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## Reactions of ditertiary phosphines with $\eta^6$ -arenetricarbonylmanganese cations

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### Abstract

Ditertiaryphosphines  $\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2$  ( $n=1-3$ ) react at room temperature with the  $\eta^6$ -arenetricarbonylmanganese cations  $[(\eta^6\text{-XYC}_6\text{H}_4)\text{Mn}(\text{CO})_3]^+$  (Ia, X = Y = H; Ib, X = Me, Y = H) by monocarbonyl substitution and formation of  $[(\eta^6\text{-XYC}_6\text{H}_4)\text{Mn}(\text{CO})_2(\eta^1\text{-PPh}_2(\text{CH}_2)_n\text{PPh}_2)]^+$ . Prolonged refluxing results in metal–ring bond breaking and formation of *cis*- and *trans*- $[\text{Mn}(\text{CO})_2(\eta^2\text{-PPh}_2\text{CH}_2\text{PPh}_2)_2]^+$  and *trans*- $[\text{Mn}(\text{CO})_2(\eta^2\text{-PPh}_2(\text{CH}_2)_2\text{PPh}_2)_2]^+$ .

Activation of a carbonyl group in  $[(\eta^6\text{-XYC}_6\text{H}_4)\text{Mn}(\text{CO})_2(\eta^1\text{-PPh}_2(\text{CH}_2)_n\text{PPh}_2)]^+$  by TMNO gives the series of chelate complexes  $[(\eta^6\text{-XYC}_6\text{H}_4)\text{Mn}(\text{CO})(\eta^2\text{-PPh}_2(\text{CH}_2)_n\text{PPh}_2)]^+$  ( $n=1-3$ ). The X-ray structure of the chelate with  $n=3$  is reported. In the case of  $[(\eta^6\text{-XYC}_6\text{H}_4)\text{Mn}(\text{CO})_3]^+$  (Ic, X = Cl, Y = H; Id, X = Cl, Y = Me), formation of *fac*- $\text{Mn}(\text{CO})_3(\eta^2\text{-PPh}_2(\text{CH}_2)_n\text{PPh}_2)\text{Cl}$  ( $n=1, 2$ ) occurs, in a reaction analogous to that with monophosphines, see D.A. Brown, W.K. Glass and K.M. Kreddan, *J. Organomet. Chem.*, 413 (1991) 233, but there was no evidence for ring adducts as intermediates.

### Introduction

The reactions between nucleophiles and metal carbonyl complexes of  $\pi$ -acids may proceed through a number of pathways to give a variety of products, including (a) addition of the nucleophile to the carbon atom of one of the carbonyl groups [1], (b) ring addition [2], (c) carbonyl substitution [1], and (d) breaking of the metal–ring bond and formation of nucleophilic-substituted metal carbonyls [1].

In the case of the  $\eta^6$ -arenetricarbonylmanganese cations, reaction with monophosphines at elevated temperatures was initially shown to be of type (c) above, i.e. carbonyl substitution [1], but subsequently ring addition was shown to occur with  $\text{P}^n\text{Bu}_3$  at lower temperatures [2]. More recently, we have used low temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy to show that  $[(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{Mn}(\text{CO})_3]^+$  forms exclusively the *meta* adduct, whereas both the chlorobenzene and *p*-chlorotoluene complexes form *meta* and *ortho* adducts [3]. In all cases the adducts are the

*exo*- $\eta^5$ -cyclohexadienylphosphonium)tricarbonylmanganese cations e.g.  $[(\eta^5\text{-XYC}_6\text{H}_4\text{PR}_3)\text{Mn}(\text{CO})_3]^+$  ( $\text{Y} = \text{X} = \text{H}$ ;  $\text{Y} = \text{H}$ ,  $\text{X} = \text{Me}$ ;  $\text{Y} = \text{H}$ ,  $\text{X} = \text{Cl}$ ;  $\text{Y} = \text{Me}$ ,  $\text{X} = \text{Cl}$ ;  $\text{R} = \text{Et}$ ,  $^n\text{Bu}$ ). When the temperature is raised the 'dead end' equilibria are reversed for the benzene and toluene adducts, and carbonyl substitution occurs with formation of  $[(\eta^6\text{-C}_6\text{H}_5\text{Y})\text{Mn}(\text{CO})_2(\text{PR}_3)]^+$  ( $\text{Y} = \text{H}$ ,  $\text{Me}$ ;  $\text{R} = \text{Et}$ , or  $^n\text{Bu}$ ), as first reported by Mawby [1]; however the chlorobenzene and chlorotoluene adducts react differently to give *fac*- $\text{Mn}(\text{CO})_3(\text{PR}_3)_2\text{Cl}$  ( $\text{R} = \text{Et}$ ,  $^n\text{Bu}$ ) involving direct attack of  $\text{PR}_3$  on the chlorine-bearing carbon atom rather than through a metal-hydride intermediate. In continuation of these studies, we report here the reactions occurring between the ditertiaryphosphines  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1$ , dppm;  $n = 2$ , dppe;  $n = 3$ , dppp) and a series of  $\eta^6$ -arenetricarbonylmanganese cations which, to the best of our knowledge, have not been reported previously, although analogous studies with both the tropyllium cation,  $[(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]^+$  and the cyclopentadienyl cation  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3\text{CN}]^+$  have been reported [4]. In those cases, three types of products were isolated: (a) monosubstituted complexes  $[\text{ringM}(\text{CO})_2(\eta^1\text{-diphosphine})]^+$ ; (b) chelated complexes  $[\text{ringM}(\text{CO})(\eta^2\text{-diphosphine})]^+$ ; and (c) binuclear complexes e.g.  $\{[(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2]_2\text{-}\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}(\text{PF}_6)_2$ .

