

Preparation, reactions, and infrared spectra of *fac*-(CO)₃(P–P)Mn–Z complexes (P–P = DEPE, DPPE, DPPP; Z = H, OTs, OMe, OC(O)OMe, NCO, Cl, Br, N₃)

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Abstract

A series of new octahedral Mn(I) complexes *fac*-(CO)₃(depe)Mn–Z (depe = 1,2-bis(diethylphosphino)ethane, Z = H, OTs, OMe, OC(O)OMe, NCO, Cl, Br, N₃) have been prepared and characterized, particularly with respect to their infrared spectra. The variations observed in the carbonyl stretching frequencies associated with the coordinated carbon monoxides are a function of the Z groups. Comparison of these spectra with similar spectra of the analogous dppp, 1,3-bis(diphenylphosphino)propane and dppe, 1,2-bis(diphenylphosphino)ethane complexes shows the effect of substituting phenyl groups for ethyl groups on the phosphorus atom. The depe azido complex (Z = N₃) reacts with alkynes to give a triazolato complex which on hydrolysis with HCl liberates the triazole and regenerates the chloro complex from which the azido complex is made. © 1997 Elsevier Science S.A.

Keywords: Manganese diphosphine complexes; Azido complexes; Triazolato complexes; Alkynes; Carbonyl stretching frequencies

1. Introduction

As part of our long-range interest in a comparison of the chemistry of functional groups bonded to a transition metal, with the chemistry of similar functional groups bonded to carbon, we have prepared and studied the reaction of a variety of cobalt and manganese carbonyl complexes. In a continuation of these studies we report herein on the synthesis, characterization, and reactions of *fac*-(CO)₃(P–P)Mn–Z complexes where (P–P) = depe, dppe, dppp; Z = H, OTs, OMe, OC(O)OMe, NCO, Cl, Br, N₃). The availability of 21 closely related complexes makes possible a comparison of their infrared spectra and a study of how the nature of the (P–P) ligand, as well as the structure of the Z substituent, affects the stretching frequencies of the coordinated carbon monoxides.

2. Results and discussion

2.1. IR spectra of *fac*-(CO)₃(P–P)MnZ where P–P = depe, dppe, dppp; Z = H, N₃, Br, Cl, OC(O)OMe, NCO, OTs

The preparation of the series of new depe complexes and the availability of the analogous series of dppe and dppp complexes permit a comparison of the properties of these three series. Of particular interest presently are the infrared spectra in the carbonyl stretching region. The fragments of the complexes consisting of the three facial COs bonded to Mn, if taken as a unit, show local C_{3v} symmetry and on this basis the CO stretches should give rise to E + 1A₁ bands. However, our *fac*-(CO)₃(P–P)Mn–Z are not molecules of C_{3v} symmetry but actually possess only a plane of symmetry. The E band in C_{3v} correlates with A' + A'' in C_s symmetry while the A₁ in C_{3v} correlates with A' in C_s and thus three bands associated with the 2A' + 1A'' stretching modes are expected and observed.

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We will discuss first the way in which the structure of the (P–P) ligand affects the IR spectra. Table 1 lists the three carbonyl stretching frequencies for each of the seven Z derivatives in each of the three (P–P) series. The first three columns of data correspond to the totally symmetric A' carbonyl stretching frequencies of the three (P–P) complexes; they show that the frequencies of the dppe and dppp complexes are very similar but both are uniformly higher than that of the depe complex. This effect is clearly associated with the replacement of the phenyl groups in dppe and dppp by the ethyl groups in depe. As has been pointed out [1], carbonyl stretching force constants and their related frequencies can be used as a measure of the electron density at the carbon atom of the carbonyl ligand in metal carbonyl and substituted metal carbonyl compounds. The greater the partial positive charge on the carbon atom of the carbonyl group, the higher the force constant and the higher the frequency. In the complexes with the depe ligand, the ethyl groups on the phosphorus atom produce an electron-releasing effect which is transmitted through the manganese atom and reduces the positive charge on the carbon of the carbonyl ligands with a resultant shift of $\nu_{C=O}$ to lower frequency. The presence of the phenyl groups (with their associated π^* systems) on the phosphorus atom in the dppe and dppp ligands causes a decrease of electron density at both the manganese and the CO ligands, resulting in an increase in the force constant (and an increase in $\nu_{C=O}$) for these complexes as compared to the depe complexes. Thus, both the presence of ethyl groups and the absence of phenyl groups in the depe complexes result in consistently lower carbonyl stretching frequencies than those of the dppe and dppp complexes.

