})_6$ with the formation of a puckered 6-membered $\text{Co}_2\text{P}_2\text{C}_2$ ring. Full details of the structural parameters of (V) will be published elsewhere.

It is evident that the substitution products $\text{L}_2\text{Co}_4(\text{CO})_8\text{L}'_2$ [(XV)–(XXII)] have terminal CO groups on Co 1 and Co 2 (Fig. 4) replaced by phosphite ligands. Furthermore, to minimise steric interactions it seems probable that the carbonyl groups C2–O2 and C5–O5 (Fig. 4) are substituted by phosphites.

The mechanism of formation of the complexes $\text{L}_2\text{Co}_4(\text{CO})_{10}$ is of interest in view of the two different nucleophilic sites in the ligands. Assuming the usual dissociative mechanism for first row metal carbonyls, reaction of $\text{R}_2\text{PC}\equiv\text{CR}'$ with $\text{Co}_2(\text{CO})_8$ may proceed via path A or B in Scheme 1. Mechanism A is presumably

SCHEME 1



analogous initially to the mechanism of formation of $\text{Co}_2(\text{CO})_7\text{PR}_3$ ² while B is comparable to the recently revised reaction path for $(\text{RC}\equiv\text{CR})\text{Co}_2(\text{CO})_6$ ³². For the ligands $(\text{C}_6\text{F}_5)_2\text{PC}\equiv\text{CR}$ ($\text{R} = \text{Me}, \text{Ph}$) we have obtained definite evidence favouring mechanism B. The complexes $[(\text{C}_6\text{F}_5)_2\text{PC}_2\text{R}]\text{Co}_2(\text{CO})_6$ [(I) and (III)] can be isolated from the reaction mixtures. (I) and (III) can be converted into complexes of the second type $[(\text{C}_6\text{F}_5)_2\text{PC}_2\text{R}]_2\text{Co}_4(\text{CO})_{10}$ by refluxing in a hydrocarbon solvent. One of these, ($\text{R} = \text{Me}$) was fully characterised by microanalysis and the other was identified by IR spectroscopy. The conversion (I) \rightarrow (II) can be followed by IR spectroscopy (Fig. 5) which shows the gradual replacement of the $(\mu\text{-alkyne})\text{Co}_2(\text{CO})_6$ peaks by those of the $\text{Co}_4(\text{CO})_{10}$ complex. However the reaction may be more complex than is represented by the Scheme 1B. Fig. 5 shows in addition to the growing peaks due to $\text{L}_2\text{Co}_4(\text{CO})_{10}$, the gradual appearance then disappearance of a band

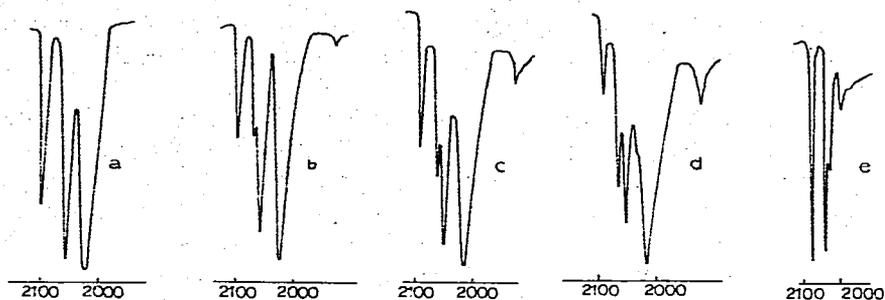


Fig. 5. $\nu(\text{CO})$ spectra in *n*-hexane showing the conversion of $[(\text{C}_6\text{F}_5)_2\text{PC}_2\text{Me}]_2\text{Co}_2(\text{CO})_6$ into $[(\text{C}_6\text{F}_5)_2\text{PC}_2\text{Me}]_2\text{Co}_4(\text{CO})_{10}$. Spectra a-d show the appearance of bands due to the tetranuclear species. Spectrum e is the spectrum obtained after complete reaction.

