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Communication

Synthesis and Structural Characterization of Cobalt Complexes Ligated by *N*-Methyl(bis(diphenylphosphino)amine)

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Abstract: The reaction of the short-bite bis(diphosphino)amine ligand Ph₂PN(Me)PPh₂ (Medppa) with an equimolar amount of [Co₂(CO)₈] in toluene solution yielded the diphosphane-bridged complex bis(μ₂-carbonyl)(μ-bis(diphenylphosphino)methylamine)-tetracarbonyl-dicobalt(0) (Co—Co) · 0.5 toluene, [Co₂(CO)₆(μ-Medppa)] **1**. Using a 3:1 ratio, the ion-pair complex [Co(CO)(η²-Medppa)₂][Co(CO)₄] **2** was formed. The ionic intermediate [Co(CO)₂(η²-Medppa)(η¹-Medppa)][Co(CO)₄] **3** was spectroscopically observed during the stoichiometric reaction involving [Co₂(CO)₈] and 2 eq. Medppa. Complexes **1** and **2** were characterized using IR and NMR spectroscopy and by single-crystal X-ray analysis performed at 100 K.

Keywords: cobalt; carbonyl; bis(diphenylphosphino)methylamine; crystal structure; chelate complex



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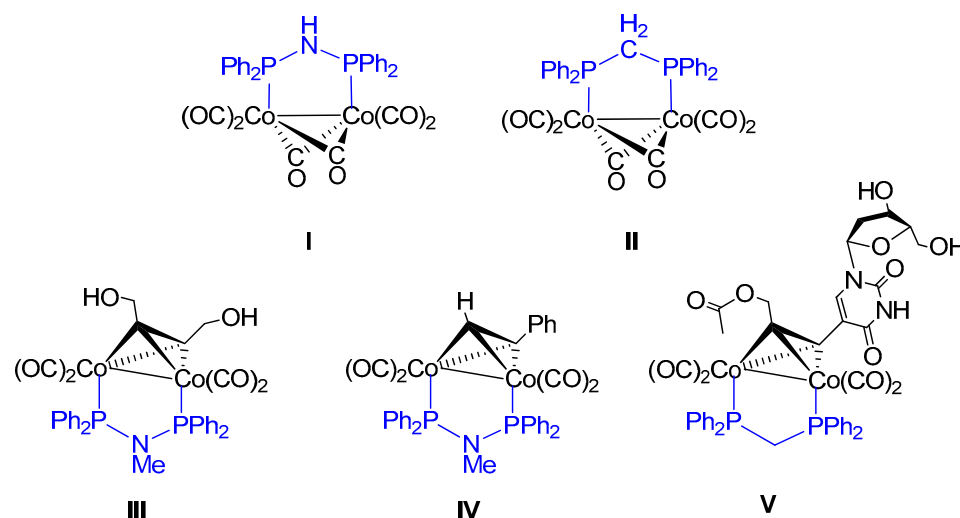
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1. Introduction

One common method to stabilize the highly reactive [Co₂(CO)₈] is the addition of two equiv. of monodentate organophosphorus donors L (L = PR₃, P(OR)₃) leading to phosphane- or phosphite-substituted dinuclear cobalt(0) carbonyl complexes of general formula [Co₂(CO)₆L₂] [1–6]. These organometallic species, often adopting a D_{3d} symmetry bearing solely terminal carbonyl ligands and two *trans*-arranged L donors, have found numerous applications in homogenous catalysis (e.g., hydroformylation, hydroalkoxycarbonylation, hydrogenation, etc.) [3,7–10] or for further transformation with unsaturated organic ligands (e.g., Pauson Khand reaction, Nicholas reaction) [11–14]. Using so-called short-bite diphosphane ligands of the type R₂PXPR₂ (X = N, C) instead, both mononuclear chelate complexes and dinuclear diphosphane-bridged complexes [Co₂(CO)₆L∩L] can be formed [15,16]. In the latter case, the geometry of the dinuclear scaffold is altered with respect to its [Co₂(CO)₆L₂] congeners, since one or two carbonyls are now μ₂-bridging and the two P atoms are *cis*-arranged, forming five-membered Co-P-X-P-Co metallacycles.

