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# Bridged Derivatives of the Heteronuclear Carbonyl Complexes $[CoM(CO)_9]$ (M = Mn, Re)

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The new heterobinuclear complexes $[CoM(CO)_5(\mu\text{-dppm})_2]$, **1**, and $[CoM(CO)_6(\mu\text{-dppm})(\eta^1\text{-dppm})]$, **2**, where M = Mn or Re and dppm = $Ph_2PCH_2PPh_2$, have been prepared by reaction of $[CoX(CO)_2(\eta^1\text{-dppm})_2]$, X = halogen, with $Na[M(CO)_5]$. Complexes **1** and **2** have been characterized by spectroscopic methods and, for **1a** (M = Mn), by an X-ray structure determination. The nature of the fluxionality of the carbonyl ligands in **1a** has also been studied; at room temperature, a merry-go-round mechanism leads to equivalence of all carbonyl ligands.

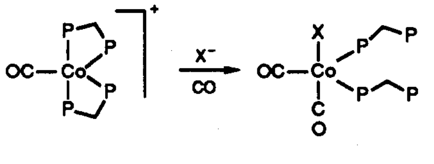
## Introduction

There is continuing interest in the synthesis and properties of organometallic complexes containing heteronuclear metal–metal bonds.[2-12] Many such compounds contain bridging phosphine ligands such as $Ph_2PCH_2PPh_2$, dppm, since the synthesis of complexes containing MM′ ($\mu$-dppm) groups is facilitated by use of precursor mononuclear complexes containing M($\eta^1$-dppm) or strained M($\eta^2$-dppm) groups. An important aspect of such complexes is that the presence of bridging dppm ligands discourages fragmentation of the binuclear unit by cleavage of the metal–metal bond, which is a common problem in the chemistry of unbridged metal–metal bonded compounds.[3] This added stability of bridged binuclear complexes allows their organometallic chemistry to be developed in a systematic way. In recent years, numerous complexes containing MM′ ($\mu$-dppm) groups, in which both M and M′ are group VIII metals, have been synthesized and there is also current interest in derivatives in which either M or M′ is an earlier transition element. Examples of known complexes include $[RhM(CO)_4(\mu\text{-dppm})_2]$ (M = Mn,Re),[5] $[(CO)_3M'(\mu\text{-dppm})_2M(CO)X]$ (M′ = Cr,Mo,W; M = Rh,Ir)[6] and $[Cl(CO)_2Mn(\mu\text{-dppm})_2M(CO)_2]PF_6$ (M = Rh,Ir)[7]. However, there appears to be no precedent for a complex containing the MnCo($\mu$-dppm) unit. Known complexes containing both a cobalt atom and a group VIIb element include the binary carbonyls $[CoM(CO)_9]$ (M = Mn,[8,9] Re,[9] or Tc[10]) and the derivatives $[MCo(CO)_5(\mu\text{-CO})(DAB)]$ (M = Mn, Re; DAB = PrN=CHCH=NPr),[11] which are prepared by displacement of halide from $[MX(CO)_5]$ or $[MBr(CO)_3(DAB)]$, respectively, by the $[Co(CO)_4]^-$ anion. The complex $[CpCo(\mu\text{-NO})_2MnCpPMe_3]$ is prepared similarly by reaction of Na[CpCoNO] with $[CpMn(CO)(NO)PMe_3]BF_4$.[12] This paper reports the synthesis and characterization of new binuclear complexes $[CoM(CO)_5(\mu\text{-dppm})_2]$ (**1a**, M = Mn; **1b**, M = Re) and derivatives of 1 containing $\eta^1$-dppm ligands.

## Synthesis of the Complex $[CoMn(CO)_5(\mu\text{-dppm})_2]$, 1a

It has previously been shown that the ionic complexes $[Co(CO)(\eta^2\text{-dppm})_2][Co(CO)_4]$ and $[Rh(CO)(\eta^2\text{-dppm})_2][Co(CO)_4]$ are easily converted, by loss of CO, to the metal–metal bonded complexes $[Co_2(CO)_4(\mu\text{-dppm})_2]$ and $[CoRh(CO)_3(\mu\text{-dppm})_2]$ respectively.[4,5] By analogy with these and other precedents, it was reasoned that reaction of $[Co(CO)(\eta^2\text{-dppm})_2]^+$ with $[Mn(CO)_5]^-$ should provide a route to dppm-substituted derivatives of the mixed metal binary carbonyl $[CoMn(CO)_9]$.[8-10] However, this reaction was unsuccessful and the reagent $[Co(CO)\ (\eta^2\text{-dppm})_2]BPh_4$ was recovered along with a low yield of an unidentified complex (see Experimental Section). The $\eta^2$-dppm to $\mu$-dppm transformation, which is a key step in the formation of binuclear complexes, evidently occurs much less easily in the precursor $[Co(CO)\ (\eta^2\text{-dppm})_2]^+$ than in the analogous rhodium and iridium cations used previously in the synthesis of dppm-bridged heterobimetallic complexes.[5]

It is known that ring opening of the chelating dppm ligands of the $[Co(CO)(dppm)_2]^+$ cation can be achieved by reaction with halide, $X^-$, and CO according to eq 1.[4]



(1)

Furthermore, $[CoX(CO)_2(\eta^1\text{-dppm})_2]$ should be a more reactive precursor than $[Co(CO)(\eta^2\text{-dppm})_2]^+$ for the

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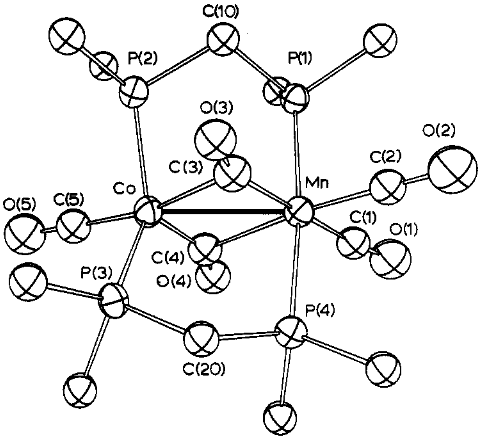
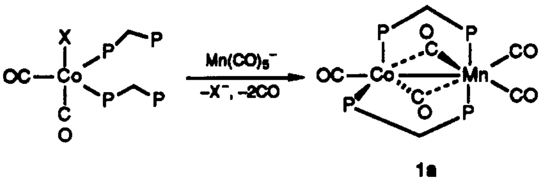


**Figure 1.** ORTEP view of complex **1a** showing 50% probability thermal ellipsoids. Only the α-carbon atoms of the phenyl rings are shown for clarity.

synthesis of binuclear complexes, since the $\eta^1$-dppm to $\mu$-dppm transformation should occur more easily than would $\eta^2$-dppm to $\mu$-dppm. Thus, halide and CO addition to form $[CoX(CO)_2(\eta^1\text{-dppm})_2]$ was carried out (eq 1) and this complex was then reacted in situ with $Na[Mn(CO)_5]$ to give a successful synthesis of the complex $[CoMn(CO)_5(\mu\text{-dppm})_2]$, **1a**, as outlined in eq 2. Complex **1a** is a red-brown solid, which is decomposed rapidly in solution and more slowly in the solid state by air. It is soluble in common organic solvents, but reacts with chloroform or carbon tetrachloride to give a product which is identified as $[(CO)Co(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2Mn(CO)_2]^+Cl^-$ and with iodine to give $[(CO)Co(\mu\text{-I})(\mu\text{-CO})(\mu\text{-dppm})_2Mn(CO)_2]^+I^-$.