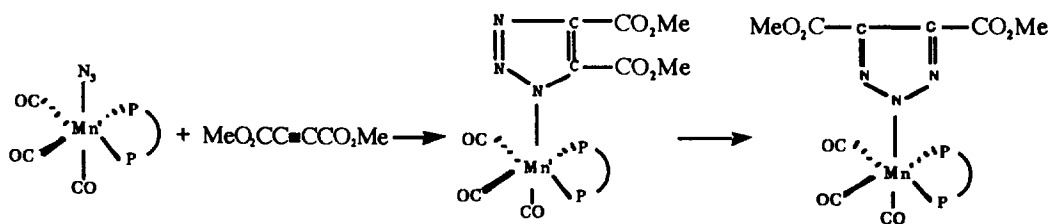
Next we consider the effect of the seven Z groups. The data in the first three columns indicate that the order of observed frequency for this A' mode is the same for all three ligands, i.e. the order of the effect of Z seems to be independent of (P–P), and therefore reflects some intrinsic properties of Z that coincide with this order. Some obvious properties are electronic effects such as relative electronegativity or relative nucleophilicity, and the relative size of the Z groups. Not enough is known presently about the steric and electronic effects of several of the Z groups listed, to permit

conclusions as to which of these properties coincide with the observed IR effect.

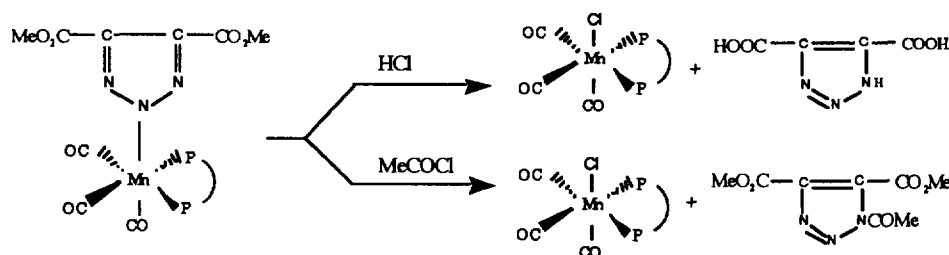
If we move now to the other stretching modes, A' and A'' , we see that the conclusions we have discussed above for the totally symmetric A' are generally applicable to these two stretching modes as well. The few irregularities may be a result of the fact that these two stretches are degenerate in C_{3v} symmetry and mix somewhat in C_s symmetry. Despite the fact that the displacement vectors of the CO stretch in A' are symmetric with respect to the symmetry plane but antisymmetric to this plane in the A'' mode, we are reluctant at this time to firmly assign which bands are which and such a decision awaits some further calculations. Although the cone angle for depe (114°) is smaller than that of either dppe (125°) or dppp (127°), and these differences may play some role, we can see no obvious correlation of these angles with all the data in Table 1.

