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REACTIONS OF NiX_2(dppe) (X = Cl, Br) WITH Na[$Co(CO)_4$]. SYNTHESIS AND CRYSTAL STRUCTURE OF $Co_2(\mu\text{-}CO)_2(CO)_4$(dppe) (dppe = $Ph_2PCH_2CH_2PPh_2$)

PIERRE BRAUNSTEIN*, INGRID PRUSKIL,

Laboratoire de Chimie de Coordination, ERA 670 CNRS, Université Louis Pasteur, 67070 Strasbourg Cedex (France)

GIOVANNI PREDIERI and ANTONIO TIRIPICCHIO

Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via M. D'Azeglio 85, 43100 Parma (Italy)

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Summary

The reaction of Na[$Co(CO)_4$] with NiX_2(dppe) (X = Cl, Br; dppe = 1,2-bis(diphenylphosphino)ethane) in THF or toluene at −30 to 0°C produces mainly $Ni(CO)_2$(dppe) and $Co_2(CO)_6$(dppe). The structure of this latter complex, determined by an X-ray analysis, can be regarded as derived from that of $Co_2(CO)_8$ by substitution of two terminal CO groups on one cobalt atom by the chelating dppe ligand. This structure could not have been predicted unambiguously solely on the basis of the interpretation of the infrared data. Crystals of $Co_2(\mu\text{-}CO)_2(CO)_4$(dppe) are monoclinic, space group $P2_1/a$, with $Z = 4$, in a unit cell of dimensions a 21.117(13), b 17.012(10), c 8.436(6) Å, β 93.76(5)°. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares to $R = 0.053$ for 1549 independent observed reflections.

Introduction

Some years ago it was observed that upon treatment of $NiX(NO)(PPh_3)_2$ (X = Cl, Br, I) with Na[$Co(CO)_4$] in THF, the mixed bimetallic complex $Ni(NO)(PPh_3)_2$-$Co(CO)_4$ was obtained, whereas when $NiX_2(PPh_3)_2$ was used the only Ni derivative isolated was $Ni(CO)_2(PPh_3)_2$ [1]. This was explained in terms of the migration of the ligands CO and PPh_3 between the metal centers. On the other hand, reaction of the same sodium tetracarbonylcobaltate with $PtCl_2$(dppe) [dppe = 1,2-bis-(diphenylphosphino)ethane] gave the triangulo cluster compound (dppe)$PtCo_2(CO)_7$ [2]. Reasoning that the bidentate nature of the dppe ligand might prevent ligand migration and have some stabilizing influence on the formation of the triangular

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species, we decided to examine the reaction of $NiX_2(dppe)$ ($X = Cl, Br$) with two equivalents of $Na[Co(CO)_4]$. To our surprise, no mixed metal complex could be isolated, even at low temperature. We observed instead a redox reaction, and the redistribution of the ligands, leading mainly to $Ni(CO)_2(dppe)$ and $Co_2(CO)_6(dppe)$, according to the following equation:

$$NiX_2(dppe) + 2\ NaCo(CO)_4 \rightarrow 2\ NaX + Ni(CO)_2(dppe) + Co_2(CO)_6(dppe) + \ldots$$

Such a facile migration (see Experimental) of a bidentate ligand such as dppe from one metal center to another seems to us unprecedented. Infrared data for the solid dicobalt complex indicated a structure in which the cobalt atoms are bridged by two carbonyl groups, the dppe ligand bridging the two metals or chelating one cobalt atom, as suggested by Ellermann [3,4]. But while the structure of dicobalt octacarbonyl derivatives with various chelating ligands has given rise to some discussion in the past, interpretation of their infrared spectra being not a simple matter [3–6], to our knowledge, no X-ray crystal structure determination has previously been reported for any compound of the general formula $Co_2(CO)_6(dppe)$. In view of the general interest in this class of complexes for homogeneous catalysis [7] we report here the crystal structure of $Co_2(\mu\text{-}CO)_2(CO)_4(dppe)$ and describe the new reactions by which it was synthesized.