(2)

## Structural Characterization of $[CoMn(CO)_5(\mu\text{-dppm})_2]$, 1a

Complex **1a** can be recrystallized from $CH_2Cl_2$/EtOH to give dark red, air-sensitive crystals suitable for an X-ray structure determination. The structure is shown in Figure 1 and selected bond distances and angles are listed in Table I. The geometry about each metal, ignoring the metal-metal interaction, is best described as distorted octahedral and distorted trigonal bipyramidal for the manganese and cobalt atoms respectively. Similar geometries for cobalt and manganese are found in the homodinuclear complexes $[Co_2(CO)_4(\mu\text{-dppm})_2]$ and $[Mn_2(CO)_6(\mu\text{-dppm})_2]$ respectively.[13] At the manganese centre, the two phosphines occupy trans positions with the angle P(4)–Mn–P(1) of 172.08(7)°. A similar geometry at manganese is present in the complex $[RhMn(CO)_4(\mu\text{-dppm})_2]$.[5] The angles associated with the *trans*-$Mn(CO)_2$ units are C(4)–Mn–C(2) = 171.9(3)° and C(3)–Mn–C(1) = 177.9(3)°. At the trigonal bipyramidal cobalt center, the phosphorus atoms and C(4) are equatorial and C(5) and C(3) are axial but the distortions are severe. For example, the angle C(5)–Co–C(3) of 162.2(3)° deviates significantly from linearity.

**Table I. Bond Distances (Å) and Angles (deg) in 1a**

| | | | |
|---|---|---|---|
| Mn–Co | 2.726(1) | P(2)–Co | 2.216(2) |
| P(3)–Co | 2.214(2) | C(3)–Co | 2.277(6) |
| C(4)–Co | 1.766(6) | C(5)–Co | 1.732(7) |
| P(1)–Mn | 2.300(2) | P(4)–Mn | 2.319(2) |
| C(1)–Mn | 1.786(6) | C(2)–Mn | 1.757(6) |
| C(3)–Mn | 1.879(6) | C(4)–Mn | 2.400(6) |
| C(10)–P(1) | 1.829(5) | C(111)–P(1) | 1.842(5) |
| C(121)–P(1) | 1.852(4) | C(10)–P(2) | 1.854(6) |
| C(211)–P(2) | 1.851(4) | C(221)–P(2) | 1.844(4) |
| C(20)–P(3) | 1.833(5) | C(311)–P(3) | 1.839(4) |
| C(321)–P(3) | 1.834(4) | C(20)–P(4) | 1.838(5) |
| C(411)–P(4) | 1.848(4) | C(421)–P(4) | 1.851(4) |
| O(1)–C(1) | 1.183(7) | O(2)–C(2) | 1.169(7) |
| O(3)–C(3) | 1.186(6) | O(4)–C(4) | 1.184(7) |
| O(5)–C(5) | 1.171(7) | | |
| P(2)–Co–Mn | 97.06(5) | P(3)–Co–Mn | 97.87(5) |
| C(3)–Co–Mn | 43.0(2) | C(4)–Co–Mn | 60.2(2) |
| C(5)–Co–Mn | 154.8(2) | P(3)–Co–P(2) | 130.68(7) |
| C(3)–Co–P(2) | 78.5(2) | C(3)–Co–P(3) | 81.3(2) |
| C(4)–Co–P(2) | 118.9(2) | C(4)–Co–P(3) | 109.3(2) |
| C(4)–Co–C(3) | 103.1(3) | C(5)–Co–P(2) | 92.9(2) |
| C(5)–Co–P(3) | 93.0(2) | C(5)–Co–C(3) | 162.2(3) |
| C(5)–Co–C(4) | 94.8(3) | P(1)–Mn–Co | 86.72(5) |
| P(4)–Mn–Co | 87.65(5) | C(1)–Mn–Co | 122.6(2) |
| C(2)–Mn–Co | 148.4(2) | C(3)–Mn–Co | 55.7(2) |
| C(4)–Mn–Co | 39.7(2) | P(4)–Mn–P(1) | 172.08(7) |
| C(1)–Mn–P(1) | 92.0(2) | C(1)–Mn–P(4) | 95.8(2) |
| C(2)–Mn–P(1) | 90.7(2) | C(2)–Mn–P(4) | 91.2(2) |
| C(2)–Mn–C(1) | 89.0(3) | C(3)–Mn–P(1) | 86.8(2) |
| C(3)–Mn–P(4) | 85.4(2) | C(3)–Mn–C(1) | 177.9(3) |
| C(3)–Mn–C(2) | 92.8(3) | C(4)–Mn–P(1) | 91.1(2) |
| C(4)–Mn–P(4) | 88.2(2) | C(4)–Mn–C(1) | 83.0(3) |
| C(4)–Mn–C(2) | 171.9(3) | C(4)–Mn–C(3) | 95.3(2) |
| C(10)–P(1)–Mn | 110.7(2) | C(111)–P(1)–Mn | 116.5(2) |
| C(121)–P(1)–Mn | 123.9(1) | C(111)–P(1)–C(10) | 104.1(2) |
| C(121)–P(1)–C(10) | 101.7(2) | C(121)–P(1)–C(111) | 97.3(2) |
| C(10)–P(2)–Co | 112.5(2) | C(211)–P(2)–Co | 114.9(1) |
| C(221)–P(2)–Co | 120.5(1) | C(211)–P(2)–(10) | 102.0(2) |
| C(221)–P(2)–C(10) | 102.5(2) | C(221)–P(2)–C(211) | 102.2(2) |
| C(20)–P(3)–Co | 112.1(2) | C(311)–P(3)–Co | 119.7(2) |
| C(321)–P(3)–Co | 116.5(1) | C(311)–P(3)–C(20) | 103.9(2) |
| C(321)–P(3)–C(20) | 101.3(2) | C(321)–P(3)–C(311) | 101.2(2) |
| C(20)–P(4)–Mn | 110.7(2) | C(411)–P(4)–Mn | 116.1(1) |
| C(421)–P(4)–Mn | 122.1(1) | C(411)–P(4)–C(20) | 102.0(2) |
| C(421)–P(4)–C(20) | 104.0(2) | C(421)–P(4)–C(411) | 99.6(2) |
| P(2)–C(10)–P(1) | 109.8(3) | P(4)–C(20)–P(3) | 110.6(3) |
| O(1)–C(1)–Mn | 174.7(5) | O(2)–C(2)–Mn | 179.3(6) |
| Mn–C(3)–Co | 81.4(2) | O(3)–C(3)–Co | 124.9(5) |
| O(3)–C(3)–Mn | 153.7(5) | Mn–C(4)–Co | 80.2(2) |
| O(4)–C(4)–Co | 151.9(5) | O(4)–C(4)–Mn | 127.8(5) |
| O(5)–C(5)–Co | 176.3(6) | C(112)–C(111)–P(1) | 123.5(1) |
| C(116)–C(111)–P(1) | 116.3(1) | C(122)–C(121)–P(1) | 121.6(1) |
| C(126)–C(121)–P(1) | 118.4(1) | C(212)–C(211)–P(2) | 118.5(1) |
| C(216)–C(211)–P(2) | 121.5(1) | C(222)–C(221)–P(2) | 123.4(1) |
| C(226)–C(221)–P(2) | 116.4(1) | C(312)–C(311)–P(3) | 117.0(1) |
| C(316)–C(311)–P(3) | 122.9(1) | C(322)–C(321)–P(3) | 119.5(1) |
| C(326)–C(321)–P(3) | 120.4(1) | C(412)–C(411)–P(4) | 122.7(1) |
| C(416)–C(411)–P(4) | 117.3(1) | C(422)–C(421)–P(4) | 120.0(1) |
| C(426)–C(421)–P(4) | 120.0(1) | | |