Representative examples are [Co₂(CO)₄(μ-CO)₂(μ₂-dppa)] **I** (dppa = bis(diphenylphosphino)amine) [17], [Co₂(CO)₄(μ-CO)₂(μ₂-dppm)] **II** (dppm = bis(diphenylphosphino)methane) [18] (Scheme 1) and [Co₂(CO)₄(μ-CO)₂(μ₂-dmpm)] (dmpm = bis(dimethylphosphino)methane) [19]. These, in turn, have been employed as precursors for further carbonyl substitution reactions with other diphosphanes [20,21] or to construct dicobaltatetrahedrane clusters

$[\text{Co}_2(\text{CO})_4\text{L}\cap\text{L}(\mu\text{-RC}\equiv\text{CR}')]]$ by treatment with internal and terminal alkynes [22–24]. Nowadays, dicobalttetrahedranes $[\text{Co}_2(\text{CO})_6(\mu\text{-RC}\equiv\text{CR}')]]$ constitute an emerging class of organometallic compounds relevant in bio-organometallic chemistry, since they display promising biological activity [25–27]. Surprisingly, the only structurally characterized $\text{Co}_2(\text{CO})_4\text{L}\cap\text{L}(\mu\text{-RC}\equiv\text{CR}')]]$ -type complex featuring biological activity is compound **V** [28], depicted in Scheme 1. We recently screened a series of dicobalttetrahedranes bearing butynediol in silico by molecular docking studies for their potential as anticancer agents [29]. Among them, we synthesized complex **III** by treatment of in situ-prepared $[\text{Co}_2(\text{CO})_6(\mu\text{-Medppa})]]$ with butynediol [29]. Along with **IV** [30], compound **III** constitutes, so far, the only representatives of Co-Co complexes spanned by Medppa.

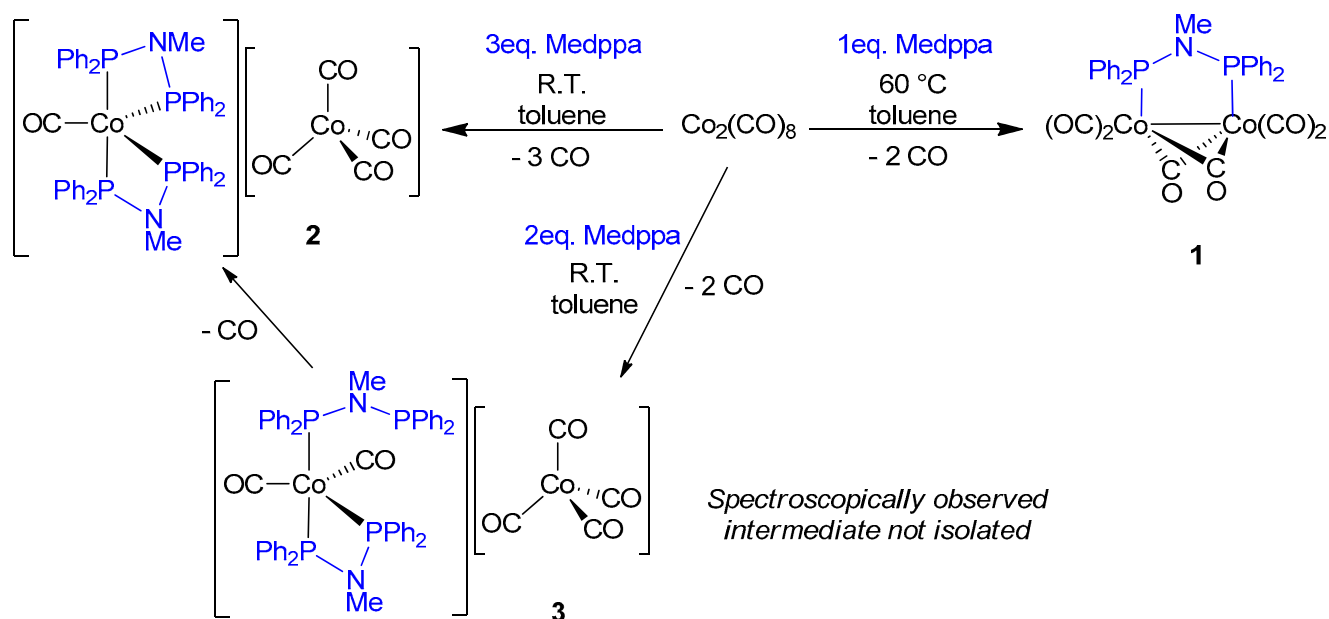


Scheme 1. Examples of diphosphane-spanned dicobalthexacarbonyl and dicobalttetrahedrane complexes [17,18,28–30].

With the idea in mind to prepare further Medppa-spanned $[\text{Co}_2(\text{CO})_4(\mu\text{-Medppa})(\mu\text{-RC}\equiv\text{CR}')]]$ complexes as metallodrugs, in this communication, we describe the synthesis and spectroscopic characterization of $[\text{Co}_2(\text{CO})_4(\mu\text{-CO})_2(\mu_2\text{-Medppa})]]$ **1**, including its crystal structure. This study uses crystallographic characterization of the hitherto unknown ion-pair complex $[\text{Co}(\text{CO})(\eta^2\text{-Medppa})_2][\text{Co}(\text{CO})_4]]$ **2**, obtained by reaction of $[\text{Co}_2(\text{CO})_8]]$ with an excess of Medppa.