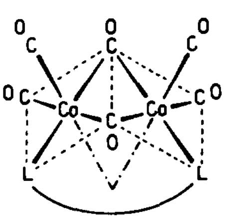
Results and discussion

Attempts to prepare $Co_2(CO)_6(dppe)$ generally start with $Co_2(CO)_8$ and dppe, and date back to 1963 when Sacco reacted these two compounds together in benzene or petroleum ether at room temperature. But, instead of the neutral complex $Co_2(CO)_6(dppe)$, he isolated the ionic product $[Co_2(CO)_4(dppe)_3][Co(CO)_4]_2$ [8]. Ellerman modified the experimental conditions [3,4] and isolated a complex of the general formula $Co_2(CO)_6(dppe)$, whose infrared absorptions showed no evidence for any bridging carbonyl group. On the basis of the IR spectra, Ellermann postulated a structure with three terminal CO ligands on each cobalt atom and the dppe bridging the two metal centers. In order to check this, crystals for X-ray diffraction were grown from benzene/n-heptane. It was recognized that isomerisation had occurred during the process, but the structure determination showed that these crystals contained the doubly bridged carbonyl complex $[Co_2(\mu\text{-}CO)_2(CO)_4(\mu\text{-}Ph_2P\text{-}NH\text{-}PPh_2)]$ [9] and not the expected complex $[Co_2(\mu\text{-}CO)_2(CO)_4(\mu\text{-}dppe)]$ (type B, see below). Thus at this point there was no certain assignment of the structure of any $Co_2(CO)_6(dppe)$ complex.

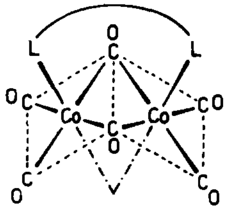
It may be of interest in this context to note that when we treated $Co_2(CO)_8$ with a stoichiometric amount of dppe in dioxane at 30°C for about 45 min, we observed the formation of a mixture of a large amount of $[Co_2(CO)_4(dppe)_3][Co(CO)_4]_2$, as described by Sacco [8], and of a minimal quantity of the $Co_2(CO)_6(dppe)$ complex which we are dealing with in this paper.

Previous structural assignment based on IR spectroscopy [5] used the solid state structure of $Co_2(CO)_8$ [10] as a model and deduced the following three possibilities for ligand coordination in $Co_2(CO)_6(L\text{–}L)$ systems ($L\text{–}L$ = bidentate P or As containing ligand).

Crow and Cullen [5] expected a single isolated peak in the IR spectrum of C, due to the lower energy absorption of the unique terminal carbonyl group of the



(A)



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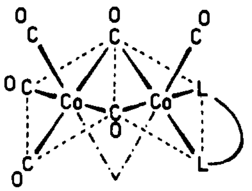

(C)

substituted cobalt atom, but did not observe it in any of their complexes, and therefore excluded that structure. They further distinguished between A and B on the basis of the energy difference between the bridging carbonyl stretching frequencies, expecting a larger difference for structure A and a smaller one in the case of B. This was shown to be correct by an X-ray crystal structural analysis of μ-[1,2-bis-(dimethylarsino)tetrafluorocyclobutene-*AsAs*]-di-μ-carbonyl-bis(dicarbonylcobalt)(*Co–Co*) [11], a complex which showed both structure A and a large difference between the bridging ν(CO) frequencies (56 cm^{-1}; C_6H_{12} solution [5]). This kind of assignment is also confirmed by the B-type solid-state structure of $[Co_2(\mu\text{-}CO)_2(CO)_4(\mu\text{-}Ph_2PNHPPh_2]$ [9] and the small difference (9 cm^{-1}; KBr pellet) between its bridging ν(CO) frequencies.

In 1972, Stephens reported the X-ray crystal structure of $Co_2(CO)_6$(nbd) (nbd = norbornadiene) [12]. This compound has structure C in which the diene acts as a chelating ligand replacing two equatorial terminal CO groups on one cobalt atom. Its terminal CO absorptions in the infrared are at 2076, 2024, 2012, and 2009sh cm^{-1} [13]. As the frequency of the infrared band due to the unique terminal