Also, the equatorial ligands subtend angles distorted from 120° as follows: P(2)–Co–P(3) = 130.68(7)°, P(2)–Co–C(4) = 118.9(2)° and P(3)–Co–C(4) = 109.3(2)°.

The structure contains a roughly planar $(CO)Co(\mu\text{-}CO)_2Mn(CO)_2$ arrangement. The carbonyl C(3)O(3) and C(4)O(4) are semibridging, being bound more strongly to manganese and cobalt, respectively. This is clearly shown by differences in angles M–C–O of 28.8° and 24.1° and in distances M–C of 0.398 and 0.634 Å for the ligands C(3)O(3) and C(4)O(4), respectively (Table I).

The Co–Mn distance of 2.726(1) Å is indicative of a weak metal–metal bond. Several other compounds containing cobalt–manganese bonds have been structurally characterized and all have shorter Co–Mn bond distances. Examples of such distances include 2.444(1) Å in [CpCo-

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$(\mu\text{-NO})_2MnCp(PMe_3)]$,[12] 2.561 Å (average) in $[(\eta^5\text{-}C_5H_4Me)MnCo_2(\eta^5\text{-}C_5H_4Me)(\mu\text{-}CO)_3(\mu_3\text{-}CO)]$,[2] 2.639(3) Å in $[CoMn(CO)_5(\mu\text{-}CO)(DAB)]$,[11] and 2.656(4) Å in $[(\mu\text{-}{}^tBuP)FeCo(CO)_6Mn(CO)_4]$.[14] The observed long M–M distances in the related complexes $[RhM(\mu\text{-dppm})_2(CO)_n]$ ($n = 3$, M = Co,[3] Rh,[15] or Ir;[16] $n = 4$, M = Mn, Re[5]) have been interpreted in terms of dative M(–I)→M(I) bonds but it is less obvious that this interpretation can be applied to **1a**. The structure of $[RhMn(CO)_4(\mu\text{-dppm})_2]$[5] is fundamentally different from that of **1a** since it contains one less carbonyl ligand and since all of the carbonyls are terminal. The difference in the chemical formulae of the complexes $[MMn(CO)_n(\mu\text{-dppm})_2]$ (M = Co, $n = 5$; M = Rh, $n = 4$) reflects the tendency of cobalt and rhodium to have 18-electron and 16-electron configurations, respectively.[17] The manganese and rhodium atoms in $[RhMn(CO)_4(dppm)_2]$ have trigonal bipyramidal and square planar geometries, respectively, and the long Rh–Mn distance is consistent with the presence of a Mn(–I)→Rh(I) dative bond. It is likely that the metal-metal bond in complex **1a** is a weak covalent bond, since there is no reason to prefer either of the dative Mn(–I)→Co(I) or Co(–I)→Mn(I) formulations.

## NMR Spectra and Fluxionality of 1a

The $^{31}P$ NMR spectrum of $[CoMn(CO)_5(\mu\text{-dppm}_2]$, **1a**, contains equal intensity resonances at $\delta = 59.6$ (m) and $\delta = 34.3$ (m, br), which are assigned to the phosphorus atoms on manganese and cobalt, respectively. The assignment is based on comparisons with other dppm-bridged complexes of manganese and cobalt.[7,17-20] At room temperature, the P(Mn) resonance appears as a complex multiplet as expected for an AA′XX′ spin system, while only a broad doublet is observed for the P(Co) resonance. At –90 °C the P(Co) resonance is sharper and further fine structure is resolved, consistent with lower quadrupolar broadening by cobalt at lower temperatures due to thermal decoupling,[21] but otherwise the spectrum is unchanged.

In the $^1H$ NMR spectrum of **1a**, only a broad singlet at $\delta = 5.33$ is observed for the $CH_2P_2$ protons of the dppm ligands, although two such peaks are expected. This is indicative of fluxionality as described below.

At room temperature the $^{13}C$ NMR spectrum of **1a**, enriched with $^{13}CO$, Figure 2, contains a single broad resonance at $\delta = 239$, indicating the effective equivalence of all five carbonyl ligands and so confirming that the complex is fluxional. At –65 °C, three broad resonances are observed at $\delta = 255$, 240, and 225. At –75 °C, the signal at 225 ppm sharpens considerably and the signal at 255 ppm partially splits. At –90 °C, both the peaks at 255 and 240 ppm in the –65 °C spectrum split, such that five equal intensity resonances at $\delta = 294$, 249, 233, 225, and 218 are resolved. This spectrum is consistent with the solid state structure of $[CoMn(CO)_5(dppm)_2]$ in which all five carbonyls are inequivalent.