2. Results and Discussion

$[\text{Co}_2(\text{CO})_6(\mu\text{-Medppa})]]$ **1** was obtained via treatment of $[\text{Co}_2(\text{CO})_8]]$ with an equimolar amount of bis(diphenylphosphino)methylamine in toluene solution at 60 °C, as shown in Scheme 2. Upon cooling, small red-brown crystals of air-stable **1** were isolated, and elemental analysis confirmed their composition as toluene adduct. A few crystals of a minor product were also collected as yellow plates and identified as ion-pair complex $[\text{Co}(\text{CO})(\eta^2\text{-Medppa})_2][\text{Co}(\text{CO})_4]]$ **2**. Such salt-like species are commonly observed as initial products during the reactions of PR_3 , $\text{P}(\text{OR})_3$, and diphosphanes with dicobalt octacarbonyl, evolving into neutral dinuclear complexes [1,2,21,31–34].



Scheme 2. Synthesis of compounds **1**, **2** and spectroscopic detection of **3**, featuring chelating, dangling and bridging bonding modes of Medppa.

Using a 3:1 ligand-to- $[\text{Co}_2(\text{CO})_8]$ ratio, exclusively, **2** was formed. The disproportionation of $[\text{Co}_2(\text{CO})_8]$ leading to cobalt homonuclear ionic species is well established during reactions with other diphosphane ligands such as dppm, dppa, and *i*Budppa... [21,32–35], and, varying the condition reactions (solvent polarity, temperature, molar ratio), different ionic or neutral compounds have been characterized.

Initially, when employing a stoichiometric Medppa/ $[\text{Co}_2(\text{CO})_8]$ 2:1 ratio, we evidenced, by spectroscopic characterization, formation of the intermediate $[\text{Co}(\text{CO})_2(\eta^1\text{-Medppa})(\eta^2\text{-Medppa})][\text{Co}(\text{CO})_4]$ **3** (Scheme 2). This finding is in line with the observation of Ellermann et al. (i) that during the reaction of dppa with $[\text{Co}_2(\text{CO})_8]$, stoichiometric molar conditions induce only partial conversion and (ii) that for the complete reaction leading to $[\text{Co}(\text{CO})(\eta^2\text{-dppa})_2][\text{Co}(\text{CO})_4]$, an excess of diphosphane is needed [21]. Therefore, for a straightforward preparation of the ion-pair complex **2**, a 3:1 ratio of Medppa/ $[\text{Co}_2(\text{CO})_8]$ was required.

The IR spectra of the isolated products recorded in CH_2Cl_2 , shown in Figure 1, are very distinctive in the carbonyl region. The infrared spectrum of **1** reveals three intense terminal carbonyl vibrations at 2043, 2010 and 1984 cm^{-1} , along with two characteristic $\nu(\text{CO})$ bands at 1817 and 1785 cm^{-1} , attributed to bridging COs. A simpler spectrum is obtained for **2** displaying a $\nu(\text{CO})$ absorption at 1942 cm^{-1} ascribed to the cationic $[\text{Co}(\text{CO})(\eta^2\text{-Medppa})_2]^+$ part and an intense band at 1884 cm^{-1} for the tetracarbonylcobaltate anion, coordinated by four tetrahedrally arranged carbonyls. These patterns are reminiscent of those reported for $[\text{Co}_2(\text{CO})_6(\mu\text{-dppa})]$ (**I**) in CH_2Cl_2 (2048, 2014, 1989, 1817 and 1796 cm^{-1}) and $[\text{Co}(\text{CO})_2(\eta^2\text{-dppa})_2][\text{Co}(\text{CO})_4]$ recorded in THF (1944 and 1882 cm^{-1}) [35]. Compared to **I**, a slight shift to lower wavenumbers is observed for carbonyl stretching frequencies in **1**, reflecting the stronger electron-donating propensity of Medppa vs. dppa.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra recorded in CDCl_3 consist of singlets for **1** and **2** at δ 119.7 and 80.2 ppm, respectively. These values are in concordance with the ones reported for the Medppa-bridged dicobaltatetrahedrane $[\text{Co}_2(\text{CO})_4(\mu\text{-Medppa})(\mu\text{-PhC}\equiv\text{CH})]$ **IV** (δ 114.9 ppm) [30] and in the Medppa-chelate complex $[(\eta^2\text{-Medppa})\text{CpCo}(\text{MeCN})][\text{PF}_6]_2$ (δ 77.9 ppm) [36]. During the disproportion reaction using a 2:1 ligand-to- $[\text{Co}_2(\text{CO})_8]$ ratio, a sample solution was analyzed using $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The more complex

spectrum (Figure S1) shows the coexistence of $[\text{Co}(\text{CO})(\eta^2\text{-Medppa})_2]^+$ at δ 80.2 ppm and a set of multiplets attributed to the intermediate **3**. Three signals are observed at δ 120.6 ppm (doublet of triplet, $J_{\text{PP}} = 143$ Hz, 32 Hz), 75.3 ppm as a broad singlet (including free Medppa) and 61.7 ppm (d, $J_{\text{PP}} = 143$ Hz). This A_2MX fluxional system is consistent with the formation of a cationic trigonal bipyramidal $[\text{Co}(\text{CO})(\eta^1\text{-Medppa})(\eta^2\text{-Medppa})]^+$ species, giving rise to a doublet of triplets and a doublet due to the dangling monocoordinated Medppa and a broad signal to the chelating ligand [35,37].