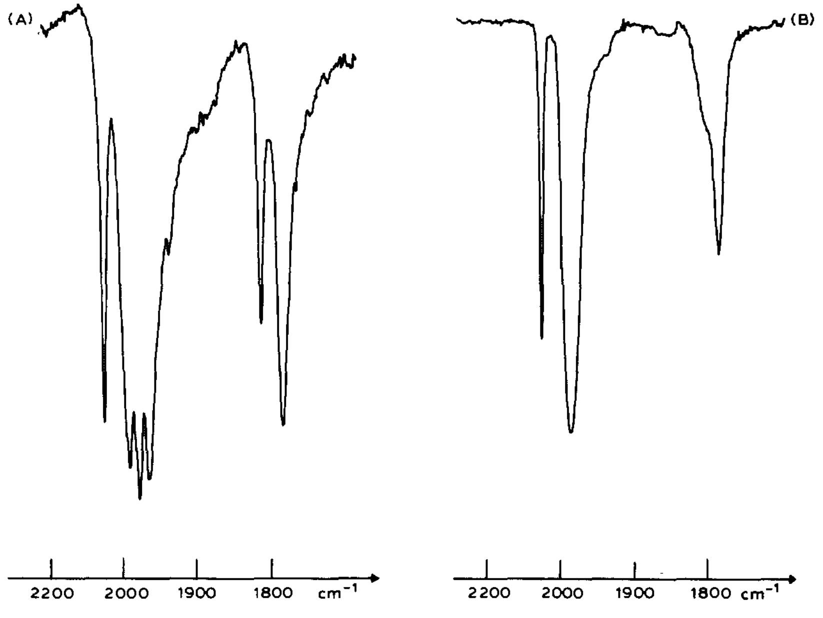

Fig. 1. Infrared spectrum of $Co_2(\mu\text{-}CO)_2(CO)_4$(dppe): (A) in KBr pellet; (B) in toluene solution.

TABLE 1

COMPARISON OF THE IR SPECTRA OF SEVERAL $Co_2(CO)_6(L{-}L)$ COMPLEXES

Compound	$\nu(CO)$ (cm^{-1})									Solvent	Reference
$Co_2(CO)_6$(dppe) non-bridged	2050sh	2035s	1998vs	1970sh						KBr	[4]
	2037s	2001vs	1975sh							CH_2Cl_2	
$Co_2(\mu\text{-}CO)_2(CO)_4\mu\text{-}(PPh_2NHPPh_2)$	2045s	2005s	1993vs	1980s	1965sh	1811ms	1801s	1767sh		KBr	[9]
	2055ms	2022s	1993s	1828sm		1799m				CH_2Cl_2	
$Co_2(\mu\text{-}CO)_2(CO)_4$(ffars)[a]	2022s	2020s	1996vs	1842m		1786m				C_6H_{12}	[5]
$Co_2(\mu\text{-}CO)_2(CO)_4$(nbd)[b]	2076s	2024vs	2012s	2009sh		1949vw	1834s			C_7H_{16}	[13]
$Co_2(\mu\text{-}CO)_2(CO)_4$(dppe)[c]	2049s	1989s	1975vs	1962s		1935sh	1809m	1780s	1762sh	KBr[d]	This work
	2057m	1984vs	1807sh	1788m						THF	This work
	2057s	1988vs	1804sh	1783m						CH_2Cl_2	This work
	2054s	1988vs	1809sh	1709m						toluene[e]	This work
	2055m	1985s	1812sh	1788m						dioxane	This work

[a] ffars = $(CH_3)_2As\overline{C{=}CAs(CH_3)_2CF_2C}F_2$. [b] nbd = norbornadiene. [c] No infrared spectrum could be taken in acetonitrile, the complex decomposing immediately and showing only the absorption band of the $[Co(CO)_4]^-$ anion at 1893 cm^{-1}. [d] See Fig. 1(A). [e] See Fig. 1(B).

carbonyl ligand on the substituted metal atom was not, in contrast to previous expectations [5], very different from that of the terminal CO groups on the other cobalt atom, the authors [13] concluded that structure C could not be excluded for the other $Co_2(CO)_6$(L–L) complexes.

At this point, the three structures A–C were still possible for the present $Co_2(CO)_6$(dppe) compound. Indeed, applying Cullen's criterion [5], the difference of 29 cm^{-1} (KBr) between the ν(CO) frequencies of the bridging carbonyls lies at the borderline of structures A and B. (Fig. 1). Furthermore, structure C could not be ruled out in view of the known propensity of dppe to act as a chelate and in the light of the X-ray structure of $Co_2(\mu\text{-}CO)_2(CO)_4$(nbd) [12].