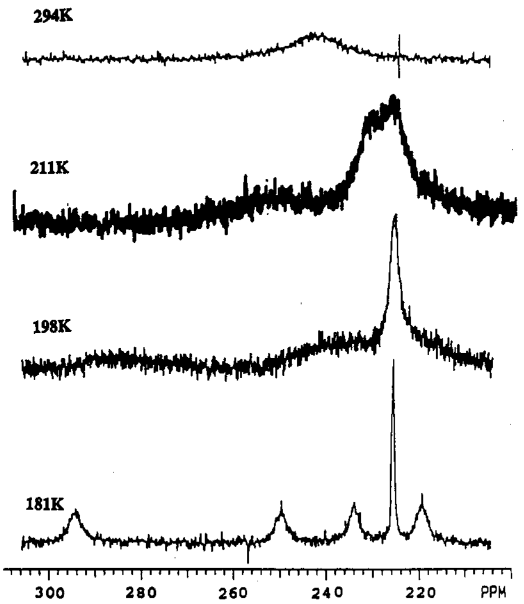
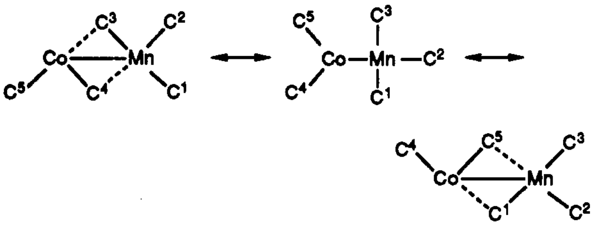


**Figure 2.** Variable temperature $^{13}C$ NMR spectra (75 MHz) of **1a**, $^{13}CO$ enriched, in the carbonyl region.

There appear to be two levels of fluxionality. A lower energy process gives three carbonyl environments in a 2:2:1 ratio, while a higher energy process leads to complete exchange. The lower energy process causes coalescence of the resonances at $\delta = 294$ and 218 [(294 + 218)/2 = 256 at –65 °C] and those at $\delta = 249$ and 233 [(249 + 233)/2 = 241 at –65 °C] signals but does not affect the resonance at $\delta = 225$. These data do not define a unique mechanism. Two possibilities might involve the two semibridging carbonyls moving either to terminal positions, thus leading to equivalence of the pairs of carbonyls C(4)O(4), C(5)O(5) and C(1)O(1), C(3)O(3) (eq 3), or to symmetrical bridging positions, thus leading to equivalence of C(3)O(3), C(4)O(4) and C(1)O(1), C(2)O(2) pairs (eq 4, first step); the unique carbonyl would be C(2)O(2) or C(5)O(5), respectively. Since cobalt causes much greater quadrupolar broadening than manganese in the $^{31}P$ NMR, it is likely also to give broadening in the $^{13}C$ NMR. Since the unique carbonyl resonance at $\delta = 225$ is sharp (Figure 2), it is probably due to a MnCO group and so that mechanism of equation (3) is preferred. Of course, the merry-go-round mechanism which leads to complete exchange of carbonyls requires transfer of carbonyls between cobalt and man-



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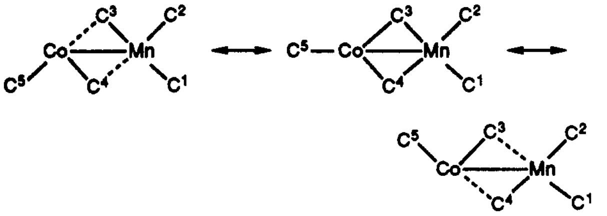

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**Table II. $^{13}$CO Chemical Shifts in Selected Cobalt and Manganese Carbonyl Complexes**

| complex | $\delta^{13}$C (ppm) | ref |
|---|---|---|
| $[Co_4(CO)_8(dppm)_2]$ | 260.1, 258.2, 206.9, 203.2, 201.7 | 27 |
| $[Co_4(CO)_8(dmpm)_2]$ | 260.5, 259.8, 259.4, 258.1, 250.7, 250.0, 210.0, 208.5, 203.8, 203.1 | 27 |
| $[Mn_2(CO)_{10}]$ | 223.1, 212.9 | 25 |
| $[Mn_2(CO)_5(dppm)_2]$ | 239.8, 237.5, 233.8, 226.8, 224.9 | 18 |
| $[CoMn(CO)_6(L)](L{=}iPr{-}N{=}CH{-}CH{=}N{-}iPr)$ | 209.3, 218.5, 222.2, 223.3 | 24 |

ganese (eq 4) and the intermediate with symmetrical $\mu$-CO groups is proposed for this higher energy process. The coplanarity of the $CoMn(CO)_5$ atoms can be maintained throughout the exchange. This type of concerted migration is common and has also been observed in $[Co_2(CO)_4(\mu\text{-dppm})_2]$,[22] $[Fe_2(CO)_5[\mu\text{-}(EtO)_2POP(OEt)_2]_2]$,[23] and $[Mn_2(CO)_6(\mu\text{-dppm})_2]$.[18]

Another interesting feature of the limiting low temperature $^{13}$C NMR spectrum of **1a** is the chemical shift of the resonance at $\delta = 294$. Most carbonyl ligands have chemical shifts which fall in the range $\delta = 190$–$260$, with the downfield part of that range being associated with bridging carbonyls. As the structure of **1a** contains only terminal and semibridging carbonyls, the shift of $\delta = 294$ is unprecendented and unexpected. Related cobalt and manganese carbonyl complexes exhibit $^{13}$CO chemical shifts in the conventional range $\delta = 190$–$260$, as illustrated in Table II.[18,24-27] There appear to be no unusual interactions between phenyl substituents and $\mu$-CO groups to account for the unusual chemical shift.

## Synthesis and Characterization of $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})Mn(CO)_4]$, 2a

Complex **2a** was prepared by reaction of $[Co(CO)(\eta^2\text{-dppm})_2]^+$ with $[Mn(CO)_5]^-$ in the presence of NaI and CO. Formation of **2a** from the immediate precursor, $[CoI(CO)_2(\eta^1\text{-dppm})_2]$, requires displacement of $I^-$ by $[Mn(CO)_5]^-$ followed by substitution of a carbonyl on manganese by the free phosphorus donor of an $\eta^1$-dppm group. It is likely that **2a** is an intermediate in the formation of **1a**, since only a second phosphine for CO substitution is required for this transformation.

The IR spectrum of **2a** contains several bands in the range 2058–1863 cm$^{-1}$, which are assigned to $\nu$(CO). The lowest energy band at 1863 cm$^{-1}$ could indicate that a semibridging carbonyl is present, though the $\nu$(CO) values of the semibridging carbonyls in **1a** are at still lower energy (1759 and 1700 cm$^{-1}$).