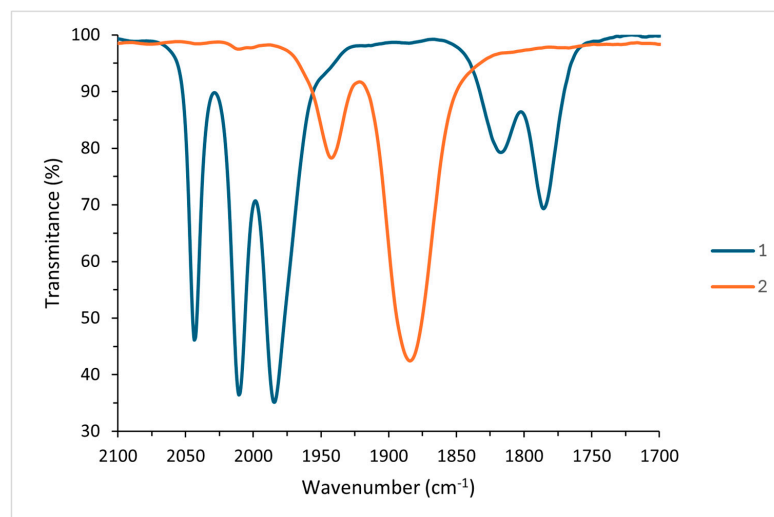


Figure 1. Comparison of the IR spectra of $[\text{Co}_2(\text{CO})_6(\mu\text{-Medppa})]$ **1** (blue) and $[\text{Co}(\text{CO})(\eta^2\text{-Medppa})_2][\text{Co}(\text{CO})_4]$ **2** (red) in the carbonyl region (recorded in CH_2Cl_2).

In addition to the spectroscopic characterization of **1** in solution, the dinuclear complex was also unambiguously analyzed using X-ray diffraction performed at 100 K. Complex **1** crystallizes in the triclinic space group $P\bar{1}$, containing a half molecule of disordered toluene (Table S1). As shown in Figure 2, in this organometallic species, the two crystallographically non-equivalent Co1 and Co2 centers are linked through a metal–metal bond and spanned by the Medppa ligand forming a five-membered cycle. The Co–Co bond is further spanned by two μ_2 -carbonyls, and the coordination sphere around each Co atom is completed by two terminal carbonyls, which are *cis*-arranged with respect to the Co–P bonds. Therefore, the overall structure is quite reminiscent of those of $[\text{Co}_2(\text{CO})_4(\mu\text{-CO})_2(\mu_2\text{-dppa})] \cdot 0.5$ benzene (CSD refcode JAZFUM), $[\text{Co}_2(\text{CO})_4(\mu\text{-CO})_2(\mu_2\text{-dppm})]$ (CSD refcode PPACCP) and $[\text{Co}_2(\text{CO})_4(\mu\text{-CO})_2(\mu_2\text{-dcpm})]$ (dcpm = bis(dicyclohexylphosphino)methane; CSD refcode PAJRUP) [17,18,38]. The Co–Co bond length of 2.4595(5) Å is similar to that of its dppa-, dppm- and dcpm-analogues (2.457(3), 2.4568(5)) and 2.4618(7) Å. Other relevant averaged bond lengths of **1** are listed in Table 1 and compared with those of analogous diphosphane-spanned compounds. The observation that the P–X–P angles of the P–C–P-spanned derivatives are considerably more acute than those of the P–N–P-spanned complexes is noteworthy. This difference between the P–C–P and P–N–P angles is already present in the free diphosphine ligands. The P–C–P bond angle in dppm is 106.2(3)° [39] and the P–N–P angles are 118.9(2)° and 114.86(4)° in the nitrogen-bridged diphosphines dppa and Medppa, respectively [30,40,41]. Based on the structural data, the authors of [30] discuss a partial double bond character of the P–N bond and a trigonal planar arrangement around the N atom of the diphosphinoamines, while the sp^3 -hybridized C center in dppm has a tetrahedral geometry of 106.3°.