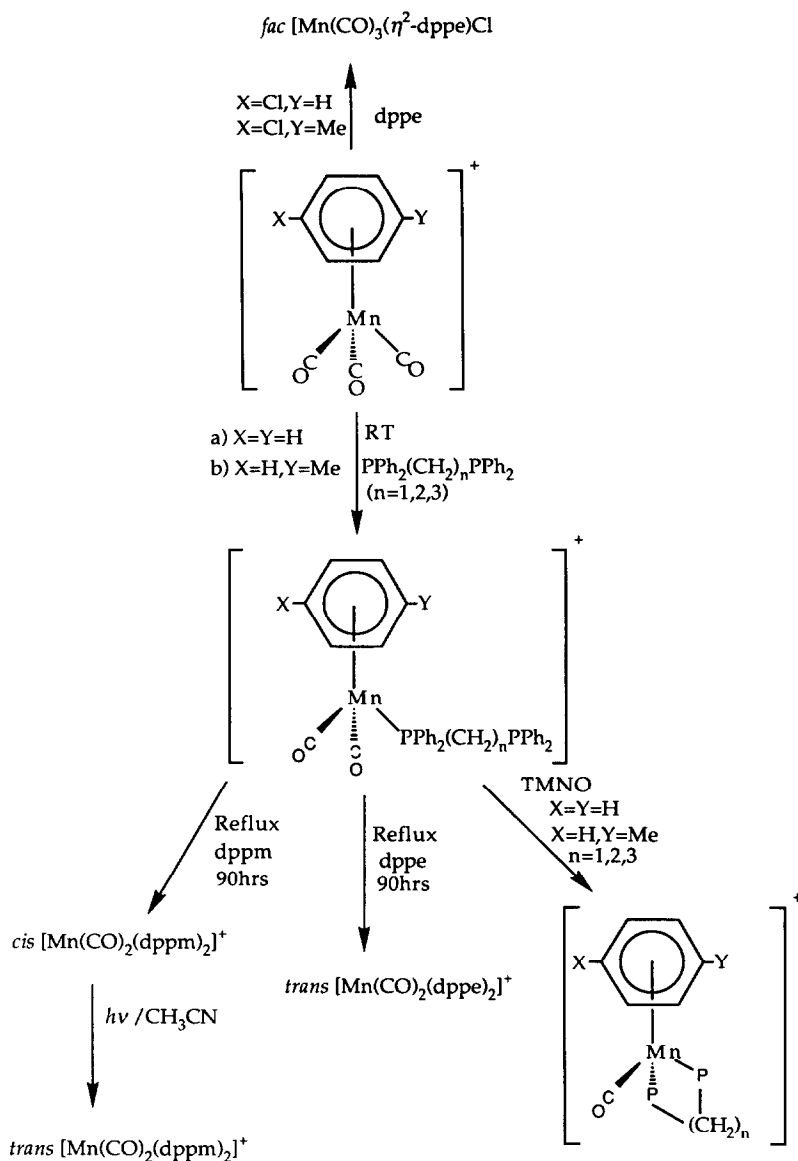
## Results and discussions

### *Low temperature reaction between $[(\eta^6\text{-C}_6\text{H}_6\text{Mn}(\text{CO})_3]\text{PF}_6$ and ditertiaryphosphines*

Monitoring of the reaction between  $[(\eta^6\text{-XYC}_6\text{H}_4)\text{Mn}(\text{CO})_3]\text{PF}_6$  ( $\text{X} = \text{Y} = \text{H}$ ;  $\text{X} = \text{Me}$ ,  $\text{Y} = \text{H}$ ;  $\text{X} = \text{Cl}$ ,  $\text{Y} = \text{H}$ ), and ditertiary phosphines  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1\text{--}3$ ) at low temperatures ( $-20^\circ\text{C}$ ) in acetone by I.R. spectroscopy gave no evidence for ring-addition adducts and formation of ( $\eta^5$ -cyclohexadienyl)diphosphonium)tricarbonylmanganese cations, in contrast to the reaction with monophosphines [2,3].

### *Formation of $\eta^6$ -arenedicarbonyl-bis-(diphenylphosphino)alkanemanganesehexafluorophosphate*

The reaction of  $[(\eta^6\text{-XYC}_6\text{H}_4)\text{Mn}(\text{CO})_3]\text{PF}_6$  ( $\text{X} = \text{Y} = \text{H}$ ;  $\text{X} = \text{Me}$ ,  $\text{Y} = \text{H}$ ) with the ditertiary phosphines  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1\text{--}3$ ) at room temperature gave the monosubstituted derivatives  $[(\eta^6\text{-arene})\text{Mn}(\text{CO})_2(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)]\text{PF}_6$  ( $n = 1\text{--}3$ ), (Scheme 1). The reaction was monitored by the disappearance of the  $\nu(\text{CO})$  stretching bands of the starting cation, e.g.  $[(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3]\text{PF}_6$ , at 2081 and 2024  $\text{cm}^{-1}$  and their replacement by those of the monosubstituted product e.g.  $[(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_2(\eta^1\text{-dppm})]\text{PF}_6$  at 2003 and 1958  $\text{cm}^{-1}$ . Microanalytical and spectroscopic data are given in Tables 1–3. In all cases, the spectroscopic properties are very similar to those for the analogous monophosphines [1,3]. The  $^{31}\text{P}$  NMR spectra for this series demonstrate conclusively that the potentially bidentate phosphine ligands are co-ordinated in a monodentate mode to the metal atom; this is because of the presence of two mutually coupled non-equivalent phosphorus NMR resonances and the fact that the high field signal has a chemical shift very similar to that of the free ligand [5,6]. As expected, the coordinated phosphorus atom shows a downfield shift compared to that of the free ligand, defined as the coordination shift ( $\delta_{\text{complex}} - \delta_{\text{free ligand}}$ ; see Table 3) [4,7,8]; for example,  $[(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_2(\eta^1\text{-dppm})]\text{PF}_6$  has two  $^{31}\text{P}$  resonances, one at high field,  $\delta - 23.97$  ppm, assigned to the



Scheme 1.

uncoordinated phosphorus atom, and one at the lower field,  $\delta$  69.37 ppm, assigned to the co-ordinated phosphorus atom being split by  $J(P_a, P_b) = 82.2$  Hz. This large coupling constant may be due to the small bite angle between the two phosphorus atoms in the dppm complex than in the analogous dppe complex  $[(C_6H_5)_Mn(CO)_2(\eta^1-dppe)]PF_6$ , which shows a coupling constant of only  $J(P_a, P_b) = 35.1$  Hz, and then in the case of  $[(C_6H_5)_Mn(CO)_2(\eta^1-dppp)]PF_6$  where no coupling is observed.

