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One-pot synthesis of *fac*-[$Mn(CO)_3(P–P)Cl$] from $Mn_2(CO)_{10}$, [P–P] and chlorinated solvents: [P–P] = 1,2-bis(diethylphosphino)ethane (depe), 1,2-bis(diphenylphosphino)ethane (dppe) or 1,3-bis(diphenylphosphino)propane (dppp). The X-ray crystal structure of *fac*-[$Mn(CO)_3$(depe)Cl]

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Abstract—In a one-pot reaction, the three titled manganese chloride complexes were prepared by refluxing $Mn_2(CO)_{10}$ with (P–P) in 2-chloroethanol for two hours. The new compounds were characterized by IR, ^1H NMR, mass spectra and microanalyses. The X-ray crystal structure of *fac*-$Mn(CO)_3$(depe)Cl is also reported. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: manganese; phosphine; manganese carbonyl; manganese complexes; 2-chloroethanol; crystal structure.

The presence of a halogen atom covalently bonded to a Mn and/or Re atom in complexes of these metals provides an entry into other functionalities attached directly to the metal atom. Although the preparation of the pentacarbonyl halides $M(CO)_5X$ (M = Mn, Re; X = Cl, Br, I) have been reported elsewhere, the replacement of the halogen by other functionalities is complicated by the relative instability of such pentacarbonyl complexes. Substitution of the carbonyl ligands by other ligands enhances the stability of such complexes. Accordingly the carbonyl halides have been treated with a variety of monodentate tertiary phosphine and arsine ligands (L) to form compounds of the types $M(CO)_4LX$ and $M(CO)_3L_2X$ [1–5]. These complexes may be prepared alternatively by the cleavage of $Mn_2(CO)_8(L)_2$ by halogens [6–9]; by halogen–hydrogen exchange reactions starting with $MnH(CO)_{5-n}(L)_n$ [6,7,10,11]; or by photolysis of various $Mn_2(CO)_8(L)_2$ species in chlorinated solvents [12,13]. Reactions of $M(CO)_5X$ with diphosphine ligands (P–P) have also been reported and lead to some of the same chlorides [14–16] that we report here. In our previous papers [17–19], we described the syntheses of a series of mononuclear tricarbonyl complexes, *fac*-$M(CO)_3$(P–P)Z [M = Mn, Re; (P–P) = dppe, dppp) and Z is a variety of functional groups, namely, –H, –OTs, –OMe, –CHO, –COOH, –COOR, $-CO_3R$, $-CH_2OR$, CH_2X, etc.]. These complexes were all prepared by substitution of CO ligands by (P–P) prior to carrying out the reactions on the metal.

We report here a new methodology for preparing *fac*-$(CO)_3$(P–P)MnCl directly in a one-pot reaction by refluxing a 2-chloroethanol solution of $Mn_2(CO)_{10}$ and (P–P) [where (P–P) = depe, dppe, dppp]. This ready availability of the manganese chloride complex should now facilitate the preparation of derivatives with other functional groups directly bonded to manganese and permit us to extend our long-range general studies of comparing the chemistry of functional groups directly bonded to a transition metal with the chemistry of the same functional groups bonded to carbon in traditional organic chemistry.

EXPERIMENTAL

All reactions were carried out under argon. Solvents were purified by standard methods. CH_2Cl_2, CCl_4 and

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$ClCH_2CH_2OH$ were purchased from Aldrich Chemical Company. 1,2-Bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp) and 1,2-bis(diethylphosphino)ethane (depe) were purchased from commercial sources (either Pressure or Strem Chemical Company). $Mn_2(CO)_{10}$ [20] and *fac*-$MnH(CO)_3$(P–P) [21] were prepared according to literature methods. IR spectra were recorded on a Perkin–Elmer 1600 Series FT-IR instrument. ^1H NMR spectra were performed on a Bruker AC 250 instrument with $CDCl_3$ as solvent. All peak positions are relative to TMS. Mass spectra were recorded on a Kratos MS-80 for high resolution and HP 6890 for low resolution. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc.

Preparation of fac-$Mn(CO)_3$(P–P)Cl

The three chloride complexes [(P–P) = dppe, dppp, depe] were each prepared *via* three independent methods and each particular (P–P) complex, regardless of the method of preparation, showed identical solubility, melting point, IR, ^1H NMR, and mass spectrum.