2.2. Reaction of *fac*-(CO)₃(depe)MnN₃ with dimethyl acetylenedicarboxylate

Fac-(CO)₃(depe)MnN₃ reacts with MeO₂CC≡CCO₂Me under mild conditions (20°C) in a 1,3-dipolar reaction to produce a triazolato complex. The mass spectrum of this complex shows a parent peak at m/z 529. The infrared spectrum associated with the triazolato moiety shows $\nu(C=O)$, $\nu(C-O)$ and ring bands similar to those observed for analogous complexes derived from (R₃P)Co(DH)₂(N₃) [2] and CpFe(CO)₂N₃ [3]. The single broad carbonyl ester band indicates a high degree of local symmetry consistent with the N(2) isomer. Furthermore, the ¹H NMR spectrum shows a singlet resonance at δ 3.87 for the six methoxycarbonyl protons as expected for the N(2) isomer, whereas the N(1)-bound isomer would be expected to exhibit two methyl proton resonances for the non-equivalent methoxycarbonyl groups. The N(1) isomer (Scheme 1) is possibly the kinetic product of the reaction but the isolated product is the thermodynamically stable N(2) isomer. Isomerization from N(1)- to N(2)-bound triazole is most likely a result of steric factors as has been found for analogous tetrazolato complexes [4]. The final structure proof as to the position of attachment awaits the X-ray analysis.



Scheme 1.



Scheme 2.

Treatment of the triazolato complex with HCl results in cleavage of the Mn–N bond, release of the triazole, and regeneration of the chloro complex which was the starting material from which the triazolato complex was prepared (Scheme 2). Treatment of the triazolato complex with acetyl chloride produces acetyltriazole illustrated in Scheme 2. The ^1H NMR spectrum of the acetyltriazole shows two methyl proton resonances for the non-equivalent methoxycarbonyl groups as expected for the N(1) triazole. These cleavage reactions permit recycling of the starting chloride complex and both occur readily at room temperature.

3. Experimental

3.1. General

All reactions were carried out under an atmosphere of argon. Solvents were purified by standard methods. HBr (48% aqueous solution), *p*-toluenesulfonic acid monohydrate, NaN_3 , NaOMe and $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ were purchased from Aldrich Chemical Company. $\text{Mn}_2(\text{CO})_{10}$, 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp) and 1,2-bis(diethylphosphino)ethane (depe) were purchased from either Pressure Chemicals or Strem Chemical Company. *Fac*-(CO) $_3$ (P–P)MnZ (P–P = dppe, dppp; Z = H, OTs, OMe, OC(O)OMe, Cl) were prepared by published procedures [5–8]. IR spectra were recorded on a Perkin–Elmer 1600 Series FT-IR instrument. The carbonyl stretching frequencies of these complexes as well as the new complexes in this series (21 compounds) are all recorded in Table 1. ^1H NMR spectra were recorded on CDCl_3 solutions relative to internal Me_4Si on a Bruker AC-250 spectrometer. 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. Elemental analyses were performed by Galbraith Laboratories, Inc.

3.2. Preparation of *fac*-(CO) $_3$ (depe)MnH

A mixture of 2.000 g (5.128 mmol) of $\text{Mn}_2(\text{CO})_{10}$, 2.113 g (10.256 mmol) of depe and 75 cm^3 of 1-penta-

nol was refluxed for 5 h. The solvent was removed under reduced pressure. The residue was dissolved in 100 cm^3 of benzene and stirred with 2 g of silica gel for 15 min, whereupon the mixture was filtered. The filtrate was evaporated to give an air-sensitive yellow oil. Satisfactory analysis could not be obtained because the compound slowly decomposed at room temperature.

3.3. Preparation of *fac*-(CO) $_3$ (depe)MnOTs

To 2.4 mmol of *fac*-(CO) $_3$ (depe)MnH in methylene chloride (100 cm^3) was added an excess of *p*-toluenesulfonic acid. After hydrogen evolution ceased, the excess acid was removed by extraction with water. The methylene chloride solution was concentrated and diluted with hexane and the solution cooled to 0°C overnight. The yellow solid which precipitated was collected by filtration, washed with hexane, and dried in vacuo; m.p. 184–186°C. ^1H NMR (δ , CDCl_3): 7.17–7.69 (m, 4H, aromatic), 2.36 (s, 3H, CH_3), 1.91 (m, 12H, CH_2), 1.19 (m, 12H, CH_3). MS (m/z): 432 ($[\text{Mn}(\text{depe})\text{OTs}]^+$, 11.2), 262 ($[\text{Mn}(\text{depe}) + \text{H}]^+$, 1.9), 206 ($[\text{depe}]^+$, 7.5), 177 ($[\text{EtPCH}_2\text{CH}_2\text{PEt}_2]^+$, 100), 149 ($[\text{P}_2\text{Et}_3]^+$, 5.9), 121 ($[\text{P}_2\text{Et}_2\text{H}]^+$, 19.6), 90 ($[\text{PEt}_2\text{H}]^+$, 12.2), 61 ($[\text{PEtH}]^+$, 8.2). No parent molecular ion peak was observed.