The reaction between the ditertiaryphosphines and  $[(\eta^6-XYC_6H_4)Mn(CO)_3]PF_6$  ( $X = Cl, Y = H$ ;  $X = Cl, Y = Me$ ) followed a different course and the outcome

Table 1

Analytical and IR ( $\nu(\text{CO})$ ) data for diphosphonium complexes

| Complex                                                                                                                                        | Analysis (Found (calc.) (%)) |             | IR spectra                         |           |
|------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|-------------|------------------------------------|-----------|
|                                                                                                                                                | C                            | H           | $(\nu(\text{CO}), \text{cm}^{-1})$ |           |
| $[(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_2(\eta^1\text{-dppm})]\text{PF}_6$                                                                | 55.29 (55.15)                | 4.27 (3.90) | 2003                               | 1958      |
| $[(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_2(\eta^1\text{-dppe})]\text{PF}_6 \cdot 2\text{C}_6\text{H}_5\text{CN} \cdot 2\text{H}_2\text{O}$ | 53.96 (53.65)                | 4.22 (4.71) | 2001                               | 1956      |
| $[(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_2(\eta^1\text{-dppp})]\text{PF}_6$                                                                | 56.34 (56.30)                | 4.48 (4.29) | 2001                               | 1956      |
| $[(\text{C}_6\text{H}_5\text{CH}_3)\text{Mn}(\text{CO})_2(\eta^1\text{-dppm})]\text{PF}_6$                                                     | 55.59 (55.70)                | 4.27 (4.10) | 1998                               | 1953      |
| $[(\text{C}_6\text{H}_5\text{CH}_3)\text{Mn}(\text{CO})_2(\eta^1\text{-dppe})]\text{PF}_6$                                                     | 56.15 (56.30)                | 4.32 (4.29) | 1996                               | 1951      |
| $[(\text{C}_6\text{H}_5\text{CH}_3)\text{Mn}(\text{CO})_2(\eta^1\text{-dppp})]\text{PF}_6$                                                     | 57.12 (57.38)                | 4.61 (4.64) | 1997                               | 1951      |
| $[(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})(\eta^2\text{-dppm})]\text{PF}_6$                                                                  | 54.51 (54.40)                | 4.19 (3.97) |                                    | 1933      |
| $[(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})(\eta^2\text{-dppe})]\text{PF}_6 \cdot \text{CH}_3\text{CN} \cdot 3\text{H}_2\text{O}$             | 52.72 (52.57)                | 4.75 (4.88) |                                    | 1928      |
| $[(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})(\eta^2\text{-dppp})]\text{PF}_6 \cdot 2\text{CH}_3\text{CN}$                                      | 57.21 (57.00)                | 4.57 (4.75) |                                    | 1914      |
| $[(\text{C}_6\text{H}_5\text{CH}_3)\text{Mn}(\text{CO})(\eta^2\text{-dppm})]\text{PF}_6$                                                       | 55.37 (55.00)                | 4.35 (4.16) |                                    | 1927      |
| $[(\text{C}_6\text{H}_5\text{CH}_3)\text{Mn}(\text{CO})(\eta^2\text{-dppe})]\text{PF}_6$                                                       | 56.44 (56.82)                | 4.51 (4.46) |                                    | 1924      |
| $[(\text{C}_6\text{H}_5\text{CH}_3)\text{Mn}(\text{CO})(\eta^2\text{-dppp})]\text{PF}_6 \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$   | 56.34 (56.13)                | 4.85 (4.93) |                                    | 1904      |
| $[\text{cis-Mn}(\text{CO})_2(\eta^2\text{-dppm})_2]\text{PF}_6$                                                                                | 61.12 (60.94)                | 4.35 (4.30) | 1958                               | 1904      |
| $[\text{trans-Mn}(\text{CO})_2(\eta^2\text{-dppm})_2]\text{PF}_6$                                                                              | 61.34 (60.94)                | 4.42 (4.30) |                                    | 1865      |
| $[\text{trans-Mn}(\text{CO})_2(\eta^2\text{-dppe})_2]\text{PF}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$                                          | 61.09 (61.07)                | 4.79 (4.62) |                                    | 1897      |
| <i>fac</i> - $\text{Mn}(\text{CO})_2(\eta^2\text{-dppe})\text{Cl}$                                                                             | unsatisfactory               |             | 2021                               | 1950 1915 |

being similar to that of reactions with monophosphines [3], the  $[\text{areneMn}(\text{CO})_3]^+$  cation undergoing breaking of the C–Cl bond, migration of the chlorine atom to the metal, and breaking of the metal–ring bond with formation of *fac*- $\text{Mn}(\text{CO})_3(\eta^2\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)\text{Cl}$ , which was identified by  $\nu(\text{CO})$  stretching frequencies at 2021vs, 1950s, and 1915s  $\text{cm}^{-1}$  by comparison with the data reported for *fac*- $\text{Mn}(\text{CO})_3(\eta^2\text{-dppe})\text{Br}$  prepared by reaction of  $\text{Mn}(\text{CO})_5\text{Br}$  and dppe [9].

Finally, the fact that  $[(p\text{-C}_6\text{H}_4\text{Y})\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2]\text{PF}_6$  and  $[\text{Ph}_3\text{PC}_2\text{H}_4\text{PPh}_2]\text{PF}_6$  were also obtained (identified by microanalytical and spectroscopic data) suggests that although there was no spectroscopic evidence for ring addition by ditertiaryphosphines to the  $[(\eta^6\text{-arene})\text{Mn}(\text{CO})_3]^+$  cation in the case of the chlorobenzene and *p*-chlorotoluene complexes, direct attack by the diphosphine at the carbon atom bearing the chlorine substituent must occur as in the case of monophosphines [3]. Interestingly, recent studies in our laboratories of the reactions between ditertiaryphosphines and both the  $[(\eta^5\text{-cycloheptadienyl})\text{tricarboxyliron}]$  cation [10] and the  $[(\eta^7\text{-tropyllium})\text{tricarboxylchromium}]$  cation [11] have revealed the first examples of formation of stable ring adducts.