Method 1 [*preparation from the respective hydrides*]. $MnH(CO)_3$(P–P) (1.0 mmol) and CCl_4 (20.0 mmol) were refluxed under argon for 3 h. After cooling, the solvent was removed on a rotary evaporator and the residue was chromatographed on a column of silica gel with benzene as eluent. The yellow solid product was recrystallized from 1 : 1 dichloromethane/hexane to give the crystalline product in 60–68% yield. The reactions were repeated in 2-chloroethanol under reflux for only 15 min whereupon the desired chloroderivative was obtained pure in 87–90% yield.

Method 2 [*preparation directly from* $Mn_2(CO)_{10}$]. A mixture of $Mn_2(CO)_{10}$ (5 mmol), (P–P) (10 mmol) and $ClCH_2CH_2OH$ (75 cm^3) was refluxed under argon for 2 h. After cooling, the solvent was removed on a rotary evaporator. The residue was chromatographed on a column of silica gel with CH_2Cl_2 as eluent and the product was recrystallized from a dichloromethane/hexane mixture. The resulting yellow crystals were filtered, washed with 2 × 5 cm^3 portions of hexane and air-dried giving a pure product in 58–60% yield. A sample for X-ray diffraction study was crystallized from CH_2Cl_2/hexane (1 : 1).

Data for $Mn(CO)_3$(depe)Cl: m.p. 128–130°C. IR (cm^{-1}, CH_2Cl_2): ν(CO) 2019s, 1948s, 1897s. ^1H NMR (δ, $CDCl_3$): 1.95 (m, 12H, CH_2), 1.22 (m, 12H, CH_3). MS (*m/z*): 380 ($[MnCl(CO)_3(depe)]^+$, 8.4), 296 ($[MnCl(depe)]^+$, 96.7), 261 ($[Mn(depe)]^+$, 8.6), 206 ($[depe]^+$, 7.5), 177 ($[EtPCH_2CH_2PEt_2]^+$, 100), 149 ($[P_2Et_3]^+$, 21.1), 121 ($[P_2Et_2H]^+$, 29.2), 90 ($[PEt_2H]^+$, 7.1), 61 ($[PEtH]^+$, 5.1). Found: C, 41.0; H, 6.5; Cl, 9.3. Calc. for $C_{13}H_{24}ClMnO_3P_2$: C, 41.0; H, 6.4; Cl, 9.3%.

Data for $Mn(CO)_3$(dppe)Cl: m.p. 174–175 °C. IR (cm^{-1}, CH_2Cl_2): ν(CO) 2025s, 1955s, 1914s. ^1H NMR (δ, $CDCl_3$): 7.53 (m, 20H, aromatic), 2.89 (m, 4H, CH_2). MS (*m/z*): 538 ($[Mn(CO)_3(dppe) + H]^+$, 15.6), 454 ($[Mn(dppe) + H]^+$, 21.6), 398 ($[(dppe)]^+$, 87.5), 370 ($[P_2Ph_4]^+$, 44.1), 262 ($[PPh_3]^+$, 100), 185 ($[PPh_2]^+$, 92.5), 108 ($[PPh]^+$, 29.9). Found: C, 59.4; H, 4.2; Cl, 7.6. Calc. for $C_{29}H_{24}ClMnO_3P_2 \cdot 0.25ClCH_2CH_2OH$: C, 59.7; H, 4.3; Cl, 7.5%. An expanded ^1H NMR spectrum of the complex showed CH_2 resonances owing to $HOCH_2CH_2Cl$ solvate, which when intergrated were consistent with the empirical formula.

Data for $Mn(CO)_3$(dppp)Cl: m.p. 215°C dec. IR (cm^{-1}, CH_2Cl_2): ν(CO) 2028s, 1959s, 1909s. ^1H NMR (δ, $CDCl_3$): 7.43 (m, 20H, aromatic), 3.16 (t, 4H, CH_2), 2.19 (q, 2H, CH_2). MS (*m/z*): 586 ($[MnCl(CO)_3(dppp)]^+$, 1.3), 551 ($[Mn(CO)_3(dppp)]^+$, 4.2), 467 ($[Mn(dppp]^+$, 12.9), 412 ($[dppp]^+$, 29.2), 335 ($[P_2Ph_3Pr]^+$, 100.0), 262 ($[PPh_3]^+$, 7.9). Found: C, 61.6; H, 4.3; Cl, 6.5. Calc. for $C_{30}H_{26}ClMnO_3P_2$: C, 61.4; H, 4.4: Cl, 6.0%.