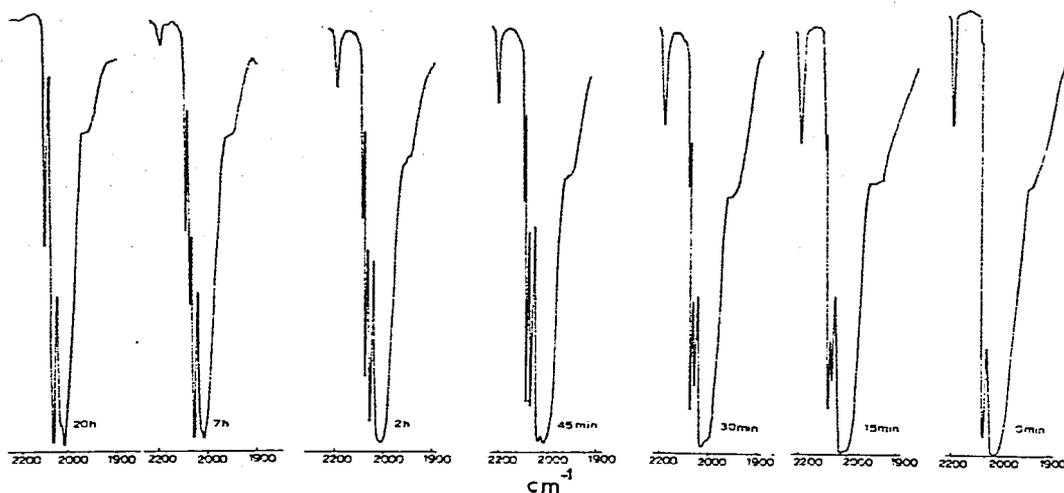


Fig. 6. $\nu(\text{CO})$ IR spectra in chloroform showing the intermediate stages in the reaction of $\text{PhMePC}\equiv\text{CMe}$ with $\text{Co}_2(\text{CO})_8$.

at ca. 1950 cm^{-1} . As shown later (section C) this band may be characteristic of a disubstituted $\text{Co}_2(\text{CO})_6\text{L}'_2$ complex ($\text{L}' = \text{phosphine}$). Thus we cannot entirely rule out the intermediacy of a third complex in the conversion of $\text{LCo}_2(\text{CO})_6$ to $\text{L}_2\text{Co}_4(\text{CO})_{10}$ even for $\text{L} = (\text{C}_6\text{F}_5)_2\text{PC}\equiv\text{CR}$.

We have also followed the reaction of $\text{PhMePC}\equiv\text{CMe}$ with $\text{Co}_2(\text{CO})_8$ by IR spectroscopy (Fig. 6). This experiment was of interest since we had not isolated any of the simple $(\mu\text{-alkyne})\text{Co}_2(\text{CO})_6$ species with this ligand. The spectra provide excellent evidence however that a complex of this type is indeed a reaction intermediate. Consider the $\nu(\text{CO})$ spectrum at 0 min. The spectrum shows quite clearly the presence of $\nu(\text{C}\equiv\text{C})$ of the free ligand at 2200 cm^{-1} and the appearance of a distinct shoulder at 2092 cm^{-1} . The latter band grows into the spectrum concurrent with the disappearance of the band due to $\nu(\text{C}\equiv\text{C})$ of the free ligand. As pointed out previously this high frequency $\nu(\text{CO})$ band is undoubtedly due to ν_1 of a $\mu\text{-alkyne}$ complex $(\text{PhMePC}_2\text{Me})\text{Co}_2(\text{CO})_6$. Even after 20 h this band was still present, however work up failed to yield the solid complex. Good yields of (X) were obtained from this reaction mixture. Although (X) was present in solution according to infrared spectra

there is also the possibility that the simple μ -alkyne species converts to (X) on the column.

Further analysis of the spectra in Fig. 6 revealed an additional complication. Consider again the $\nu(\text{CO})$ spectrum at 0 min. A broad band encompassing the region between $1990\text{--}2040\text{ cm}^{-1}$ consists of absorptions due to $\text{Co}_2(\text{CO})_8$ which occur at 2030 cm^{-1} and 2040 cm^{-1} ³³ as well as those arising from the reaction products. Now $(\text{PhMePC}_2\text{Me})_2\text{Co}_4(\text{CO})_{10}$ exhibits a band at 2012 cm^{-1} (Table 2). Hence the region from $2000\text{--}1975\text{ cm}^{-1}$ should not contain any strong or medium absorption bands due to $\text{Co}_2(\text{CO})_8$ ³³ or complex (X). Any strong bands in this region are therefore likely due to intermediate products.

The spectra of $\text{Co}_2(\text{CO})_7\text{L}$ complexes contain strong bands at 1996 cm^{-1} for $\text{L} = \text{Ph}_3\text{P}$ and 1992 cm^{-1} for $\text{L} = \text{Bu}_3\text{P}^2$. It is reasonable to assume therefore that a band in this region would occur for an intermediate $\text{Co}_2(\text{CO})_7(\text{PhMePC}_2\text{Me})$. Inspection of Fig. 6 reveals that the broad band in this region gradually narrows and moves to higher frequency as the reaction proceeds. If $\text{Co}_2(\text{CO})_7(\text{PhMePC}_2\text{Me})$ is in fact formed initially then by analogy with the spectra of $\text{Co}_2(\text{CO})_7(\text{PR}_3)$ complexes² other bands in the $\nu(\text{CO})$ region attributed to this complex should appear at ca. 2080 s , 2025 s , and 1960 m cm^{-1} . The 1960 cm^{-1} band appears as a shoulder which decreases in intensity with time while the 2080 and 2025 cm^{-1} bands are obscured by $\text{Co}_2(\text{CO})_8$, $(\text{PhMePC}_2\text{Me})\text{Co}_2(\text{CO})_6$ and eventually $(\text{PhMePC}_2\text{Me})_2\text{Co}_4(\text{CO})_{10}$ absorptions. The complex $(\text{PhMePC}_2\text{Me})\text{Co}_2(\text{CO})_7$ should also exhibit a $\nu(\text{C}\equiv\text{C})$ band due to the uncoordinated acetylene moiety. The spectra in Fig. 6 yield no evidence for a "free" $\nu(\text{C}\equiv\text{C})$ other than that of the free ligand. However this is not surprising since $\nu(\text{C}\equiv\text{C})$ of these phosphines shifts little if at all on complexing of phosphorus and in CHCl_3 solution two $\nu(\text{C}\equiv\text{C})$ bands could remain unresolved. On balance we believe the spectral evidence favours a second intermediate having a skeleton $\text{Co}_2(\text{CO})_7\text{L}'$ ($\text{L}' = \text{phosphorus donor}$). However this could be a simple dinuclear, monosubstituted $\text{Co}_2(\text{CO})_8$ complex or alternatively a tetranuclear species of type (iv).