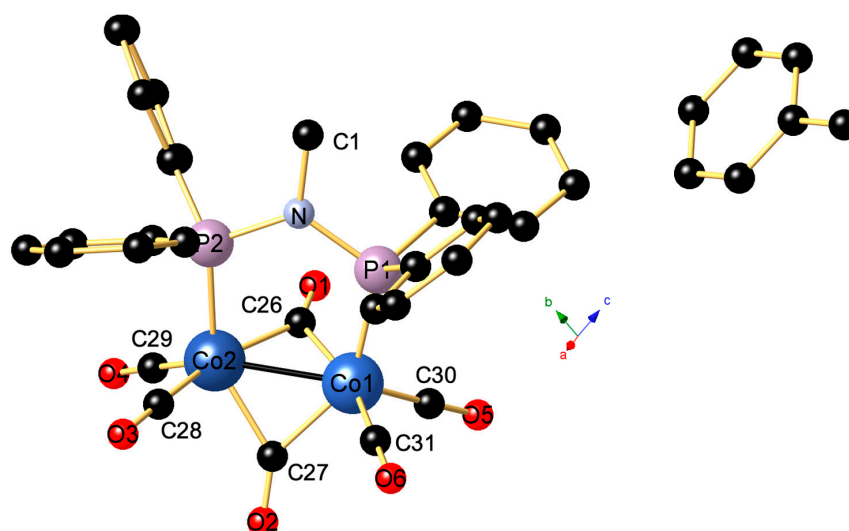


Figure 2. Molecular structure of **1**. All H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Co1–Co2 2.4595(5), Co1–P1 2.2273(5), Co1–C26 1.9493(16), Co1–C27 1.9514(18), Co1–C30 1.7843(18), Co1–C31 1.8096(17), Co2–P2 2.2456(5), Co2–C26 1.9206(16), Co2–C27 1.9514(19), Co2–C28 1.8174(19), Co2–C29 1.7846(17), P1–N 1.7047(14), P2–N 1.7031(16), P1–Co1–Co2 96.439(18), C26–Co1–P1 84.86(5), C27–Co1–P1 144.93(6), C27–Co1–C26 82.24(7), C30–Co1–P1 107.14(6), C30–Co1–C26 90.72(7), C30–Co1–C27 105.50(8), C30–Co1–C31 104.01(8), C31–Co1–P1 95.89(5), C31–Co1–C26 164.24(7), C31–Co1–C27 88.35(7), P2–Co2–Co1 97.338(19), C26–Co2–P2 86.95(5), C26–Co2–C27 82.51(7), C27–Co2–P2 144.36(5), C28–Co2–P2 92.87(7), C28–Co2–C26 161.74(8), C28–Co2–C27 87.13(9), C29–Co2–P2 112.46(6), C29–Co2–C26 93.91(7), C29–Co2–C27 102.98(8), C29–Co2–C28 103.98(8).

Table 1. Comparison of relevant bond lengths (Å) and angles (°) in **1** with those of other crystallographically characterized $[\text{Co}_2(\text{CO})_6(\mu\text{-dppx})]$ complexes.

	1	dppa	dppm	dcpm
Co–Co	2.4595(5)	2.4569	2.4569(4)	2.4618(7)
Co–P	2.234	2.229	2.252	2.262
Co– μC	1.939	1.914	1.938	1.927
Co–C	1.799	1.765	1.793	1.805
P–X	1.704	1.689	1.850	1.843
PXP	123.19(9)	126.22	115.9(1)	117.73(17)
CSD reference	This work	PPACCP [17]	JAZFUM [18]	PAJRUP [38]

There are no particular supramolecular features; the disordered toluene molecule is intercalated between two neighbored dicobalt species through weak C–H \cdots O and aromatic contacts ($d(\text{O6}\cdots\text{H33}) = 2.600$, $d(\text{O6}\cdots\text{H37}) = 2.640$, $d(\text{O2}\cdots\text{H34}) = 2.670$, $d(\text{H21}\cdots\text{C38}) = 2.779$ Å). Further weak intermolecular interactions occur in the crystal between the dinuclear moieties ($d(\text{H10}\cdots\text{C17}) = 2.774$, $d(\text{H11}\cdots\text{C27}) = 2.791$, $d(\text{H1C}\cdots\text{C5}) = 2.670$ Å).

An X-ray diffraction investigation was performed at 100 K on crystals of compound **2** crystallizing in the monoclinic space group $P2_1/n$ (Table S1). The asymmetric unit contains one $[\text{Co}(\text{CO})(\eta^2\text{-Medppa})_2]^+$ cation and one anion $[\text{Co}(\text{CO})_4]^-$ (Figure 3). The tetracarbonylcobaltate anion adopts a tetrahedral geometry with C–Co–C angles ranging from 107.01(10) to 111.52(10) $^\circ$ (average angle of 109.45 $^\circ$). These values and other geometrical parameters fit well with those reported for complexes including the $[\text{Co}(\text{CO})_4]^-$ anion [9,33,37]. Selected bond lengths and angles of the cationic moiety $[\text{Co}(\text{CO})(\eta^2\text{-Medppa})_2]^+$ are listed in Table 2 and compared with those reported for other $[\text{Co}(\text{CO})(\eta^2\text{-dppx})_2][\text{Co}(\text{CO})_4]$ complexes. The cationic cobalt center in **2** is five-coordinated by one equatorially arranged CO and by two chelating Medppa ligands, with P2 and P3 occupying the axial site and P1 and P4 occupying the equatorial sites of the polyhedron. The Co–P distances vary from 2.1870(5) Å