Method 3 [*preparation from* $Mn_2(CO)_{10}$ *by autoclave treatment*]. All pressure reactions were carried out in a Parr 4560 series 300 cm^3 magnedrive autoclave. In a typical experiment, the autoclave was charged with $Mn_2(CO)_{10}$ (1.950 g, 5.000 mmol), dppe (3.984 g, 10.000 mmol) and CH_2Cl_2 (100 cm^3) and the autoclave sealed. After appropriate flushing, the autoclave was pressurized to 100 psi nitrogen. The mixture was heated to 130°C for 2 h. On cooling, the autoclave was vented, and the solution was transferred into a 250 cm^3 round-bottomed flask. Removal of the solvent and recrystallization from dichloromethane/hexane (1 : 1) gave yellow crystals of $Mn(CO)_3$(dppe)Cl in almost quantitative yield. An analogous reaction between $Mn_2(CO)_6(dppe)_2$ (prepared as described below) and CH_2Cl_2 gave $Mn(CO)_3$(dppe)Cl as yellow crystals (98% yield).

Preparation of $Mn_2(CO)_6(dppe)_2$

$Mn_2(CO)_{10}$ (0.600 g, 1.539 mmol) and dppe (1.295 g, 3.251 mmol) were mixed with 2-propanol (50 cm^3) and refluxed under an argon atmosphere for about 2 h. On cooling, the yellow crystals that precipitated were collected by filtration, washed with hexane (3 × 10 cm^3) and dried *in vacuo* (0.860 g, 52% yield). Data: m.p. 173–180°C. IR (cm^{-1}, CH_2Cl_2): ν(CO) 1896s, 1860s. These data match those previously reported for this compound [22].

X-ray diffraction measurements

A bright yellow, rod crystal was sealed in a glass capillary. Intensity data were collected at 23.5°C on a Siemens P3 diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Lattice parameters were obtained by least-squares refinement of the angular settings from 25 reflections lying in a 2θ range of 10–30°. Intensity data were collected using θ–2θ scans in the range $3.5 \leqslant 2\theta \leqslant 55°$

($+h$, $+k$, $+l$). A decay correction (minimum 0.9739 and maximum 1.0027) was applied to the unique reflections (2149 reflections) based on three standard reflections monitored every 250 reflections. The data were also corrected for Lorentz and polarization effects. No absorption correction was applied. The structure was solved by a combination of direct methods using SHELXTL v5.03 [23] and the difference Fourier technique and refined by full-matrix least squares on F^2. Three reflections were omitted from the refinement, $F_0^2 \ll < F_c^2$ for [2 0 0], and [0 2 0] and [22 0 4] had a very negative F^2 value. The non-hydrogen atoms were refined with anisotropic displacement parameters. Atoms Mn, Cl, C(1) and O(1) lie on special positions along the crystallographic mirror plane which coincides with the molecular mirror symmetry. Weights were assigned as $W^{-1} = \sigma^2(F_0^2) + (aP)^2 + bP$, where $a = 0.0420$, $b = 8.6141$ and $P = 0.33333\ F_0^2 + 0.66667\ F_c^2$. All hydrogen atom positions were calculated based on geometric criteria, after at least one H atom per C atom was located directly from the electron density maps, and allowed to ride on their respective atoms (C—H = 1.0 Å). Hydrogen atom isotropic temperature factors were defined as $U(\mathrm{C})*a = U(\mathrm{H})$ where $a = 1.5$ for methyl hydrogens and $a = 1.2$ for methylene hydrogens. The disorder in the P–C–C–P backbone was sorted out and the occupancies of the two conformations refined to 49.82% : 50.18%. The refinement converged with crystallographic agreement factors of $R1 = 4.50\%$, $wR2 = 8.75\%$ and $S = 1.013$ for 1270 reflections with $I \geqslant 2\sigma(I)$ and 107 variable parameters. A final difference Fourier map showed maximum residual electron density of 0.314 eÅ^{-3}.