The $^{31}$P NMR spectrum of **2a** contains four resonances and bears a striking resemblance to that of $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})BH_2]$,[20] as expected since both contain the $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})X]$ unit (X = $BH_2$ or $Mn(CO)_4$). The resonances of phosphorus atoms bonded to the quadrupolar $^{59}$Co and $^{55}$Mn in **2a** are broad relative to the resonance due to the free end of the $\eta^1$-dppm ligand, which is sharp and well resolved. The conversion of **2a** to **1a** in solution was readily monitored by $^{31}$P NMR. The isolation and characterization of this intermediate **2a** allows a reasonable mechanism for the overall formation of **1a** from $[CoX(CO)_2(\eta^1\text{-dppm})_2]$ to be proposed, as shown in eq 5.

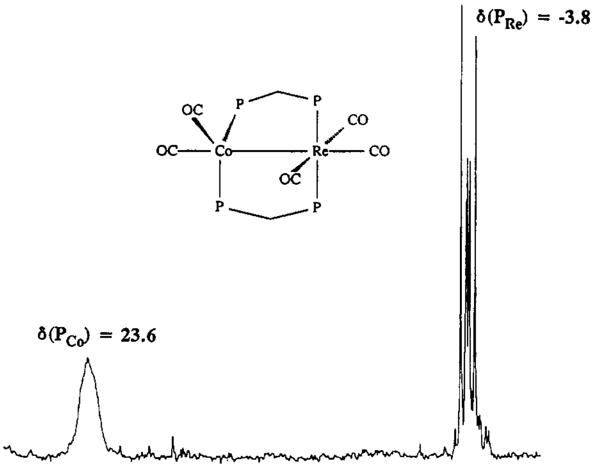
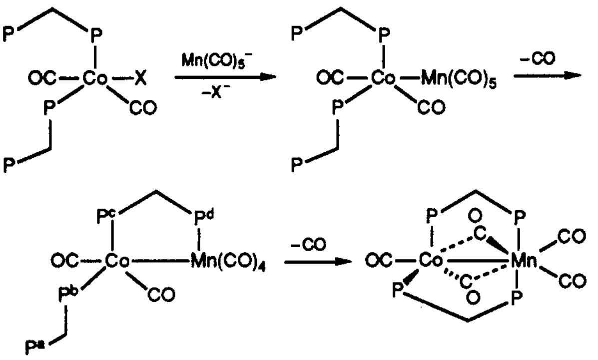


**Figure 3.** $^{31}$P NMR spectrum of **1b**. The broad P(Co) resonance is typical for complexes 1 and 2.



(5)

## Synthesis and Characterization of $[CoRe(CO)_5(\mu\text{-dppm})_2]$, 1b, and $[CoRe(CO)_6(\eta^1\text{-dppm})(\eta^2\text{-dppm})]$, 2b

These complexes were prepared in the same way as the manganese analogs **1a** and **2a**. Complex **1b** was isolated in pure form but **2b** was identified only by its NMR spectra.

The $^{31}$P NMR spectrum of **1b** consists of two sets of resonances at $\delta = 23.6$ (br) and $-3.8$ (m), assigned to the phosphorus atoms on cobalt and rhenium, respectively (Figure 3). As in **1a**, the PCo resonance is broadened by the quadrupolar cobalt but the PRe resonance shows the multiplet structure expected for an AA′XX′ spin system. The room temperature $^1$H NMR spectrum of **1b** contains a singlet resonance at $\delta = 4.43$ due to the methylene protons on dppm, and this becomes broader at −90 °C. This suggests that **1b** is fluxional but attempts to study this in detail failed since a $^{13}$CO enriched sample of $[CoRe(CO)_5(\mu\text{-dppm})_2]$ could not be prepared.

The IR spectrum of **1b** contains bands due to $\nu$ (CO) in the range 2010–1840 cm$^{-1}$. It is possible that the band at 1840 cm$^{-1}$ is due to a semibridging carbonyl, but this value is very high when compared to those assigned to the

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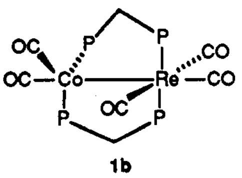

**1b**

semibridging carbonyls (1700, 1760 cm$^{-1}$) in **1a**. Also, low $\nu$ (CO) values for terminal carbonyls are common in complexes of electron-rich third-row transition elements, and carbonyl bridging is less common for heavier transition metals. Thus it is likely that **1b** contains only terminal and weakly semibridging carbonyls.

The complex [(CO)$_2$($\eta^1$-dppm)Co($\mu$-dppm)Re(CO)$_4$], **2b**, has been identified by $^{31}$P and $^1$H NMR in reactions of [Co(CO)(dppm)$_2$]$^+$ with [Re(CO)$_5$]$^-$ in the presence of LiCl or NaI and CO, but it has not been completely separated from **1b**. The $^{31}$P NMR spectrum of **2b** contains four resonances, two of which overlap, and is very similar to the spectra of **2a** and [(CO)$_2$($\eta^1$-dppm)Co($\mu$-dppm)BH$_2$].[20] The $^1$H NMR specrum of **2b** contained two multiplets at $\delta$ = 4.03 and 3.78 ppm, assigned to the CH$_2$ protons of the two dppm ligands. Again, the spectrum closely resembled the $^1$H NMR spectrum of **2a**.

## Conclusions

The reaction of [M(CO)($\eta^2$-dppm)$_2$]$^+$ with [Mn(CO)$_5$]$^-$ or [Re(CO)$_5$]$^-$, which is known to be a good method for synthesis of dppm-bridged heterobimetallic complexes when M = Rh or Ir,[5] is not successful when M = Co. However, the cobalt precursor can be activated by reaction with halide and CO, forming the more reactive precursor [CoX(CO)$_2$($\eta^1$-dppm)$_2$],[4] and reactions with [Mn(CO)$_5$]$^-$ and [Re(CO)$_5$]$^-$ are then successful.

## Experimental Section

All syntheses were carried out under an atmosphere of dry nitrogen, using either Schlenk line or dry box techniques, unless otherwise specified.