*Formation of bis-chelated ditertiaryphosphine compounds  $[\text{Mn}(\text{CO})_2(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)_2]\text{PF}_6$  ( $n = 1, 2$ )*

It was expected that reaction of the ditertiaryphosphines with  $[(\eta^6\text{-XYC}_6\text{H}_4)\text{Mn}(\text{CO})_3]\text{PF}_6$  under more vigorous conditions would lead to dicarbonyl substitution and formation of the chelated series  $[(\eta^6\text{-arene})\text{Mn}(\text{CO})(\eta^2\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)]\text{PF}_6$ , as in the case of analogous tropyllium complex [4]. This did not occur and it was found necessary to activate the second carbonyl leaving group with trimethylamine-*N*-oxide (TMNO) (see below); however, prolonged reflux of  $[(\eta^6\text{-XYC}_6\text{H}_4)\text{Mn}(\text{CO})_3]\text{PF}_6$  ( $\text{X} = \text{Y} = \text{H}$ ;  $\text{X} = \text{Me}$ ,  $\text{Y} = \text{H}$ ) with  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1, 2$ ) in acetone for 90 h led instead to breaking of the arene–metal bond and

Table 2

<sup>1</sup>H and (<sup>13</sup>C) NMR spectral data for diphosphonium complexes <sup>a</sup>

| Complex                                                                                                     | Chemical shift                              | Assignments                             |
|-------------------------------------------------------------------------------------------------------------|---------------------------------------------|-----------------------------------------|
| [(C <sub>6</sub> H <sub>6</sub> )Mn(CO) <sub>2</sub> (η <sup>1</sup> -dppm)]PF <sub>6</sub>                 | 7.44 (c, 20) (133.01, c)                    | C <sub>6</sub> H <sub>5</sub> (phenyls) |
|                                                                                                             | 6.23 (s, 6) (99.75, s)                      | C <sub>6</sub> H <sub>6</sub>           |
|                                                                                                             | 3.68 (d, 2, <i>J</i> = 10.1 Hz) (33.50, c)  | CH <sub>2</sub>                         |
| [(C <sub>6</sub> H <sub>6</sub> )Mn(CO) <sub>2</sub> (η <sup>1</sup> -dppe)]PF <sub>6</sub>                 | 7.44 (c, 20) (134.99, c)                    | C <sub>6</sub> H <sub>5</sub> (phenyls) |
|                                                                                                             | 5.81 (s, 6) (99.84, d, <i>J</i> = 15.0 Hz)  | C <sub>6</sub> H <sub>6</sub>           |
|                                                                                                             | 2.42 (m, 2) (28.63, d, <i>J</i> = 21.5 Hz)  | CH <sub>2</sub> (α)                     |
|                                                                                                             | 1.95 (m, 2) (23.03, m)                      | CH <sub>2</sub> (β)                     |
| [(C <sub>6</sub> H <sub>6</sub> )Mn(CO) <sub>2</sub> (η <sup>1</sup> -dppp)]PF <sub>6</sub>                 | 7.46 (c, 20) (133.14, c)                    | C <sub>6</sub> H <sub>5</sub> (phenyls) |
|                                                                                                             | 6.20 (s, 6) (99.67, s)                      | C <sub>6</sub> H <sub>6</sub>           |
|                                                                                                             | 2.83 (m, 2) (34.98, m)                      | CH <sub>2</sub> (α)                     |
|                                                                                                             | 2.19 (m, 2) (21.92, d, <i>J</i> = 17.2 Hz)  | CH <sub>2</sub> (γ)                     |
|                                                                                                             | 1.45 (m, 2) (29.26, d, <i>J</i> = 13.19 Hz) | CH <sub>2</sub> (β)                     |
| [(C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )Mn(CO) <sub>2</sub> (η <sup>1</sup> -dppm)]PF <sub>6</sub> | 7.43 (c, 20) (133.43, c)                    | C <sub>6</sub> H <sub>5</sub> (phenyls) |
|                                                                                                             | (116.01, s)                                 | C <sup>1</sup> -CH <sub>3</sub>         |
|                                                                                                             | 6.26 (t, 2)                                 | H <sup>3,5</sup>                        |
|                                                                                                             | (101.90, s)                                 | C <sup>3,5</sup>                        |
|                                                                                                             | 5.94 (d, 2, <i>J</i> = 6.78 Hz)             | H <sup>2,6</sup>                        |
|                                                                                                             | (97.93, s)                                  | C <sup>2,6</sup>                        |
|                                                                                                             | 5.80 (t, 1)                                 | H <sup>4</sup>                          |
|                                                                                                             | (97.45, s)                                  | C <sup>4</sup>                          |
|                                                                                                             | 3.67 (d, 2, <i>J</i> = 10.2 Hz) (33.49, c)  | CH <sub>2</sub>                         |
|                                                                                                             | 2.38 (s, 3) (20.18, s)                      | CH <sub>3</sub>                         |
| [(C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )Mn(CO) <sub>2</sub> (η <sup>1</sup> -dppe)]PF <sub>6</sub> | 7.39 (c, 20) (135.10, c)                    | C <sub>6</sub> H <sub>5</sub> (phenyls) |
|                                                                                                             | (116.04, s)                                 | C <sup>1</sup> -CH <sub>3</sub>         |
|                                                                                                             | 6.25 (t, 2)                                 | H <sup>3,5</sup>                        |
|                                                                                                             | (101.66, s)                                 | C <sup>3,5</sup>                        |
|                                                                                                             | 5.99 (d, 2, <i>J</i> = 6.41 Hz)             | H <sup>2,6</sup>                        |
|                                                                                                             | (98.29, s)                                  | C <sup>2,6</sup>                        |
|                                                                                                             | 5.93 (t, 1)                                 | H <sup>4</sup>                          |
|                                                                                                             | (97.80, s)                                  | C <sup>4</sup>                          |
|                                                                                                             | 2.60 (m, 2) (30.15, d, <i>J</i> = 20.4 Hz)  | CH <sub>2</sub> (α)                     |
|                                                                                                             | 1.96 (m, 2) (22.87, d, <i>J</i> = 22.9 Hz)  | CH <sub>2</sub> (β)                     |
| [(C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )Mn(CO) <sub>2</sub> (η <sup>1</sup> -dppp)]PF <sub>6</sub> | 7.14 (c, 20) (133.84, c)                    | C <sub>6</sub> H <sub>5</sub> (phenyls) |
|                                                                                                             | (116.09, s)                                 | C <sup>1</sup> -CH <sub>3</sub>         |
|                                                                                                             | 5.81 (b, 2)                                 | H <sup>3,5</sup>                        |
|                                                                                                             | (101.54, s)                                 | C <sup>3,5</sup>                        |
|                                                                                                             | 5.57 (b, 2)                                 | H <sup>2,6</sup>                        |
|                                                                                                             | (97.75, s)                                  | C <sup>2,6</sup>                        |
|                                                                                                             | 5.45 (b, 1)                                 | H <sup>4</sup>                          |
|                                                                                                             | (97.18, s)                                  | C <sup>4</sup>                          |
|                                                                                                             | 2.55 (b, 2) (33.91, m)                      | CH <sub>2</sub> (α)                     |
|                                                                                                             | <sup>b</sup> ( <sup>b</sup> )               | CH <sub>2</sub> (β)                     |
|                                                                                                             | <sup>b</sup> ( <sup>b</sup> )               | CH <sub>2</sub> (γ)                     |
|                                                                                                             | 21.4 (s, 3) (20.26, s)                      | CH <sub>3</sub>                         |