3.4. Preparation of *fac*-(CO) $_3$ (depe)MnOCH $_3$

To 1.00 g (1.94 mmol) of *fac*-(CO) $_3$ (depe)MnOTs suspended in 50 cm^3 of methanol was added NaOMe (0.10 g, 1.94 mmol), freshly prepared from the reaction of sodium with methanol. After stirring for 12 h, the solvent was removed on a rotary evaporator. The residue was extracted with benzene (25 cm^3), the benzene solution diluted with 25 cm^3 of hexane and cooled. The resulting yellow microcrystals were collected by filtration, washed with hexane, and dried in vacuo; m.p. 162°C dec. ^1H NMR (δ , CDCl_3): 3.80 (s, 3H, OCH_3), 1.53 (m, 12H, CH_2), 1.05 (m, 12H, CH_3). This compound is extremely air-sensitive, decomposes even in an argon atmosphere and also readily absorbs carbon dioxide from the atmosphere and thus is very difficult to characterize.

3.5. Preparation of *fac*-(CO)₃(depe)MnOC(O)OCH₃

A stream of pure CO₂ was bubbled for 2 h through a 0.2 M methanol solution of *fac*-(CO)₃(depe)MnOCH₃ prepared as above without isolation. The solvent was removed on a rotary evaporator. The residue was chromatographed on a column of silica gel with 5:1 diethyl ether–acetone as eluent and the product was recrystallized from a methylene chloride–hexane mixture. The resulting yellow crystals were filtered, washed with hexane and dried in vacuo; m.p. 109–112 °C. IR (cm⁻¹, CH₂Cl₂): ν(C=O) 1655m. ¹H NMR (δ, CDCl₃): 3.54 (s, 3H, OCO₂CH₃), 1.79–1.93 (m, 12H, CH₂), 1.08–1.31 (m, 12H, CH₃). MS (*m/z*): 438 ([Mn(CO)₃(depe)CO₃Me + H₂O]⁺, 5.0), 376 ([Mn(CO)₃(depe)OMe]⁺, 11.1), 346 ([Mn(CO)₃(depe) + H]⁺, 17.2), 292 ([Mn(depe)OMe]⁺, 27.1), 262 ([Mn(depe) + H]⁺, 91.4), 206 ([depe]⁺, 13.4), 177 ([EtPCH₂CH₂PEt₂]⁺, 100), 149 ([P₂Et₃]⁺, 34.9), 121 ([P₂Et₂H]⁺, 50.2), 90 ([PEt₂H]⁺, 11.8), 61 ([PEtH]⁺, 10.9). Anal. Found: C, 43.11; H, 6.70; P, 14.03; Mn, 13.05. C₁₅H₂₇MnO₆P₂ Calc.: C, 42.86; H, 6.48; P, 14.74; Mn, 13.07%.

3.6. Preparation of *fac*-(CO)₃(P–P)MnBr (P–P = depe, dppe, dppp)

A solution of 1.0 g of *fac*-MnH(CO)₃(P–P) in 50 cm³ of dichloromethane was stirred with a five-fold excess of HBr (48%) at room temperature for 1 h. The excess acid was removed by extraction with water. The dichloromethane solution was dried over CaSO₄ and evaporated to dryness. The crude product was chromatographed on a column of silica gel with dichloromethane as eluent. The analytical sample was obtained by recrystallization from a dichloromethane–hexane (1:1) mixture. The melting points and spectral properties of the compounds were consistent with those previously reported [9,10].