**[CoMn(CO)$_5$($\mu$-dppm)$_2$], 1a.** A solution of [Co(CO)(dppm)$_2$]-BPh$_4$ (2.40 g) and LiCl (0.20 g) in THF (40 mL) under a CO atmosphere was heated under reflux for 30 min. To this solution was added a mixture prepared by reaction of [Mn$_2$(CO)$_{10}$] (0.86 g) in freshly distilled THF (20 mL) with Na/Hg amalgam (0.59g Na/3 mL Hg) for 12 h. The mixture was heated under reflux under a CO atmosphere for an additional 45 min and then under N$_2$ atmosphere for 2 h. The solvent was removed under vacuum and the resulting solid was washed with EtOH (30 mL) and recrystallized from C$_6$H$_6$/EtOH: yield, 48%. NMR in CD$_2$Cl$_2$ at -90 °C: $\delta$ ($^{31}$P) = 59.6 [m, PMn], 34.3 [br, m, PCo]; $\delta$ ($^{13}$C) = 294, 249, 233, 225, 218; $\delta$ ($^1$H) = 5.33 [s, PCH$_2$P]. IR (Nujol): $\nu$ (CO) = 1954 (m), 1937 (s), 1902 (w), 1885 (s), 1759 (w), 1700 (s) cm$^{-1}$. Anal. Calcd for C$_{55}$H$_{44}$CoMnO$_5$P$_4$: C, 64.59; H, 4.34. Found: C, 63.35; H, 3.52%. $^{13}$CO enrichment of [CoMn(CO)$_5$(dppm)$_2$] was accomplished by stirring a solution of the compound under a $^{13}$CO atmosphere for 24 h. From comparison of selected bands due to $\nu$ (CO) in the IR spectra of normal and $^{13}$CO-enriched samples, the degree of enrichment was determined to be approximately 50%. Both before and after the variable temperature $^{13}$C NMR experiment, a $^{31}$P NMR spectrum of the sample was recorded to confirm its purity.

When a similar attempt to prepare **1a** was made in the absence of LiCl, most of the [Co(CO)($\eta^2$-dppm)$_2$]BPh$_4$ reagent was recovered. In addition, a low yield of an unidentified complex having the following spectroscopic properties was obtained. NMR in CH$_2$Cl$_2$/CD$_3$CN mixture: $\delta$ ($^{31}$P) = 80.8 [dd, $J$(PP) = 71, 63 Hz, PMn], 28.0 [ddd, $J$(PP) = 132, 71, 63 Hz, PCo]. IR (Nujol): $\nu$ (CO) = 1968 (m), 1933 (s), 1898 (m), 1815 (m), 1777 (m) cm$^{-1}$.

**[CoMn($\mu$-Cl)(CO)$_3$($\mu$-dppm)$_2$]Cl.** A sample of **1a** was dissolved in CDCl$_3$ and the $^{31}$P NMR spectrum was recorded. This showed that **1a** had reacted to give a single product, which was isolated by evaporation of the solvent and tentatively identified as [(CO)Co($\mu$-Cl)($\mu$-CO)($\mu$-dppm)$_2$Mn(CO)$_2$]Cl. NMR in CDCl$_3$: $\delta$ ($^{31}$P) = 52.9 [t, $^2J$(PP) = 41 Hz, PMn], 39.7 [t, $^2J$(PP) = 41 Hz, PCo]. IR (Nujol): $\nu$ (CO) = 1993 (w), 1970 (s), 1915 (s), 1805 (m) cm$^{-1}$. Anal. Calcd for C$_{54}$H$_{44}$Cl$_2$CoMnO$_4$P$_4$: C, 60.87; H, 4.16. Found: C, 60.98; H, 4.01%.

**[CoMn($\mu$-I)(CO)$_3$($\mu$-CO)($\mu$-dppm)$_2$]I.** A mixture of complex **1a** (0.040 g) and I$_2$ (0.10 g) in CH$_2$Cl$_2$ (10 mL) was stirred for 1 h. The solvent was evaporated under vacuum, and the residue was washed with EtOH (10 mL) and recrystallized from CH$_2$Cl$_2$/EtOH: yield, 0.043 g. NMR in CD$_2$Cl$_2$: $\delta$ ($^{31}$P) = 51.4 [t, $^2J$(PP) = 40 Hz, PMn], 41.8 [t, $^2J$(PP) = 40 Hz, PCo]. IR (Nujol): $\nu$ (CO) = 1991 (w), 1968 (s), 1916 (s), 1802 (m) cm$^{-1}$. Anal. Calcd for C$_{54}$H$_{44}$CoI$_2$MnO$_4$P$_4$: C, 51.95; H, 3.55. Found: C, 52.2; H, 3.6%.

**[(CO)$_2$($\eta^1$-dppm)Co($\mu$-dppm)Mn(CO)$_4$], 2a.** To a solution of [Co(CO)(dppm)$_2$]BPh$_4$ (2.73 g) and NaI (0.36 g) in THF (40 mL), that had been heated under reflux under an atmosphere of CO for 45 min, was added a solution prepared by reaction of [Mn$_2$(CO)$_{10}$] (0.70 g) in THF (30 mL) with Na/Hg amalgam (0.37 g of Na, 3 mL of Hg) for 2 h. The solution was refluxed under N$_2$ for an additional 30 min and the solvent was then removed under vacuum. The resulting solid was extracted with EtOH (25 mL), and the filtered solution was set aside for 24 h, during which period dark red crystals of **2a** precipitated: yield, 31%. NMR in CH$_2$Cl$_2$: $\delta$ ($^{31}$P) = 53.8 [d, br, $^2J$(P$^c$P$^d$) = 105 Hz, P$^c$], 30.2 [d, $^2J$(P$^c$P$^d$) = 105 Hz, P$^d$], 52.5 [br, P$^b$], -30.8 [d, $^2J$(P$^a$P$^b$) = 20.5 Hz, P$^a$]. IR (Nujol): $\nu$ (CO) = 2058 (w), 2024 (m), 1962 (s), 1952 (m), 1931 (s), 1892 (m), 1864 (m) cm$^{-1}$. FAB-MS: $m/z$ = 1050, 912, 883, 855, 827; Calcd for C$_{56}$H$_{44}$CoMnO$_6$P$_4$, [P]: 1050, P-4CO: 910, P-Mn(CO)$_4$: 883, P-Mn(CO)$_5$: 855, P-Mn(CO)$_6$: 827. Anal. Calcd for C$_{56}$H$_{44}$CoMnO$_6$P$_4$: C, 64.01; H, 4.22. Found: C, 63.75; H, 4.26%.

The ethanol-insoluble fraction of product was shown to contain a mixture of [Co(CO)(dppm)$_2$]BPh$_4$ and **1a**.

**[CoRe(CO)$_5$($\mu$-dppm)$_2$], 1b.** To a solution of [Co(CO)-(dppm)$_2$]BPh$_4$ (1.00 g) and NaI (0.19 g) in THF (30 mL), that had been heated under reflux under a CO atmosphere for 20 min, was added a solution prepared by reaction of [Re$_2$(CO)$_{10}$] (1.11 g) in THF (30 mL) with Na/Hg amalgam (0.092 g Na/5 mL of Hg) for 16 h. The solution was refluxed for an additional 10 min under N$_2$ and the solvent was removed by vacuum. The solid residue was recrystallized from C$_6$H$_6$/EtOH to give pure **1b**: yield, 15%. NMR in acetone-$d_6$: $\delta$ ($^{31}$P) = 23.6 [br, PCo], -3.82 [m, PRe]; $\delta$ ($^1$H) = 4.43 [s, CH$_2$P$_2$]. IR (Nujol): $\nu$ (CO) = 2010 (m), 1979 (w), 1923 (s), 1885 (s), 1840 (m). FAB-MS: 1042; Calcd for C$_{55}$H$_{44}$CoReP$_4$O$_5$: [P] = 1153, P-4CO: 1041. Anal. Calc. for C$_{55}$H$_{44}$CoO$_5$P$_4$Re: C, 57.24; H, 3.84. Found: C, 56.93; H, 3.81%.