C. Complexes of the type $\text{L}_2\text{Co}_2(\text{CO})_6$

The sealed tube reaction of $\text{Ph}_2\text{PC}\equiv\text{CC}(\text{Me})_3$ with $\text{Co}_2(\text{CO})_8$ in benzene yielded a product analysing as $\text{L}_2\text{Co}_2(\text{CO})_6$ (XIII). The IR spectrum of (XIII) shows two bands due to $\nu(\text{C}\equiv\text{C})$ of the ligand. Hence the alkyne groups are uncoordinated. The $\nu(\text{CO})$ IR spectrum of this derivative compares very well with the spectra of several $(\text{PR}_3)_2\text{Co}_2(\text{CO})_6$ complexes having predominantly non-bridged structures in solution³. X-ray studies of $(\text{Bu}_3\text{P})_2\text{Co}_2(\text{CO})_6$ ^{34,35} have established a non-bridged D_{3d} solid state structure for this compound and Vohler³⁶ and Manning³ came to a similar conclusion from IR studies. The similarity between (XIII) and the phosphine complexes $\text{L}_2\text{Co}_2(\text{CO})_6$ is further emphasised by an examination of spectra in highly concentrated solutions (Fig. 7). Weak bands at 1826 cm^{-1} and 1793 cm^{-1} (sh) due to $\nu(\text{CO})$ bridging appear in concentrated solutions. Thus an equilibrium between bridged and non-bridged isomers exists, analogous to $(\text{Et}_3\text{P})_2\text{Co}_2(\text{CO})_6$ and other complexes of the type $(\text{PR}_3)_2\text{Co}_2(\text{CO})_6$ ^{3,4}. By bubbling CO through solutions of (XIII), partial conversion to $[\text{Ph}_2\text{PC}\equiv\text{CC}(\text{Me})_3]\text{Co}_2(\text{CO})_7$ occurred which could be followed by IR spectroscopy. Spectrum (c) Fig. 7 illustrates this result. The spectrum can be compared with that of other $\text{LCo}_2(\text{CO})_7$ complexes².

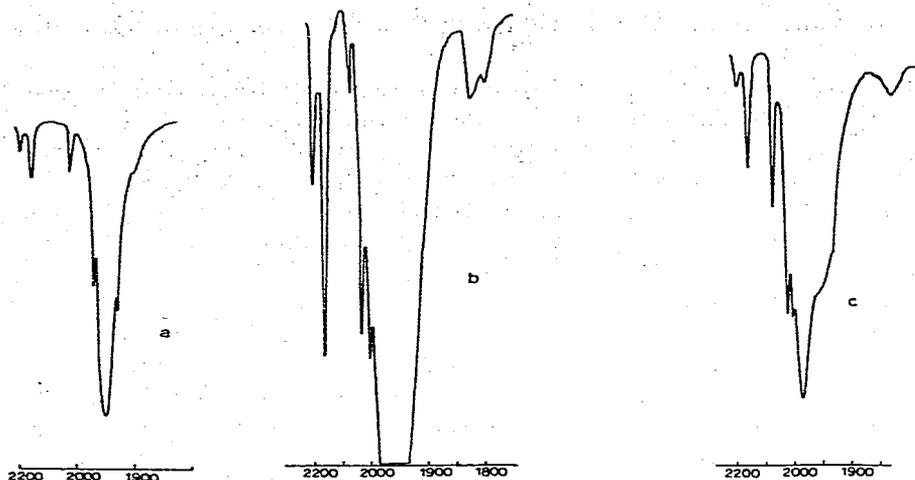


Fig. 7. $\nu(\text{CO})$ IR spectra of $[\text{Ph}_2\text{PC}_2\text{C}(\text{Me})_3]_2\text{Co}_2(\text{CO})_6$: (a) As a nujol mull; (b) in a concentrated benzene solution showing the presence of $\nu(\text{CO})_{\text{bridging}}$; (c) after passing carbon monoxide into a concentrated benzene solution for several hours. The appearance of bands due to $\text{Co}_2(\text{CO})_7$, $[\text{Ph}_2\text{PC}_2\text{C}(\text{Me})_3]$ can be seen.

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