We therefore decided to determine the crystal structure of the complex. It was revealed to be of type C, representing the first example of its kind for $Co_2(CO)_6$(L–L) complexes involving a phosphorous-containing bidentate ligand.

Noteworthy is the close similarity of the IR spectra in the ν(CO) region between $[Co_2(\mu\text{-}CO)_2(CO)_4(\mu\text{-}PPh_2NHPPh_2)]$ [9] and our $Co_2(\mu\text{-}CO)_2(CO)_4$(dppe) (see Table 1 and Fig. 1), although the former has B and the latter a C-type structure. This observation may cast some doubt on structural assignments based solely on IR vibrations, at least in this class of molecules.

Description of the crystal structure of $Co_2(\mu\text{-}CO)_2(CO)_4$(dppe)

A perspective view of the complex together with the labelling of the atoms is shown in Fig. 2. Selected bond distances and angles in the complex are given in

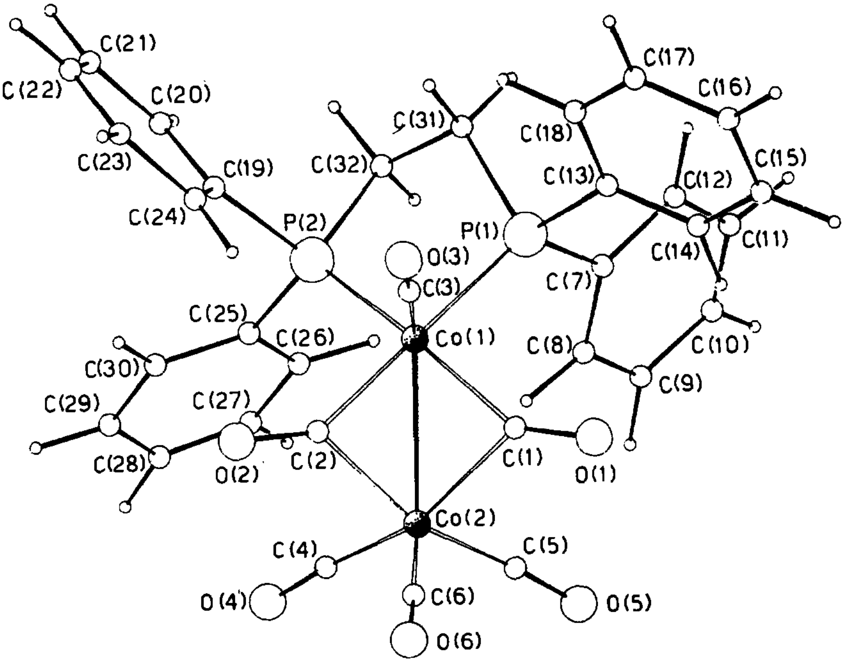

Fig. 2. View of the structure of the complex $Co_2(\mu\text{-}CO)_2(CO)_4(Ph_2PCH_2CH_2PPh_2)$ with the atomic labelling system.