Table 2 (continued)

| Complex                                                                                               | Chemical shift                                                                | Assignments                             |
|-------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|-----------------------------------------|
| [(C <sub>6</sub> H <sub>5</sub> )Mn(CO)( $\eta^2$ -dppm)]PF <sub>6</sub> <sup>c</sup>                 | 7.57 (c, 20) (133.99, c)                                                      | C <sub>6</sub> H <sub>5</sub> (phenyls) |
|                                                                                                       | 5.58 (t, 6, $J(\text{H-P}) = 2.01$ Hz) (92.20, s)                             | C <sub>6</sub> H <sub>6</sub>           |
|                                                                                                       | 5.09 (st, 1)                                                                  | CH <sub>2</sub> (H <sub>A</sub> )       |
|                                                                                                       | 3.93 (st, 1)                                                                  | CH <sub>2</sub> (H <sub>B</sub> )       |
|                                                                                                       | $J(\text{H}_{\text{AB}}) = 16.3$ , $J(\text{P-CH}_2) = 10.4$ Hz<br>(46.17, t) | CH <sub>2</sub>                         |
| [(C <sub>6</sub> H <sub>5</sub> )Mn(CO)( $\eta^2$ -dppe)]PF <sub>6</sub> <sup>c</sup>                 | 7.52 (c, 20) (134.63, c)                                                      | C <sub>6</sub> H <sub>5</sub> (phenyls) |
|                                                                                                       | 5.37 (s, 6) (93.39, s)                                                        | C <sub>6</sub> H <sub>6</sub>           |
|                                                                                                       | 2.83 (m, 2) (29.66, m)                                                        | CH <sub>2</sub> ( $\alpha$ )            |
|                                                                                                       | 2.45 (m, 2) (29.66, m)                                                        | CH <sub>2</sub> ( $\beta$ )             |
| [(C <sub>6</sub> H <sub>5</sub> )Mn(CO)( $\eta^2$ -dppp)]PF <sub>6</sub> <sup>c</sup>                 | 7.45 (c, 20) (136.30, c)                                                      | C <sub>6</sub> H <sub>5</sub> (phenyls) |
|                                                                                                       | 5.41 (t, 6, $J(\text{H-P}) = 1.83$ Hz) (94.43, s)                             | C <sub>6</sub> H <sub>6</sub>           |
|                                                                                                       | 2.60 (m, 4) (30.09, m)                                                        | CH <sub>2</sub> ( $\alpha$ )            |
|                                                                                                       | 2.11 (m, 2) (20.75, s)                                                        | CH <sub>2</sub> ( $\beta$ )             |
| [(C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )Mn(CO)( $\eta^2$ -dppm)]PF <sub>6</sub> <sup>c</sup> | 7.51 (c, 20) (133.61, c)                                                      | C <sub>6</sub> H <sub>5</sub> (phenyls) |
|                                                                                                       | (106.90, s)                                                                   | C <sup>1</sup> -CH <sub>3</sub>         |
|                                                                                                       | 5.56 (m, 4)                                                                   | H <sup>2,3,5,6</sup>                    |
|                                                                                                       | (93.96, s)                                                                    | C <sup>3,5</sup>                        |
|                                                                                                       | (89.89, s)                                                                    | C <sup>2,6</sup>                        |
|                                                                                                       | 5.18 (m, 1)                                                                   | H <sup>4</sup>                          |
|                                                                                                       | (93.67, s)                                                                    | C <sup>4</sup>                          |
|                                                                                                       | 5.08 (m, 1)                                                                   | CH <sub>2</sub> (H <sub>A</sub> )       |
|                                                                                                       | 3.94 (m, 1)                                                                   | CH <sub>2</sub> (H <sub>B</sub> )       |
|                                                                                                       | (46.55, t, $J(\text{C-P}) = 23.7$ Hz)                                         | CH <sub>2</sub>                         |
|                                                                                                       | 2.31 (s, 3)                                                                   | CH <sub>3</sub>                         |
|                                                                                                       | (20.53, s)                                                                    |                                         |
| [(C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )Mn(CO)( $\eta^2$ -dppe)]PF <sub>6</sub> <sup>c</sup> | 7.55 (c, 20) (134.76, c)                                                      | C <sub>6</sub> H <sub>5</sub> (phenyls) |
|                                                                                                       | (107.21, s)                                                                   | C <sup>1</sup> -CH <sub>3</sub>         |
|                                                                                                       | 5.58 (d, 2)                                                                   | H <sup>3,5</sup>                        |
|                                                                                                       | (95.92, s)                                                                    | C <sup>3,5</sup>                        |
|                                                                                                       | 5.17 (t, 2)                                                                   | H <sup>2,6</sup>                        |
|                                                                                                       | (90.29, s)                                                                    | C <sup>2,6</sup>                        |
|                                                                                                       | 4.54 (t, 1)                                                                   | H <sup>4</sup>                          |
|                                                                                                       | (95.05, s)                                                                    | C <sup>4</sup>                          |
|                                                                                                       | 2.77 (m, 2) (29.63, m)                                                        | CH <sub>2</sub> ( $\alpha$ )            |
|                                                                                                       | 2.45 (m, 2) (29.63, m)                                                        | CH <sub>2</sub> ( $\beta$ )             |
|                                                                                                       | 2.31 (s, 3) (20.25, s)                                                        | CH <sub>3</sub>                         |
| [(C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )Mn(CO)( $\eta^2$ -dppp)]PF <sub>6</sub> <sup>c</sup> | 7.46 (c, 20) (136.24, c)                                                      | C <sub>6</sub> H <sub>5</sub> (phenyls) |
|                                                                                                       | (109.48, s)                                                                   | C <sup>1</sup> -CH <sub>3</sub>         |
|                                                                                                       | 5.66 (t, 2)                                                                   | H <sup>3,5</sup>                        |
|                                                                                                       | (96.46, s)                                                                    | C <sup>3,5</sup>                        |
|                                                                                                       | 5.55 (t, 1)                                                                   | H <sup>4</sup>                          |
|                                                                                                       | (94.67, s)                                                                    | C <sup>4</sup>                          |
|                                                                                                       | 4.72 (d, 2)                                                                   | H <sup>2,6</sup>                        |
|                                                                                                       | (92.57, s)                                                                    | C <sup>2,6</sup>                        |
|                                                                                                       | 2.63 (m, 4) (30.23, m)                                                        | CH <sub>2</sub> ( $\alpha$ )            |
|                                                                                                       | 2.15 (m, 2) (20.82, s)                                                        | CH <sub>2</sub> ( $\beta$ )             |
|                                                                                                       | 1.97 (s, 3) (20.10, s)                                                        | CH <sub>3</sub>                         |
| <i>cis</i> -[Mn(CO) <sub>2</sub> ( $\eta^2$ -dppm) <sub>2</sub> ]PF <sub>6</sub> <sup>c</sup>         | 7.85–6.54 (c, 40) (131.11, m)                                                 | C <sub>6</sub> H <sub>5</sub> (phenyls) |
|                                                                                                       | 4.97 (m, 2)                                                                   | CH <sub>2</sub> (H <sub>A</sub> )       |
|                                                                                                       | 4.52 (m, 2)                                                                   | CH <sub>2</sub> (H <sub>B</sub> )       |
|                                                                                                       | (41.28, m)                                                                    | CH <sub>2</sub>                         |