RESULTS AND DISCUSSION

Our first encounter with a Mn(CO)$_3$(P–P)Cl complex occurred during some experiments designed to improve the synthesis of Mn(CO)$_3$(dppe)H from Mn$_2$(CO)$_{10}$ and dppe by substituting refluxing 1-propanol [24] (b.p. 97°C) with refluxing 1-pentanol [21] (b.p. 137°C) as the hydrogen donor. Recrystallization of the product from CH$_2$Cl$_2$ led to an impurity which was identified as Mn(CO)$_3$(dppe)Cl. Chlorine atom abstraction from the solvent was demonstrated by treatment of the pure Mn(CO)$_3$(dppe)H in refluxing CCl$_4$, which led to almost quantitative hydrogen–chlorine exchange; over 90% of the expected CHCl$_3$ was found in the recovered CCl$_4$ (GLC), and Mn(CO)$_3$(dppe)Cl was isolated in about 68% yield. These facts suggested the possibility of using an appropriate (b.p.) solvent that might furnish both the hydrogen and the chlorine necessary to convert Mn$_2$(CO)$_{10}$ plus (P–P) directly to Mn(CO)$_3$(P–P)Cl. The use of 2-chloroethanol (b.p. 129°C) fulfilled this expectation. These and other experiments leading to the preparation of pure Mn(CO)$_3$(P–P)Cl are summarized in Scheme 1.

The chlorine atom abstraction from chlorinated solvents is most probably a free radical chain process and can be illustrated by the Mn(CO)$_3$(dppe)H/CCl$_4$ exchange noted above:

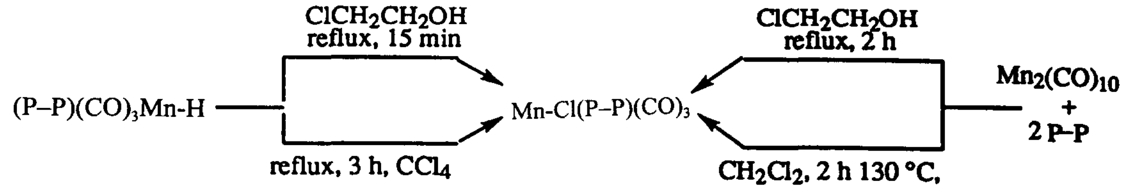
$$\mathrm{CCl_4} \rightleftharpoons {}^{\cdot}\mathrm{CCl_3} + {}^{\cdot}\mathrm{Cl}$$

$$ {}^{\cdot}\mathrm{CCl_3} + \mathrm{Mn(CO)_3(dppe)H} \rightleftharpoons \mathrm{HCCl_3} + \mathrm{Mn(CO)_3(dppe)}^{\cdot}$$

$$\mathrm{Mn(CO)_3(dppe)}^{\cdot} + \mathrm{CCl_4} \rightleftharpoons {}^{\cdot}\mathrm{CCl_3} + \mathrm{Mn(CO)_3(dppe)Cl}$$

The initiation step to give a small quantity of radicals is probably a thermal process, although no precautions were taken to exclude adventitious light. Other manganese hydrides have been shown to undergo a similar reaction [25,26]. Although we do not have conclusive evidence that the reactions of Mn$_2$(CO)$_{10}$ and (P–P) with 2-chloroethanol to give the chloride proceed through the intermediate hydride, it is quite likely that this is the case in view of the very rapid conversion of the pure hydride to chloride.