TABLE 2

SELECTED BOND DISTANCES (Å) AND ANGLES (°) WITH E.S.D.'S IN PARENTHESES

Around the Co atom

Co(1)–Co(2)	2.541(3)	Co(2)–C(1)	2.01(2)
Co(1)–P(1)	2.211(4)	Co(2)–C(2)	1.96(2)
Co(1)–P(2)	2.234(5)	Co(2)–C(4)	1.77(2)
Co(1)–C(1)	1.85(2)	Co(2)–C(5)	1.76(2)
Co(1)–C(2)	1.85(2)	Co(2)–C(6)	1.77(2)
Co(1)–C(3)	1.76(2)		
Co(2)–Co(1)–P(1)	123.7(1)	C(1)–Co(2)–C(2)	85.7(7)
Co(2)–Co(1)–P(2)	111.5(2)	C(1)–Co(2)–C(4)	157.0(7)
Co(2)–Co(1)–C(1)	51.5(5)	C(1)–Co(2)–C(5)	85.3(8)
Co(2)–Co(1)–C(2)	50.2(5)	C(1)–Co(2)–C(6)	94.3(7)
Co(2)–Co(1)–C(3)	121.5(6)	C(1)–Co(2)–Co(1)	46.1(5)
P(1)–Co(1)–P(2)	85.1(2)	C(2)–Co(2)–C(4)	87.0(8)
P(1)–Co(1)–C(1)	87.5(5)	C(2)–Co(2)–C(5)	160.0(8)
P(1)–Co(1)–C(2)	167.0(5)	C(2)–Co(2)–C(6)	92.3(7)
P(1)–Co(1)–C(3)	97.0(6)	C(2)–Co(2)–Co(1)	46.3(5)
P(2)–Co(1)–C(1)	150.7(5)	C(4)–Co(2)–C(5)	94.3(9)
P(2)–Co(1)–C(2)	87.4(5)	C(4)–Co(2)–C(6)	107.8(8)
P(2)–Co(1)–C(3)	112.1(6)	C(4)–Co(2)–Co(1)	116.0(6)
C(1)–Co(1)–C(2)	94.0(7)	C(5)–Co(2)–C(6)	106.5(8)
C(1)–Co(1)–C(3)	97.0(7)	C(5)–Co(2)–Co(1)	116.6(7)
C(2)–Co(1)–C(3)	95.7(7)	C(6)–Co(2)–Co(1)	113.7(5)

In the carbonyl groups

O(1)–C(1)	1.15(2)	O(4)–C(4)	1.14(2)
O(2)–C(2)	1.18(2)	O(5)–C(5)	1.17(3)
O(3)–C(3)	1.14(2)	O(6)–C(6)	1.12(2)
Co(1)–C(1)–Co(2)	82.4(7)	Co(2)–C(2)–O(2)	134(1)
Co(1)–C(2)–Co(2)	83.6(7)	Co(1)–C(3)–O(3)	179(1)
Co(1)–C(1)–O(1)	145(1)	Co(2)–C(4)–O(4)	175(2)
Co(2)–C(1)–O(1)	132(1)	Co(2)–C(5)–O(5)	176(2)
Co(1)–C(2)–O(2)	143(1)	Co(2)–C(6)–O(6)	179(2)

In bis(diphenylphosphine)ethane ligand

P(1)–C(31)	1.82(2)	P(2)–C(32)	1.86(2)
P(1)–C(7)	1.82(1)	P(2)–C(19)	1.83(2)
P(1)–C(13)	1.83(1)	P(2)–C(25)	1.83(2)
C(31)–P(1)–C(7)	101.1(7)	C(32)–P(2)–C(19)	102.9(7)
C(31)–P(1)–C(13)	104.3(7)	C(32)–P(2)–C(25)	105.0(7)
C(31)–P(1)–Co(1)	107.4(5)	C(32)–P(2)–Co(1)	108.9(5)
C(7)–P(1)–C(13)	106.2(7)	C(19)–P(2)–C(25)	102.9(7)
C(7)–P(1)–Co(1)	121.7(5)	C(19)–P(2)–Co(1)	117.5(5)
C(13)–P(1)–Co(1)	114.1(5)	C(25)–P(2)–Co(1)	118.0(5)

Table 2. The structure can be regarded as derived from that of $Co_2(CO)_8$ [10] by replacing two terminal carbonyl groups on one cobalt by a chelating dppe ligand, and is comparable with that of $Co_2(CO)_6(nbd)$ [12] in which the norbornadiene (nbd) ligand bonded to a cobalt through the two double bonds replaces the dppe chelating ligand. The Co–Co distance (2.541 Å) is only slightly longer than in $Co_2(CO)_8$ (2.524 Å) and in $Co_2(CO)_6(nbd)$ (2.531 Å). Two carbonyls asymmetri-

cally bridge the two metal atoms (Co(1)–C(1) 1.85, Co(2)–C(1) 2.01, Co(1)–C(2) 1.85, Co(2)–C(2) 1.96 Å). This situation is similar to that found in the nbd complex (where the Co–C bond values are 1.867, 1993, 1.875, 1.980 Å), and differs from that found in $Co_2(CO)_8$ in which the two carbonyl bridges are symmetrical (mean value of the Co–C distances 1.92 Å). The asymmetry of these bridges also influences the corresponding Co–C–O angles (mean values Co(1)–C–O 144, Co(2)–C–O 133°, compared with values of 142 and 136° found in the nbd complex). The two Co(1)C(1)O(1)Co(2) and Co(1)C(2)O(2)Co(2) systems are planar, and the angle between the two planes passing through the two Co(1)(μ-CO)Co(2) systems is 141.2°, greater than the corresponding "butterfly angle" in $Co_2(CO)_6$(nbd) (135.0°) and in $Co_2(CO)_8$ (127°).