3.7. Reaction of *fac*-(CO)₃(depe)MnCl with KNCO

A suspension consisting of 0.57 g (1.50 mmol) of *fac*-(CO)₃(depe)MnCl [7] and 0.12 g (1.50 mmol) of potassium cyanate in 50 cm³ of methanol was stirred at room temperature for 40 days. The solvent was removed on a rotary evaporator. The residue was chromatographed on a column of silica gel with diethyl ether as eluent and recrystallized from a dichloromethane–hexane mixture; m.p. 121–123 °C. IR (cm⁻¹, CH₂Cl₂): ν(NCO) 2237s. ¹H NMR (δ, CDCl₃): 1.73 (m, 12H, CH₂), 1.16 (m, 12H, CH₃). MS (*m/z*): 387 ([Mn(NCO)(CO)₃(depe)]⁺, 9.2), 303 ([Mn(NCO)(depe)]⁺, 13.5), 261 ([Mn(depe)]⁺, 1.2), 206 ([depe]⁺, 2.3), 177 ([EtPCH₂CH₂PEt₂]⁺, 100), 149 ([P₂Et₃]⁺, 12.7), 121 ([P₂Et₂H]⁺, 29.1), 90 ([PEt₂H]⁺,

12.6), 61 ([PEtH]⁺, 21.5). Anal. Found: C, 43.36; H, 6.61; N, 3.33. C₁₄H₂₄MnNO₄P₂ Calc.: C, 43.42; H, 6.25; N, 3.62%.

3.8. Preparations of *fac*-(CO)₃(P–P)MnN₃ (P–P = depe, dppe, dppp)

Approximately 1.5 mmol of *fac*-(CO)₃(P–P)MnX (X = Cl, Br; P–P = depe, dppe, dppp) was slurried with 50 cm³ of methanol, and the mixture was stirred at room temperature with 2 molar equiv. of NaN₃ for 30–40 days. The solvent was removed in vacuo and the resulting solid was extracted with benzene. The benzene solution was evaporated to dryness. The crude product was chromatographed on a column of silica gel with diethyl ether as eluent and the product was recrystallized from a benzene–hexane mixture.

Data for *fac*-(CO)₃(depe)MnN₃: m.p. 120–121 °C. IR (cm⁻¹, CH₂Cl₂): ν(N₃) 2053s. ¹H NMR (δ, CDCl₃): 1.92 (m, 12H, CH₂), 1.23 (m, 12H, CH₃). MS (*m/z*): 387 ([Mn(N₃)(CO)₃(depe)]⁺, 36.8), 303 ([Mn(N₃)(depe)]⁺, 51.2), 261 ([Mn(depe)]⁺, 9.7), 206 ([depe]⁺, 9.8), 177 ([EtPCH₂CH₂PEt₂]⁺, 100), 149 ([P₂Et₃]⁺, 25.8), 121 ([P₂Et₂H]⁺, 48.2), 90 ([PEt₂H]⁺, 19.1), 61 ([PEtH]⁺, 17.8). Anal. Found: C, 39.65; H, 6.42; N, 10.76. C₁₃H₂₄MnN₃O₃P₂ Calc.: C, 40.31; H, 6.25; N, 10.85%.

Data for *fac*-(CO)₃(dppe)MnN₃: m.p. 168–170 °C dec. IR (cm⁻¹, CH₂Cl₂): ν(N₃) 2055s. ¹H NMR (δ, CDCl₃): 7.26–7.60 (m, 20H, aromatic), 2.66–2.84 (m, 2H, CH₂), 1.29–1.56 (t, 2H, CH₂). MS (*m/z*): 537 ([Mn(CO)₃(dppe)]⁺, 0.5), 454 ([Mn(dppe) + H]⁺, 7.8), 398 ([dppe]⁺, 90.5), 370 ([P₂Ph₄]⁺, 29.1), 289 ([Ph₃PCH=CH₂]⁺, 50.4), 262 ([PPh₃]⁺, 41.9), 185 ([PPh₂]⁺, 100), 154 ([Ph–Ph]⁺, 8.7), 108 ([PPh]⁺, 26.9). Anal. Found: C, 63.07; H, 4.77; N, 6.41. C₂₉H₂₄MnN₃O₃P₂ · 0.75C₆H₁₄ Calc.: C, 62.42; H, 5.35; N, 6.52%.