to 2.2224(5) Å and the P–Co–P angles span the range 72.10(10)–171.00(2)°. This Co cation adopts a distorted trigonal bipyramidal geometry with a τ_5 value of 0.72. The τ_5 geometry index was calculated according to $\tau_5 = (\beta - \alpha)/60$, where α and β are the largest angles around the metal center with $\beta > \alpha$ [42]. The same geometry is reported for the cation in [Co(CO)(η^2 -dppm)₂][Co(CO)₄] (CSD refcode KOKTEJ, $\tau_5 = 0.64$), [Co(CO)(η^2 -*t*Budppa)₂][Co(CO)₄] (CSD refcode SAKFUJ, $\tau_5 = 0.85$) and [Co(CO)(η^2 -dppa)₂][BPh₄] · THF (CSD refcode LIQSUZ, $\tau_5 = 0.74$), while a distorted square pyramidal arrangement is observed for [Co(CO)(η^2 -dppm)₂][Co(CO)₄] · 2THF (CSD refcode LIQTAG, $\tau_5 = 0.25$) and [Co(CO)(η^2 -*i*Budppa)₂][Co(CO)₄] (CSD refcode WEYJAL, $\tau_5 = 0.16$) [9,33,35,37]. As expected, the P–N–P angles of 100.42(9) and 99.88(8)° measured for the chelating ligands are significantly smaller than those in **1**, where Medppa acts as a μ_2 -bridging ligand (P–N–P angle = 123.19(9)°).

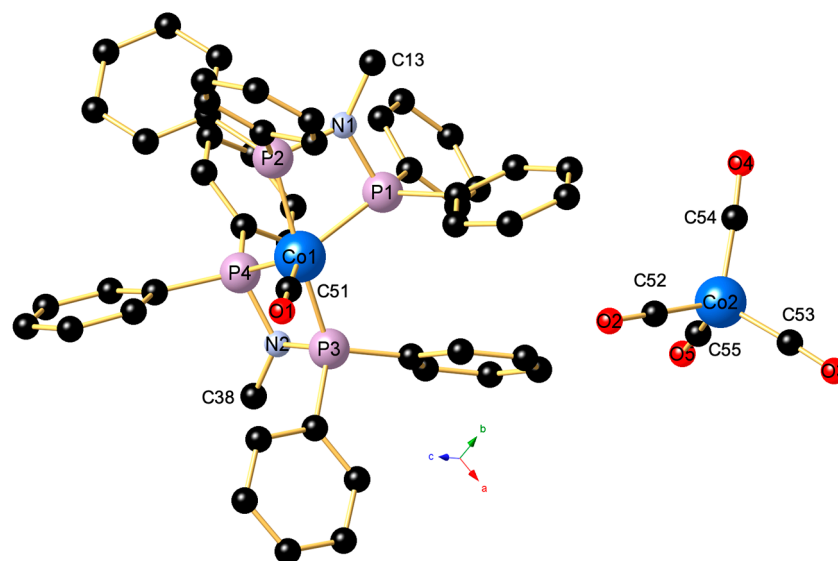


Figure 3. Molecular structure of **2**. All H atoms are omitted for clarity.

Table 2. Comparison of relevant bond lengths (Å) and angles (°) for the cationic moiety in **2** and related crystallographically characterized [Co^I(dppx)₂(CO)][Co^I(CO)₄] salts.

	2	<i>i</i> Budppa	dppm	dppm·2THF
Co–C	1.7441(19)	1.796(9)	1.735(12)	1.786(7)
Co–P	2.2224(5)	2.179(2)	2.217(3)	2.195(2)
	2.2194(5)	2.174(2)	2.208(3)	2.204(2)
	2.1870(5)	2.180(2)	2.207(3)	2.210(2)
	2.1931(5)	2.173(2)	2.227(3)	2.203(2)
	2.1870(5)	2.180(2)	2.207(3)	2.210(2)
P–Co–C	94.21(6)	100.0(2)	93.1(3)	97.7(2)
	94.79(6)	100.3(2)	94.9(3)	98.0(2)
	122.31(7)	103.8(2)	113.8(4)	104.9(2)
	127.81(7)	105.9(2)	112.5(4)	107.8(2)
	127.81(7)	105.9(2)	112.5(4)	107.8(2)
P–Co–P	171.00(2)	159.74(7)	172.05(11)	164.23(8)
	109.87(2)	150.29(7)	133.73(12)	147.26(8)
	102.36(2)	102.24(6)	102.53(11)	99.84(8)
	102.62(2)	103.17(6)	103.37(11)	103.43(8)
	72.10(2)	71.94(6)	73.73(11)	73.83(8)
P–X–P	72.215(19)	71.94(6)	73.93(11)	73.84(7)
	100.42(9)	97.3(2)	92.6(5)	93.0(3)
	99.88(8)	96.8(2)	92.4(4)	92.9(3)
CSD reference	This work	WEYJAL [33]	KOKTEJ [37]	LIQTAG [35]