Table 2 (continued)

| Complex                                                                                         | Chemical shift                                                                  | Assignments                                                                                                       |
|-------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------|
| <i>trans</i> -[Mn(CO) <sub>2</sub> ( $\eta^2$ -dppm) <sub>2</sub> ]PF <sub>6</sub> <sup>c</sup> | 7.33 (c, 40)<br>5.10 (m, 2)<br>4.95 (m, 2)                                      | C <sub>6</sub> H <sub>5</sub> (phenyls)<br>CH <sub>2</sub> (H <sub>A</sub> )<br>CH <sub>2</sub> (H <sub>B</sub> ) |
| <i>trans</i> -[Mn(CO) <sub>2</sub> ( $\eta^2$ -dppe) <sub>2</sub> ]PF <sub>6</sub> <sup>c</sup> | 7.28 (c, 40) (131.53, c)<br>2.77 (m, 8) (32.25, m)                              | C <sub>6</sub> H <sub>5</sub> (phenyls)<br>CH <sub>2</sub>                                                        |
| <i>fac</i> -Mn(CO) <sub>3</sub> ( $\eta^2$ -dppe)Cl <sup>c</sup>                                | 7.48 (c, 20)<br>(130.98, c)<br>3.24 (m, 2) (24.83, m)<br>3.04 (m, 2) (24.83, m) | C <sub>6</sub> H <sub>5</sub> (phenyls)<br><br>CH <sub>2</sub> ( $\alpha$ )<br>CH <sub>2</sub> ( $\beta$ )        |

<sup>a</sup> In acetone-*d*<sub>6</sub> solution, TMS as internal standard. <sup>b</sup> Obscured by the solvent peaks. <sup>c</sup> acetonitrile-*d*<sub>3</sub> solution.

formation of (a) in the case of dppm, [*cis*-Mn(CO)<sub>2</sub>( $\eta^2$ -dppm)<sub>2</sub>]PF<sub>6</sub>, and (b), in the case of dppe, [*trans*-Mn(CO)<sub>2</sub>( $\eta^2$ -dppe)<sub>2</sub>]PF<sub>6</sub> (Scheme 1). [*cis*-Mn(CO)<sub>2</sub>( $\eta^2$ -dppm)<sub>2</sub>]PF<sub>6</sub>, which was previously unknown, crystallizes from acetone as yellow crystals with  $\nu(\text{CO})$  bands at 1958 and 1904 cm<sup>-1</sup> and although it is stable in the solid state, undergoes isomerization in acetonitrile to the orange *trans* isomer, with a

Table 3

<sup>31</sup>P NMR spectra <sup>a</sup> of diphosphonium complexes (85% H<sub>3</sub>PO<sub>4</sub> as internal standard)