**[(CO)$_2$($\eta^1$-dppm)Co($\mu$-dppm)Re(CO)$_4$], 2b.** Evaporation of the mother liquor, after isolation of **1b** in the above synthesis, gave a solid which was identified spectroscopically as **2b**. However, subsequent recrystallization from C$_6$H$_6$/EtOH led to partial decomposition to a mixture of **1b** and **2b**, and so good analytical data for **1b** could not be obtained. NMR in acetone-$d_6$: $\delta$ ($^{31}$P) = 30.6 [br, P$^c$], -2.50 [dd, $^2J$(P$^c$P$^d$) = 145 Hz, $^2J$(P$^b$P$^c$) = 115 Hz, P$^d$], 30.6 [br, P$^b$], -31.5 [d, $^2J$(P$^a$P$^b$) = 63 Hz, P$^a$]; $\delta$($^1$H) = 3.78 and 4.03 [m, CH$_2$P$_2$].

**X-ray Structure Determination.** A dark red, air-sensitive crystal (with dimensions 0.40 × 0.35 × 0.22 mm, and indices of the six faces, [010], [110] and [11-1]) was obtained by cutting a larger crystal and was mounted in a thin-walled glass capillary tube.

The data collection was carried out at 296 K using an Enraf-Nonius CAD4F diffractometer with an incident-beam mono-

**Table III. Crystallographic Data for $[CoMn(CO)_5(\mu\text{-dppm})_2]$**

| | | | |
|---|---|---|---|
| formula | $C_{55}H_{44}O_5P_4CoMn$ | formula wt | 1022.73 |
| $a$ (Å) | 13.030(5) | space group | $P\bar{1}$ |
| $b$ (Å) | 20.545(5) | $T$ (°C) | 23 |
| $c$ (Å) | 9.921(3) | λ (Å) | 0.71073 |
| α (deg) | 103.65(2) | $\rho_{obsd}$ (g cm$^{-3}$) | 1.430(5) |
| β (deg) | 96.248(9) | $\rho_{calcd}$ (g cm$^{-3}$) | 1.423 |
| γ (deg) | 81.97(2) | $\mu$(Mo Kα) (cm$^{-1}$) | 7.33 |
| $V$ (Å$^3$) | 2393(2) | $R(F_o)$ | 0.0575 |
| $Z$ | 2 | $R_w(F_o)$ | 0.0536 |

chromator and Mo Kα radiation.[28] Cell constants and an orientation matrix were determined and refined by using the angular settings for 20 high-angle reflections with $22.1 < 2\theta < 32.6°$. Intensity data were recorded in $\omega$–$2\theta$ mode, at variable scan speeds (1.1–2.75 deg/min) with a maximum time per datum of 60 s. Background estimates were made by extending the scan by 25% on each side. Standard reflections 100, 0-20, and 00-1 were monitored every 180 min of X-ray exposure time and showed 2.5% decay over the total period of 176.5 h. A total of 6859 reflections in the range $0° < 2\theta < 46°$ and 183 standards were recorded. Corrections were applied for Lorentz, monochromator and crystal polarization, and background radiation effects using the Structure Determination Package[29] running on a PDP11/23+ computer. An empirical absorption correction was applied[30] based upon the $\psi$ scans of nine reflections with values in the range of $\Theta = 3.58$ to 14.68°. The transmission factors ranged from 88.74 to 99.98%. The equivalent reflections were averaged at $R = 0.014$.

The intensity statistics computed using NZTEST[31] suggested the space group $P\bar{1}$ and was confirmed by successful solution and refinement of the structure. The structure was solved by a combination of SHELXS-86[32] and subsequent difference Fourier techniques and refined by full-matrix least-squares techniques on $F$ using the SHELX-76 software[33] running on a SUN 3/80 workstation. Scattering factors for neutral, non-hydrogen atoms were taken from ref 34. All the Co, Mn, and P atoms were assigned anisotropic thermal parameters. The phenyl rings were treated as regular hexagons with C–C = 1.392 Å. The phenyl and the methylene hydrogen atoms in their idealized positions (C–H = 0.95 Å) were included for structure factor calculations only and were not refined in the least-squares cycles. The thermal parameters for the carbon atoms were refined isotropically, whereas common temperature factors were assigned to methylene and phenyl hydrogen atoms and were refined in the least-squares cycles. In the final cycles, the refinement of 202 variables and 4686 observations with $I \geq 2.5\sigma(I)$ the model converged at agreement factors $R = 0.0575$ and $R_w = 0.0536$, for a weighting scheme, $w = k/\sigma^2(F_o) + gF^2$ where $k = 3.0312$ and $g = 0.000185$. The extinction parameter refined to $5.78(1.18) \times 10^{-4}$.

The crystal data and the experimental conditions are shown in Table III. Positional and $U$(equiv) thermal parameters are given for the refined atoms in Table IV. Tables of hydrogen atom parameters, anisotropic thermal parameters, root-mean-square amplitudes of vibration, selected torsion angles, weighted least-squares planes, and structure amplitudes have been deposited as supplementary material.

**Acknowledgment.** We thank NSERC (Canada) for financial support and Dr. N.C. Payne for providing X-ray and computing facilities.