Data for *fac*-(CO)₃(dppp)MnN₃: m.p. 173–175 °C dec. IR (cm⁻¹, CH₂Cl₂): ν(N₃) 2056s. ¹H NMR (δ, CDCl₃): 7.40 (m, 20H, aromatic), 2.36 (m, 6H, CH₂). MS (*m/z*): 552 ([Mn(CO)₃(dppp)]⁺, 23.9), 468 ([Mn(dppp)]⁺, 9.9), 412 ([dppp]⁺, 27.1), 335 ([P₂Ph₃Pr]⁺, 100), 262 ([PPh₃]⁺, 9.1), 185 ([PPh₂]⁺, 23.5), 108 ([PPh]⁺, 49.8).

3.9. Preparation of triazolato complexes

To a solution of *fac*-(CO)₃(depe)MnN₃ (0.58 g, 1.50 mmol) in dichloromethane (30 cm³) was added 0.37 cm³ (3.00 mmol) of dimethyl acetylenedicarboxylate, and the solution was stirred at room temperature for 12 h. The solvent was removed using a rotary evaporator to yield a white solid residue (0.63 g, 80%). Recrystallization from benzene–hexane (1:1) afforded white crystals. Data: m.p. 167–168 °C dec. IR (cm⁻¹,

CH₂Cl₂): $\nu(\text{C}\equiv\text{O})$ 2025s, 1952s, 1911s and $\nu(\text{C}=\text{O})$ 1731s. ¹H NMR (δ , CDCl₃): 3.87 (s, 6H, CO₂CH₃), 1.65–1.95 (m, 12H, CH₂), 0.80–1.30 (m, 12H, CH₃). MS (*m/z*): 529 ([[(MeO₂C)₂(C₂N₃)Mn(CO)₃(depe)]⁺, 24.1), 445 ([[(MeO₂C)₂(C₂N₃)Mn(depe)]⁺, 64.1), 292 ([[(MeO)Mn(depe)]⁺, 24.6), 262 ([Mn(depe) + H]⁺, 26.5), 177 ([EtPCH₂CH₂PEt₂]⁺, 100), 149 ([P₂Et₃]⁺, 58.2), 121 ([P₂Et₂H]⁺, 72.9), 90 ([PEt₂H]⁺, 44.3), 61 ([PEtH]⁺, 40.8). Anal. Found: C, 42.72; H, 5.58; N, 7.96. C₁₉H₃₀MnN₃O₇P₂. Calc.: C, 43.11; H, 5.71; N, 7.94%.

3.10. Recovery of starting chloro complex from triazolato complexes

3.10.1. Concentrated HCl

0.529 g (1.000 mmol) of (MeO₂C)₂(C₂N₃)Mn(CO)₃(depe) was suspended in 20 cm³ of concentrated HCl, and the mixture was stirred vigorously for 2 days at room temperature. The resultant yellow solid of fac-(CO)₃(depe)MnCl (identified by its melting point 130–131 °C and IR spectrum [7]) was removed by filtration, and subsequently washed with water and hexane, and air-dried. Evaporation of the filtrate gave a pale-yellow oil which was extracted with hot ethanol (95%). Crystallization from ethanol gave 74 mg (49%) of colorless crystals of 1,2,3-triazole-4,5-dicarboxylic acid, m.p. 196–200 °C dec. (lit. [11] 200 °C dec.). 1,2,3-Triazole-4,5-dicarboxylic acid titrates as a tribasic acid with breaks at pH 3.8, 7.2 and 10.5.

3.10.2. Acetyl chloride

0.529 g (1.000 mmol) of (MeO₂C)₂(C₂N₃)Mn(CO)₃(depe) was stirred with 1 cm³ of freshly distilled acetyl chloride for 2 days at room temperature under

moisture-free conditions to produce a yellow oil. The oil was pumped under high vacuum to remove the acetyl chloride and then extracted with 20 cm³ of hexane from which 91 mg (40%) of C₈H₉N₃O₅ [$\nu(\text{C}=\text{O})$ 1789 cm⁻¹] was isolated.

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