| Compound                                                                                                                     | $\delta(\text{P}_a)$ <sup>b</sup> | $\delta(\text{P}_b)$ <sup>b</sup> | $\delta(\text{P}_c)$ <sup>b</sup> | $\Delta_{\text{co-or}}$ <sup>c</sup> | $\Delta_{\text{chel}}$ <sup>c</sup> | $J(\text{P}_a - \text{P}_b)$ <sup>c</sup> |
|------------------------------------------------------------------------------------------------------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|--------------------------------------|-------------------------------------|-------------------------------------------|
| [( $\eta^6$ -C <sub>6</sub> H <sub>6</sub> )Mn(CO) <sub>2</sub> ( $\eta^1$ -dppm)] <sup>+</sup>                              | -23.97                            | 69.37                             | -                                 | 92.97                                | -                                   | 82.4                                      |
| [( $\eta^6$ -C <sub>6</sub> H <sub>6</sub> )Mn(CO) <sub>2</sub> ( $\eta^1$ -dppe)] <sup>+</sup>                              | -11.28                            | 71.59                             | -                                 | 84.09                                | -                                   | 35.1                                      |
| [( $\eta^6$ -C <sub>6</sub> H <sub>6</sub> )Mn(CO) <sub>2</sub> ( $\eta^1$ -dppp)] <sup>+</sup>                              | -16.46                            | 67.05                             | -                                 | 84.35                                | -                                   | -                                         |
| [( $\eta^6$ -C <sub>6</sub> H <sub>6</sub> )Mn(CO)( $\eta^2$ -dppm)] <sup>+</sup>                                            | -                                 | -                                 | 58.46                             | -                                    | -10.91                              | -                                         |
| [( $\eta^6$ -C <sub>6</sub> H <sub>6</sub> )Mn(CO)( $\eta^2$ -dppe)] <sup>+</sup>                                            | -                                 | -                                 | 101.01                            | -                                    | +28.42                              | -                                         |
| [( $\eta^6$ -C <sub>6</sub> H <sub>6</sub> )Mn(CO)( $\eta^2$ -dppp)] <sup>+</sup>                                            | -                                 | -                                 | 59.41                             | -                                    | -8.64                               | -                                         |
| [( $\eta^6$ -C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )Mn(CO) <sub>2</sub> ( $\eta^1$ -dppm)] <sup>+</sup> <sup>e</sup> | -24.08                            | 70.37                             | -                                 | 93.97                                | -                                   | 85.5                                      |
| [( $\eta^6$ -C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )Mn(CO) <sub>2</sub> ( $\eta^1$ -dppe)] <sup>+</sup> <sup>e</sup> | -11.36                            | 72.29                             | -                                 | 84.79                                | -                                   | 35.1                                      |
| [( $\eta^6$ -C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )Mn(CO) <sub>2</sub> ( $\eta^1$ -dppp)] <sup>+</sup> <sup>e</sup> | -17.58                            | 67.19                             | -                                 | 84.49                                | -                                   | -                                         |
| [( $\eta^6$ -C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )Mn(CO)( $\eta^2$ -dppm)] <sup>+</sup> <sup>e</sup>               | -                                 | -                                 | 41.69                             | -                                    | -28.68                              | -                                         |
| [( $\eta^6$ -C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )Mn(CO)( $\eta^2$ -dppe)] <sup>+</sup> <sup>e</sup>               | -                                 | -                                 | 101.10                            | -                                    | +28.81                              | -                                         |
| [( $\eta^6$ -C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )Mn(CO)( $\eta^2$ -dppp)] <sup>+</sup> <sup>e</sup>               | -                                 | -                                 | 59.19                             | -                                    | -8.00                               | -                                         |

<sup>a</sup> In (CD<sub>3</sub>)<sub>2</sub>CO unless otherwise stated. <sup>b</sup> P<sub>a</sub>: uncoordinated phosphorus atoms, P<sub>b</sub>: coordinated phosphorus atoms, P<sub>c</sub>: chelated phosphorus atoms. <sup>c</sup>  $\Delta_{\text{co-or}}$  defined as  $\delta_{\text{co-ord}} - \delta_{\text{free ligand}}$ ,  $\Delta_{\text{chel}}$  defined as  $\delta_{\text{chelate}} - \delta_{\text{co-ord}}$ . <sup>d</sup> Coupling between the co-ordinated phosphorus atoms in Hz. <sup>e</sup> CD<sub>3</sub>CN solution.

Table 4

<sup>31</sup>P NMR spectra of the *cis* and *trans* complexes

| Complex                                                                            | Chemical shift and assignment                                                        |
|------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| <i>cis</i> -[Mn(CO) <sub>2</sub> ( $\eta^2$ -dppm) <sub>2</sub> ]PF <sub>6</sub>   | -143.65 (m, PF <sub>6</sub> ); 27.43 (m, P <sub>a</sub> ); 9.87 (m, P <sub>b</sub> ) |
| <i>trans</i> -[Mn(CO) <sub>2</sub> ( $\eta^2$ -dppm) <sub>2</sub> ]PF <sub>6</sub> | -143.54 (m, PF <sub>6</sub> ); 37.89 (s, P)                                          |
| <i>trans</i> -[Mn(CO) <sub>2</sub> ( $\eta^2$ -dppe) <sub>2</sub> ]PF <sub>6</sub> | 164.93 (s, P)                                                                        |

$\nu(\text{CO})$  band at  $1865\text{ cm}^{-1}$ . The *cis* configuration of the initial product with dpmm is further confirmed by the presence of two  $^{31}\text{P}$  NMR (Table 4) resonances, at  $\delta$  27.43 and  $\delta$  9.87 ppm, assigned to the two different groups of P atoms ( $\text{P}_a$  and  $\text{P}_b$ , respectively) of the *cis* isomer. In contrast, only one  $^{31}\text{P}$  resonance is observed for the *trans* isomer, as expected.