**Table IV. Positional and Thermal Parameters for 1a**

| atom | $x$ | $y$ | $z$ | $U$ or $U_{eq}$,[a] Å$^2$ |
|---|---|---|---|---|
| Co | 0.29217(7) | 0.21789(4) | 0.46521(9) | 0.0332(3)* |
| Mn | 0.13205(7) | 0.31179(4) | 0.51006(9) | 0.0289(3)* |
| P(1) | 0.0075(1) | 0.24516(8) | 0.3151(2) | 0.0302(6)* |
| P(2) | 0.1841(1) | 0.13240(8) | 0.3541(2) | 0.0314(6)* |
| P(3) | 0.4179(1) | 0.24055(8) | 0.6905(2) | 0.0310(6)* |
| P(4) | 0.2684(1) | 0.36537(8) | 0.7179(2) | 0.0292(6)* |
| C(10) | 0.0370(5) | 0.1570(3) | 0.3308(6) | 0.034(1) |
| C(20) | 0.3652(5) | 0.3039(3) | 0.8172(6) | 0.032(1) |
| C(1) | 0.0898(5) | 0.3819(3) | 0.4204(7) | 0.040(2) |
| O(1) | 0.0545(4) | 0.4291(3) | 0.3643(5) | 0.065(1) |
| C(2) | 0.0319(5) | 0.3391(3) | 0.5939(7) | 0.038(2) |
| O(2) | –0.0344(4) | 0.3580(2) | 0.6498(5) | 0.063(1) |
| C(3) | 0.1776(5) | 0.2361(3) | 0.5982(7) | 0.041(2) |
| O(3) | 0.1743(3) | 0.2007(2) | 0.6750(4) | 0.044(1) |
| C(4) | 0.2633(5) | 0.2895(3) | 0.3850(7) | 0.044(2) |
| O(4) | 0.2800(4) | 0.3234(2) | 0.3147(5) | 0.051(1) |
| C(5) | 0.3901(5) | 0.1816(3) | 0.3862(7) | 0.045(2) |
| O(5) | 0.4580(4) | 0.1546(3) | 0.3379(5) | 0.069(1) |
| C(111) | –0.1391(4) | 0.2615(2) | 0.2973(5) | 0.037(2) |
| C(112) | –0.2043(4) | 0.2131(2) | 0.2964(5) | 0.059(2) |
| C(113) | –0.3171(4) | 0.2274(2) | 0.2680(5) | 0.075(2) |
| C(114) | –0.3648(4) | 0.2901(2) | 0.2404(5) | 0.067(2) |
| C(115) | –0.2996(4) | 0.3385(2) | 0.241395) | 0.064(2) |
| C(116) | –0.1868(4) | 0.3242(2) | 0.2697(5) | 0.049(2) |
| C(121) | –0.0122(3) | 0.2399(2) | 0.1182(4) | 0.035(1) |
| C(122) | 0.0378(3) | 0.2833(2) | 0.0757(4) | 0.041(2) |
| C(123) | 0.0227(3) | 0.2771(2) | –0.0731(4) | 0.052(2) |
| C(124) | –0.0424(3) | 0.2276(2) | –0.1794(4) | 0.061(2) |
| C(125) | –0.0923(3) | 0.1842(2) | –0.1369(4) | 0.059(2) |
| C(126) | –0.0772(3) | 0.1903(2) | 0.0119(4) | 0.043(2) |
| C(211) | 0.1757(3) | 0.0958(2) | 0.1613(4) | 0.032(1) |
| C(212) | 0.1996(3) | 0.1355(2) | 0.0819(4) | 0.044(2) |
| C(213) | 0.1924(3) | 0.1098(2) | –0.0641(4) | 0.052(2) |
| C(214) | 0.1613(3) | 0.0445(2) | –0.1307(4) | 0.055(2) |
| C(215) | 0.1374(3) | 0.0048(2) | –0.0513(4) | 0.057(2) |
| C(216) | 0.1446(3) | 0.0304(2) | 0.0947(4) | 0.044(2) |
| C(221) | 0.2093(3) | 0.0572(2) | 0.4356(5) | 0.038(2) |
| C(222) | 0.1256(3) | 0.0173(2) | 0.4187(5) | 0.048(2) |
| C(223) | 0.1521(3) | –0.0415(2) | 0.4742(5) | 0.063(2) |
| C(224) | 0.2622(3) | –0.0604(2) | 0.5466(5) | 0.067(2) |
| C(225) | 0.3459(3) | –0.0205(2) | 0.5636(5) | 0.075(2) |
| C(226) | 0.3194(3) | 0.0383(2) | 0.5081(5) | 0.058(2) |
| C(311) | 0.4789(4) | 0.1727(2) | 0.7936(4) | 0.038(2) |
| C(312) | 0.5606(4) | 0.1300(2) | 0.7546(4) | 0.056(2) |
| C(313) | 0.6056(4) | 0.0752(2) | 0.8219(4) | 0.075(2) |
| C(314) | 0.5687(4) | 0.0631(2) | 0.9282(4) | 0.072(2) |
| C(315) | 0.4870(4) | 0.1057(2) | 0.9671(4) | 0.069(2) |
| C(316) | 0.4420(4) | 0.1605(2) | 0.8999(4) | 0.050(2) |
| C(321) | 0.5425(3) | 0.2787(2) | 0.7079(4) | 0.035(1) |
| C(322) | 0.6305(3) | 0.2869(2) | 0.8425(4) | 0.045(2) |
| C(323) | 0.7229(3) | 0.3193(2) | 0.8596(4) | 0.057(2) |
| C(324) | 0.7273(3) | 0.3433(2) | 0.7421(4) | 0.057(2) |
| C(325) | 0.6394(3) | 0.3350(2) | 0.6075(4) | 0.057(2) |
| C(326) | 0.5470(3) | 0.3027(2) | 0.5904(4) | 0.044(2) |
| C(411) | 0.2209(3) | 0.4187(2) | 0.8641(4) | 0.030(1) |
| C(412) | 0.2368(3) | 0.3993(2) | 0.9961(4) | 0.041(2) |
| C(413) | 0.1963(3) | 0.4409(2) | 1.1003(4) | 0.048(2) |
| C(414) | 0.1400(3) | 0.5018(2) | 1.0725(4) | 0.048(2) |
| C(415) | 0.1240(3) | 0.5212(2) | 0.9404(4) | 0.051(2) |
| C(416) | 0.1645(3) | 0.4796(2) | 0.8362(4) | 0.045(2) |
| C(421) | 0.3596(3) | 0.4236(2) | 0.7058(4) | 0.035(1) |
| C(422) | 0.4591(3) | 0.4390(2) | 0.8215(4) | 0.048(2) |
| C(423) | 0.5252(3) | 0.4852(2) | 0.8156(4) | 0.054(2) |
| C(424) | 0.4918(3) | 0.5160(2) | 0.6941(4) | 0.058(2) |
| C(425) | 0.3923(3) | 0.5006(2) | 0.5784(4) | 0.059(2) |
| C(426) | 0.3262(3) | 0.4544(2) | 0.5842(4) | 0.045(2) |

[a] Parameters with an asterisk were refined anisotropically and are given in the form of isotropic equivalent displacement parameter defined as $U_{eq} = 1/3 \sum_i \sum_j U_{ij} \cdot a^*_i \cdot a^*_j \cdot a_i \cdot a_j$.

**Supplementary Material Available:** Tables of hydrogen atom parameters, anisotropic thermal parameters, root-mean-square amplitudes, selected torsion angles, and weighted least-squares planes (4 pages). Ordering information is given on any current masthead page.

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