Each cobalt atom is in a square pyramidal environment: the Co(1) atom is coordinated to the bridged carbon atoms C(1) and C(2) and to the P(1) and P(2) atoms of the dppe ligand in the basal plane, the Co(2) atom is coordinated to the bridged carbon atoms and to two terminal carbonyl carbon atoms in the basal plane; both apices of the pyramids are occupied by terminal carbonyl carbon atoms. Deviations of C(1), C(2), P(1), P(2) atoms from the mean plane passing through them are −0.26, 0.26, 0.02, −0.02 Å, while deviations of the C(1), C(2), C(4), C(5) atoms from the mean plane through them are −0.02, 0.02, −0.03, 0.03 Å, respectively, with both Co atoms deviating by 0.35 Å from the basal plane towards the apical atoms. The greater deformation of the basal plane of the Co(1) atom is probably due to the limited flexibility of the dppe ligand. The angle between the two mean basal planes is 108.2°, while in $Co_2(CO)_6$(nbd) it is 99.8 and in $Co_2(CO)_8$ 100°, respectively. The folding of the two systems C(1), C(2), P(1), P(2) and C(1), C(2), C(4), C(5) is shown in Fig. 3 in which the phenyl rings of the dppe are omitted for clarity.

The results of this structure determination confirm [12] that the replacement of two carbonyl groups on a cobalt atom by a weaker π-acceptor ligand, such as norbornadiene or dppe, has remarkable effects on the $Co(\mu\text{-}CO)_2Co$ system: the bridge becomes asymmetric with the Co–C distances longer with the unsubstituted

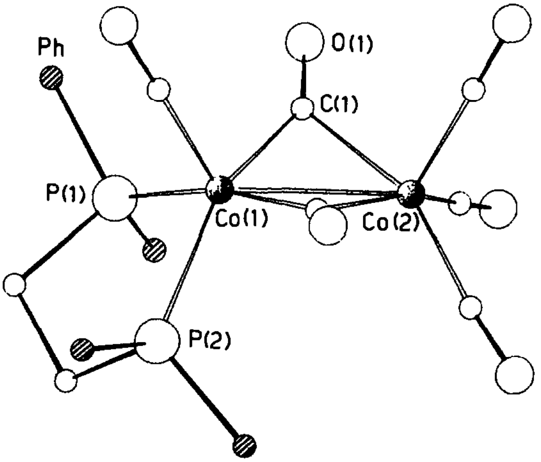

Fig. 3. View of the folding of the two basal planes of the square pyramidal arrangements of the cobalt atoms; the phenyl rings are omitted for clarity.

cobalt and shorter with the substituted Co atom; the angle between the two Co(μ-CO)Co planes increases, tending towards planarity. Since the dppe ligand is a weaker π-acceptor than nbd, this trend (greater difference in the Co–C bridge distances and larger angle between the two Co(μ-CO)Co planes) is confirmed.

Experimental

General

All operations were carried out under dry oxygen-free N_2. All solvents used were distilled under N_2. Silicagel for chromatography (Kieselgel 60, Merck) was dried under vacuum and stored under N_2.

Infrared spectra were recorded on a Perkin–Elmer 398 IR spectrometer.

The elemental analysis was performed by Analytische Laboratorien Malissa-Reuter, D-5250 Engelskirchen.

The following starting complexes were prepared by published methods: Na[Co(CO)$_4$] [14], NiCl$_2$(dppe) [15], and NiBr$_2$(dppe) [15].