The Mn(CO)$_3$(P–P)Cl complexes are air stable and soluble in organic solvents such as dichloromethane, acetone and benzene, slightly soluble in methanol, and insoluble in hexane. Their infrared spectra exhibit three strong bands in the carbonyl region consistent with facial stereochemistry. The frequencies of these bands can be compared to reported CO values of 2022, 1959, 1918 cm^{-1} for MnBr(CO)$_3$(dppe) [14], 2021, 1947, 1898 cm^{-1} for MnCl(CO)$_3$(depe) [15] and 2028, 1952, 1916 cm^{-1} for MnCl(CO)$_3$(dpm) [16]. ^{1}H NMR spectra of these complexes in CDCl$_3$ show that protons of the phenyl group appear at δ 7.43 and 7.53, methylene protons in the range of δ 1.95–3.16, and methyl protons at δ 1.22. These values are similar to our previously assigned signals for the ligands (P–P) in Mn(CO)$_3$(P–P)Z complexes (Z = OTs, OMe, etc.) [17]. The mass spectrum of Mn(CO)$_3$(dppe)Cl did not



Scheme 1.

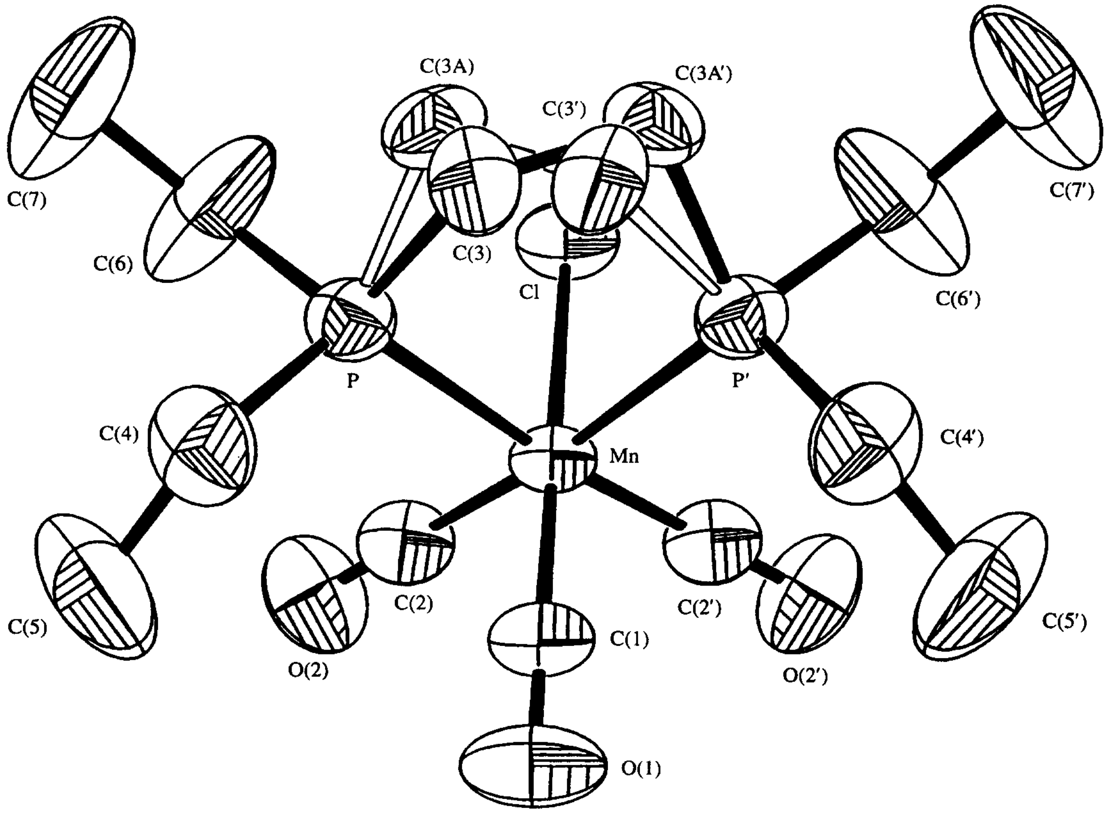


Fig. 1.

show a parent molecular ion and gave only fragments, such as $[Mn(CO)_3(dppe) + H]^+$, $[Mn(dppe) + H]^+$, $[dppe]^+$, $[P_2Ph_4]^+$, $[PPh_3]^+$, $[PPh_2]^+$ and $[PPh]^+$. The data indicate that the Mn—Cl bond is cleaved first, giving a high relative intensity peak of $[Mn(CO)_3(dppe) + H]^+$.