Weak intramolecular interactions occur between the tetracarbonylcobaltate and the phenyl groups of the cationic species ($d(\text{H}36\cdots\text{O}5) = 2.562 \text{ \AA}$, $d(\text{H}4\cdots\text{C}52) = 2.751 \text{ \AA}$), and intermolecular contacts involving the oxygen atoms of $[\text{Co}(\text{CO})_4]^-$ are observed with the PPh_2 and the NMe groups of Medppa ($d(\text{H}43\cdots\text{O}2) = 2.424 \text{ \AA}$, $d(\text{H}38\text{C}\cdots\text{O}3) = 2.524 \text{ \AA}$).

3. Materials and Methods

Dicobalt octacarbonyl was commercially purchased from Thermo Scientific. Medppa was synthesized as previously reported [43]. The reactions were performed under an argon atmosphere. The ^1H -, ^{31}P - and ^{13}C -NMR spectra were recorded on a Bruker AC 400 (Bruker, Wissembourg, France) at 400, 121.50 and 100.62 MHz, respectively, using CDCl_3 as solvent. Infrared spectra were recorded on a Vertex 70 spectrometer (Bruker, Wissembourg, France) using a Platinum ATR accessory equipped with a diamond crystal or on a Bruker Alpha II IRTF spectrometer in solution.

Bis(μ_2 -carbonyl)(μ_2 -bis(diphenylphosphino)methylamine)-tetracarbonyl-dicobalt(0)-toluene, $[\text{Co}_2(\text{CO})_6(\mu\text{-Medppa})]$ **1**: Medppa (225 mg, 0.562 mmol) was added to a stirred solution of $\text{Co}_2(\text{CO})_8$ (175.0 mg, 0.511 mmol) in toluene (10 mL). An immediate gas evolution was observed. The reaction mixture was then heated to $60 \text{ }^\circ\text{C}$ for 5 h. The solution was cooled to room temperature prior to lowering its temperature to $4 \text{ }^\circ\text{C}$. Product **1** crystallized as red-brown crystals which were collected via filtration. Yield: 69%. Anal. Calc. for $\text{C}_{31}\text{H}_{23}\text{Co}_2\text{NO}_6\text{P}_2 \cdot 0.5\text{C}_7\text{H}_8$ (M.W = $731.37 \text{ g}\cdot\text{mol}^{-1}$): C, 56.66; H, 3.72; N, 1.92%. Detected: C, 56.58; H, 3.68; N, 1.95%. ^1H -NMR (CDCl_3) at 298 K: δ 2.57 (s, 3H, CH_3), 7.05 (m, 8H, CH Ar), 7.13 (m, CH Ar), 7.60 (m, CH Ar) ppm. $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3) at 298 K: δ 32.9 (CH_3), 125.1–132.4 (Ph, Medppa and toluene), 214.7 (CO) ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3) at 298 K: δ 119.7 ppm.

Carbonylbis η^2 -bis(diphenylphosphino)methylamine)cobalt(I)-tetracarbonylcobaltate(-I) $[\text{Co}(\text{CO})(\eta^2\text{-Medppa})_2][\text{Co}(\text{CO})_4]$ **2**: Medppa (441 mg, 3 mmol) was added to a stirred solution of $\text{Co}_2(\text{CO})_8$ (342.0 mg, 1 mmol) in toluene (5 mL). An immediate gas evolution was observed. The reaction mixture was stirred at room temperature for 4 h. The solution was then cooled to $4 \text{ }^\circ\text{C}$. Product **2** crystallized as yellow plates which were collected via filtration. Yield: 58%. Anal. Calc. for $\text{C}_{55}\text{H}_{46}\text{Co}_2\text{N}_2\text{O}_5\text{P}_4$ (M.W = $1056.74 \text{ g}\cdot\text{mol}^{-1}$): C, 62.51; H, 4.38; N, 2.65%. Detected: C, 62.83; H, 4.45; N, 2.78%. ^1H -NMR (CDCl_3) at 298 K: δ 2.14 (br s, 6H, CH_3), 6.72–7.63 (m, 40H, CH Ar) ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3) at 298 K: δ 80.2 ppm.