Synthesis of di-μ-carbonyl-1,2-bis(diphenylphosphino)ethanetetracarbonyl-dicobalt(0)(Co–Co)

1 g (5.16 mmol) of dried, solid Na[Co(CO)$_4$] was added to 1.4 g (2.6 mmol) of analytically pure NiCl$_2$(dppe) in toluene at −30°C. The reaction was monitored by IR spectroscopy in the ν(CO) region. After 3 h, there was no further increase in the bands due to the products. The mixture was then filtered at low temperature (−78°C) to separate the orange-red solution from the unreacted NiCl$_2$(dppe) (0.6 g, 43%). When a large amount of hexane was added to the filtrate a red-brown precipitate formed. This was purified by column chromatography on silica gel/hexane, to give, after crystallization, white needles of Ni(CO)$_2$(dppe) (0.16 g, 11.5%). The complex was characterized by analysis and comparison of its IR spectrum with that of an authentic sample [16]. The orange-red mother liquor gave red crystals of Co$_2$(CO)$_6$(dppe) (0.35 g, 9%) after standing at −78°C for several days.

M.p. 161°C (sealed tube under N_2). Anal. Found: C, 56.19; H, 3.72; P, 8.86. $C_{32}H_{24}Co_2O_6P_2$ calcd.: C, 56.16; H, 3.53; P, 9.05%. IR ν(CO): see Table 1.

Essentially the same results were obtained when 2.13 g (3.45 mmol) of analytically pure NiBr$_2$(dppe) in THF were treated with two equivalents of freshly reduced Na[Co(CO)$_4$] in THF. At 0°C the reaction took 16 h to reach completion. After filtration to remove NaBr, the solution was taken to dryness. When the residual brown powder was extracted with hexane, the hexane solution yielded 0.28 g (19%) of Ni(CO)$_2$(dppe), whereas extraction with toluene gave the Co$_2$(CO)$_6$(dppe) complex, which was purified by column chromatography on silica gel with toluene and then crystallized from toluene/hexane. As product purity was of greatest importance, no attempt was made to optimize the yields, which ranged from 10 to 20% for Co$_2$(CO)$_6$(dppe) in three experiments.

X-Ray data collection. Solution and refinement of the structure of the complex $Co_2(\mu\text{-}CO)_2(CO)_4(dppe)$

A pink-orange crystal of the complex, having approximate dimensions of 0.10 × 0.23 × 0.30 mm, was used for the data collection. The cell parameters were obtained from a least-squares refinement of the θ values of 29 reflections accurately measured on a Siemens AED single-crystal diffractometer. The crystal data are as follows: $C_{32}H_{24}Co_2O_6P_2$, M = 684.35, monoclinic, a 21.117(13), b 17.012(10), c 8.436(6) Å, β 93.76(5)°; V 3024(3) Å^3, $Z = 4$, D_c 1.503 g cm^{-3}, Mo-K_α radiation (λ 0.71069 Å), μ(Mo-K_α) 12.40 cm^{-1}, space group $P2_1/a$ from systematic absences.

TABLE 3

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR THE NON-HYDROGEN ATOMS WITH E.S.D.'S IN PARENTHESES

Atom	x/a	y/b	z/c
Co(1)	2765(1)	1931(1)	8529(2)
Co(2)	2827(1)	440(1)	8621(3)
P(1)	3406(2)	2675(2)	7201(5)
P(2)	2008(2)	2343(3)	6747(5)
O(1)	3990(5)	1298(7)	9482(13)
O(2)	1682(5)	1154(7)	9709(12)
O(3)	2801(5)	2862(7)	11405(13)
O(4)	1804(7)	−439(8)	6956(14)
O(5)	3818(9)	−339(9)	6914(18)
O(6)	2938(6)	−192(7)	11804(16)
C(1)	3459(8)	1305(9)	9082(17)
C(2)	2186(8)	1208(10)	9193(16)
C(3)	2794(8)	2497(10)	10273(20)
C(4)	2202(10)	−70(11)	7560(22)
C(5)	3428(10)	−1(12)	7574(22)
C(6)	2902(8)	52(9)	10571(21)
C(31)	2922(7)	3419(9)	6163(19)
C(32)	2374(7)	2975(10)	5264(17)
C(7)	3843(7)	2281(10)	5586(17)
C(8)	3719(7)	1523(10)	5093(19)
C(9)	4040(8)	1216(12)	3818(22)
C(10)	4453(10)	1702(12)	3097(23)
C(11)	4574(9)	2447(12)	3591(23)
C(12)	4265(8)	2794(10)	4873(21)
C(13)	3980(7)	3236(9)	8463(17)
C(14)	4586(7)	2962(9)	8668(16)
C(15)	5031(8)	3364(10)	9665(20)
C(16)	4834(8)	4029(10)	10459(21)
C(17)	4209(8)	4299(10)	10242(19)
C(18)	3784(7)	3903(10)	9226(18)
C(19)	1384(7)	2972(10)	7457(18)
C(20)	968(8)	3355(11)	6316(20)
C(21)	518(9)	3881(11)	6871(22)
C(22)	463(9)	3984(11)	8478(23)
C(23)	844(9)	3593(11)	9548(22)
C(24)	1330(7)	3043(10)	9101(18)
C(25)	1561(7)	1602(9)	5578(17)
C(26)	1840(7)	1247(10)	4319(18)
C(27)	1505(9)	660(11)	3492(21)
C(28)	936(8)	398(10)	3951(19)
C(29)	660(8)	765(11)	5210(22)
C(30)	982(8)	1364(10)	6056(19)