Crystal structure

The molecular structure of *fac*-$Mn(CO)_3$(depe)Cl was confirmed by X-ray determination. The complex crystallized in the space group *Cmca*. A thermal ellipsoid drawing of the complex in two conformations is shown in Fig. 1. Crystal data are given in Table 1, and selected bond distances and bond angles are presented in Table 2. The molecule consists of a manganese atom octahedrally coordinated to three (facial) terminal carbonyl groups, a chlorine atom and a disordered chelating depe ligand. The chlorine ligand is *trans* to a carbonyl, while the remaining two carbonyls and the depe ligand occupy *cis* positions. The Mn—Cl bond length of 2.406 (2) Å is within the range for a Mn—Cl single bond and is comparable to that previously observed in *fac*-chloro-[1,3-bis(dimethylarsino)propane]tricarbonylmanganese [2.415

Table 1. Crystallographic data for *fac*-$Mn(CO)_3$(depe)Cl

Empirical formula	$C_{13}H_{24}ClMnO_3P_2$
Formula weight	380.65
Temperature (°C)	23.5(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Cmca* (#64)
Unit-cell dimensions	$a = 18.962(5)$ Å $\alpha = 90°$ $b = 13.615(3)$ Å $\beta = 90°$ $c = 14.205(3)$ Å $\gamma = 90°$
Volume (Å^3), Z	3667(2), 8
Density (calculated) (Mgm^{-3})	1.379
Absorption coefficient (mm^{-1})	1.043
F(000)	1584
2θ range for data collection	3.5–55.0°
Limiting indices	$0 \leqslant h \leqslant 24$, $0 \leqslant k \leqslant 17$, $0 \leqslant l \leqslant 18$
Independent reflections	2152
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	2149/0/107
Goodness-of-fit on F^2	1.013
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0450$, $wR2 = 0.0875$
R indices (all data)	$R1 = 0.1156$, $wR2 = 0.1724$
Largest diff. peak and hole (eÅ^{-3})	0.314 and −0.323

Table 2. Selected bond distances (Å) and angles (°) for *fac*-$Mn(CO)_3(depe)Cl$

Mn—C(1)	1.770(5)	Mn—C(2)	1.808(4)
Mn—P	2.309(1)	Mn—Cl	2.406(2)
P—C(3A)	1.738(9)	P—C(6)	1.811(5)
P—C(4)	1.816(4)	P—C(3)	1.956(11)
O(1)—C(1)	1.150(6)	O(2)—C(2)	1.151(4)
C(4)—C(5)	1.532(6)	C(6)—C(7)	1.516(7)
C(1)—Mn—C(2)	91.6(2)	C(1)—Mn—P	91.25(12)
C(2)—Mn—P	90.74(13)	C(1)—Mn—Cl	179.3(2)
C(2)—Mn—Cl	88.90(13)	P—Mn—Cl	88.20(4)
C(3A)—P—C(6)	93.2(6)	C(3A)—P—C(4)	111.3(5)
C(6)—P—C(4)	104.0(2)	C(6)—P—C(3)	117.1(7)
C(4)—P—C(3)	94.5(5)	C(3A)—P—Mn	111.1(3)
C(6)—P—Mn	117.0(2)	C(4)—P—Mn	117.6(2)
C(3)—P—Mn	105.0(3)	O(1)—C(1)—Mn	179.9(3)
O(2)—C(2)—Mn	178.1(4)	C(5)—C(4)—P	113.7(3)
C(7)—C(6)—P	117.8(4)		

(9) Å] [27]. The angles subtended at the manganese atom range from 83.4–94.9° and from 173.6–179.9°. The P—Mn—P′ bite angle of 83.4° and the mean value of 113.3° for the remaining ring angles essentially agree with the values of 84.1° and 109.3° for the related complex *fac*-$Mn(CO)_3(dppe)OC(O)OCH_3$ [17]. The value of the Mn—C—O angles (178–180°) and the C—C distances (1.532 and 1.516 Å) of the ethyl in the depe ligand are fairly close to the expected values. The C—C bridging distance for the chelate is 1.51 Å. The disorder in the P—C—C—P backbone is 49.82% : 50.18% for the two conformations shown in Fig. 1. This disorder gives the backbone a twisted appearance. The disorder in the two ethyl groups is not addressed because the electron densities of the individual components was not clearly defined.

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