The crystallographic data collection was performed on a Bruker D8 Venture four-circle diffractometer from Bruker AXS GmbH (Karlsruhe, Germany). Photon II from Bruker AXS GmbH was used as a CPAD detector, and the X-ray sources were a Microfocus source $\text{I}\mu\text{S}$ Mo from Incoatec GmbH with HELIOS mirror optics and a single-hole collimator from Bruker AXS GmbH. Programs used for data collection were APEX4 Suite [44] (v2021.10-0) and integrated programs SAINT (V8.40A; integration as well as SADABS (2018/7; absorption correction) from Bruker AXS GmbH [44]. The SHELX programs were used for further processing [45]. The solution of the crystal structures was analyzed with the help of the program SHELXT [46] and structure refinement was performed with SHELXL [47]. The processing and finalization of the crystal structure data were carried out with OLEX2 v1.5 [48]. All non-hydrogen atoms were refined anisotropically. All H atoms were refined freely using independent values for each $\text{Uiso}(\text{H})$.

Crystal data for $\text{C}_{34.5}\text{H}_{27}\text{Co}_2\text{NO}_6\text{P}_2$ were as follows: $M = 731.37 \text{ g}\cdot\text{mol}^{-1}$, red crystals, crystal size $0.394 \times 0.244 \times 0.211 \text{ mm}^3$, triclinic, space group $P\bar{1}$: $a = 10.4585(13) \text{ \AA}$, $b = 12.368(2) \text{ \AA}$, $c = 15.062(3) \text{ \AA}$, $\alpha = 67.600(6)^\circ$, $\beta = 87.814(7)^\circ$, $\gamma = 66.131(7)^\circ$, $V = 1631.6(5) \text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 1.489 \text{ g/cm}^3$, $T = 100 \text{ K}$, $h = -14 \leq h \leq 14$, $k = -17 \leq k \leq 17$, $l = -21 \leq l \leq 20$, $\text{GOF} = 1.014$, $R_1 = 0.0334$, $wR_2 = 0.0743$ for 9926 reflections with $I > 2\sigma(I)$ and 9926 inde-

pendent reflections. The largest diff. peak/hole was $e \text{ \AA}^{-3}$ 0.56/−0.41. The structure was solved using direct methods and refined using full-matrix least-squares against F^2 .

Crystal data for $\text{C}_{55}\text{H}_{46}\text{Co}_2\text{N}_2\text{O}_5\text{P}_4$ were as follows: $M = 1056.68 \text{ g.mol}^{-1}$, yellow plates, crystal size $0.204 \times 0.187 \times 0.164 \text{ mm}^3$, monoclinic, space group $P2_1/n$: $a = 11.7166(10) \text{ \AA}$, $b = 11.3888(7) \text{ \AA}$, $c = 37.707(3) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 98.863(3)^\circ$, $\gamma = 90^\circ$, $V = 4971.4(6) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.412 \text{ g/cm}^3$, $T = 100 \text{ K}$, $h = -16 \leq h \leq 15$, $k = -14 \leq k \leq 14$, $l = -47 \leq l \leq 53$, $\text{GOF} = 1.060$, $R_1 = 0.0402$, $wR_2 = 0.0732$ for 13,797 reflections with $I > 2\sigma(I)$ and 13,797 independent reflections. The largest diff. peak/hole was $e \text{ \AA}^{-3}$ 0.46/−0.44. The structure was solved using direct methods and refined using full-matrix least-squares against F^2 .

Data were collected using graphite-monochromated $\text{MoK}\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$ and were deposited in the Cambridge Crystallographic Data Centre as 2416934 (1) and 2416981 (2). (Supplementary Materials). The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/getstructures> (accessed on 11 February 2025).

4. Conclusions

We have demonstrated that the result of the addition of Medppa to $[\text{Co}_2(\text{CO})_8]$ depends on the metal-to-ligand ratio. Using a 1:1 ratio yields the diphosphane-bridged complex $[\text{Co}_2(\text{CO})_6(\mu\text{-Medppa})]$ **1**, whereas employing a 3:1 ratio provides the ion-pair complex $[\text{Co}(\text{CO})(\eta^2\text{-Medppa})_2][\text{Co}(\text{CO})_4]$ **2**. Using solely a 2:1 ratio also allows for the spectroscopic observation of salt $[\text{Co}(\text{CO})_2(\eta^2\text{-Medppa})(\eta^1\text{-Medppa})][\text{Co}(\text{CO})_4]$ **3** as an intermediate, in which the cation is coordinated by both a chelating and dangling Medppa ligand. The coordination of alkynes and the investigation of the biological activity of the resulting dicobalttetrahedrane clusters $[\text{Co}_2(\text{CO})_4(\mu_2\text{-Medppa})(\mu\text{-RC}\equiv\text{CR}')]]$ will be the topic of a forthcoming study.

Supplementary Materials: CIF file, Check-CIF report, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.

Author Contributions: I.J. and M.W. prepared the compound; C.S. and A.S. collected the X-ray data and solved the structure; I.J. and M.K. designed the study, analyzed the data and wrote the paper. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The X-ray data are in the CCDC as stated in the paper.

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