A complete set of intensity data was collected, with θ in the range 3–23°, on the same diffractometer using the Nb-filtered Mo-K_α radiation and the $\theta/2\theta$ scan technique. Of a total of 4335 independant reflections, 1549 having $I \geqslant 2\sigma(I)$ were considered observed and used in the analysis. One reflection was remeasured after 20 reflections as a check on crystal and instrument stability; no significant change in the measured intensity of this reflection was observed during data collection.

The structure amplitudes were obtained after the usual Lorentz and polarization reduction and the absolute scale was established by Wilson's method. No correction for absorption effect was applied in view of the low absorbance of the sample.

The structure was solved by Patterson and Fourier methods and the refinement was carried out by least-squares full-matrix cycles using the SHELX system of computer programs [17] with first isotropic and then anisotropic thermal parameters for all non hydrogen atoms except the carbon atoms of the phenyl rings, which were treated as rigid groups of D_{6h} symmetry with C–C distances of 1.395 Å. Even though a ΔF map revealed clearly the positions of almost all the hydrogen atoms, all were placed in the geometrically calculated positions and included in the final structure factor calculations. The final R value was 0.053 (observed reflections only). The function minimized in the least squares calculations was $\Sigma w|\Delta F|^2$; unit weights were used in the first cycles of refinement, the weight calculated as $w = K/[\sigma^2(F_0) + gF_0^{\,2}]$ with $K = 0.2978$ and $g = 0.0163$ in the final cycles. The atomic scattering factors (corrected for anomalous dispersion of Co and P) were taken from ref. [18].

The fractional atomic coordinates for the non-hydrogen atoms are listed in Table 3. Tables of calculated hydrogen atoms coordinates, thermal parameters, observed and calculated structure factors are available from the authors on request.

Calculations were performed on the CYBER 7600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

Conclusion

The chemistry of mononuclear complexes is often characterized by ligand redistributions between the metal centers present in the solution [1]. This is particularly the case when redox processes are involved.

Despite the "chemical labelling" achieved by the different nature of the metal centers involved, the detailed mechanism which leads to formation of $Co_2(\mu\text{-}CO)_2(CO)_4(dppe)$ from $NiX_2(dppe)$ and $[Co(CO)_4]^-$ is not known at present. The very facile dppe migration from Ni to Co observed in our case, even at low temperature, may indicate a radical pathway, involving the labile $Co(CO)_4^{\bullet}$ intermediate [19], its substitution by dppe, and further coupling with another $Co(CO)_4^{\bullet}$ radical. Such radicals could originate from the collapse of an unstable Ni–Co intermediate. Related mechanisms have recently been suggested for the redox reactions between Pd^{II} or Pt^{II} complexes and carbonylmetallate anions [20].

In conclusion, this work (i) provides evidence of facile migration of bidentate ligands between transition metal centers, a process which may be relevant to mechanisms involved in homogeneous catalysis; (ii) clearly establishes the structure of the $Co_2(\mu\text{-}CO)_2(CO)_4(dppe)$ complex, which has been much discussed in the literature.

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