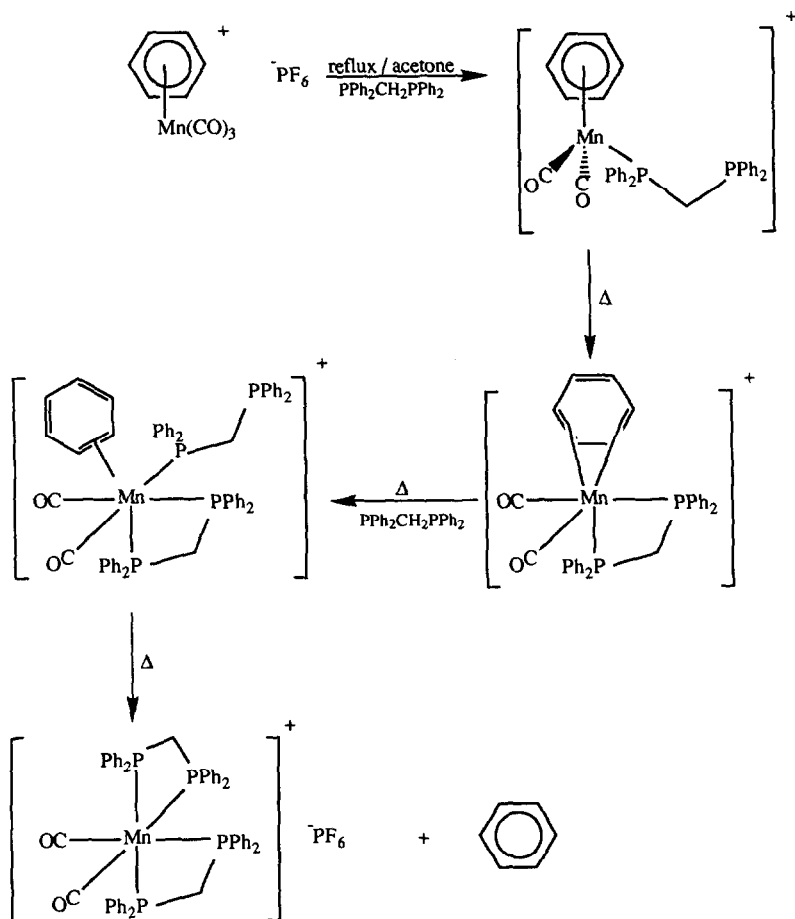
In the case of dppe, the  $[\text{trans-Mn}(\text{CO})_2(\eta^2\text{-dppe})_2]^+$  isomer is long known [12–14] with a single  $\nu(\text{CO})$  band at  $1897\text{ cm}^{-1}$ . However, in contrast to the observations when dpmm was used, monitoring of the reaction between dppe and  $[\text{arene Mn}(\text{CO})_3]^+$  by IR spectroscopy produced no evidence for initial formation of the *cis* isomer followed by isomerization to the *trans* isomer.

Formation of only the *trans* isomer in the case of the dppe complex supports the suggestion by Kuchynka and Kochi [15], based on the X-ray structures of both isomers of the dppe complexes, that the instability of the *cis* isomer is due to steric congestion in the form of a pair of rather severe non-bonded face-to-face interactions between 1- and 3-phenyl groups. In contrast, the X-ray structure of the *trans* species [15] shows a more open molecular structure, since the corresponding phenyl rings suffer only a roughly edge-to-face interaction. In the closely related cases of  $[\text{M}(\text{CO})_2(\text{dppe})_2]^{0,+1,+2}$  ( $\text{M} = \text{Mn, Cr, Mo or W}$ ) and  $[\text{M}(\text{CO})_2(\text{P-P})_2]^{0,+1}$  ( $\text{M} = \text{Cr, Mo or W}$  and  $\text{P-P} = \text{bis(diphenylphosphino)methane, ethane or propane}$ ) there has been much discussion of the factors responsible for the relative stability of the *cis* and *trans* isomers [16–18]. For example, it was noted that in the case of neutral diphosphine metal carbonyl complexes, the *cis* isomer predominates, since this structure enables both CO groups to maximise  $\pi$ -bonding with two different  $d\pi$  orbitals. In cationic systems, where  $\pi$  bonding is less important, the more symmetrical *trans* isomer is preferred. Bond and co-workers have pointed out that as a consequence of this argument, although the *trans* isomer of the cation is thermodynamically more stable, its HOMO energy is higher than of the *cis* isomer.

Although the *trans* isomer of the dppe complex is more stable than the *cis*, which was classified by Kuchynka and Kochi [15] as metastable, comparison of the *cis* isomers of dpmm and dppe complexes shows that the *cis* isomer in the case of the dpmm complex is stable in the solid state and only isomerizes to the *trans* one in solution. This order of stability,  $[(\text{cis-Mn}(\text{CO})_2(\eta^2\text{-dpmm})_2)]^+ > [\text{cis-Mn}(\text{CO})_2(\eta^2\text{-dppe})_2]^+$ , may be attributed to the smaller bite angle of dpmm, which leads to a lowering of steric interaction between the phenyl groups in the former complex. Furthermore, the formation of the *cis* isomer by reaction at the reflux temperature between  $[(\eta^6\text{-arene})\text{Mn}(\text{CO})_3]^+$  and dpmm after formation of the monosubstituted product prompts speculation that the reaction proceeds by stepwise decoordination of the arene from  $\eta^6\text{-}\eta^4\text{-}\eta^2$  modes (Scheme 2), with corresponding substitution by the bidentate ditertiaryphosphine ligand in a manner very similar to that previously suggested for the formation of  $[(\text{CH}_3\text{CN})_3\text{Mn}(\text{CO})_3]^+$  in the reaction between  $[(\eta^6\text{-arene})\text{Mn}(\text{CO})_3]^+$  and  $\text{CH}_3\text{CN}$  [1].

#### *Formation of $\eta^6\text{-arenemonocarbonyl-bis-(diphenylphosphino)alkanemanganesehexafluorophosphate}$*

No substitution of two of the carbonyl groups of  $[(\eta^6\text{-arene})\text{Mn}(\text{CO})_3]\text{PF}_6$  by ditertiary phosphines occurred upon prolonged refluxing,  $[\text{cis and trans-Mn}(\text{CO})_2(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)_2]^+$  being formed as discussed above. However, the complexes in which two carbonyl ligands have been replaced can be prepared by



Scheme 2.

activation of one of the two remaining carbonyl groups of the appropriate monosubstituted complex, i.e.  $[(\eta^6\text{-arene})\text{Mn(CO)}_2(\eta^1\text{-Ph}_2\text{P(CH}_2)_n\text{PPh}_2)]^+$  by use of trimethylamine-*N*-oxide (TMNO), which results in rapid formation of the chelates  $[(\eta^6\text{-arene})\text{Mn(CO)}(\eta^2\text{-PPh}_2(\text{CH}_2)_n\text{PPh}_2)]^+$  (Scheme 1) which were characterized by both analytical data and IR (Table 1) and NMR spectroscopy (Tables 2 and 3). A single infrared  $\nu(\text{CO})$  peak is observed, with frequencies increasing in the sequence  $[(\eta^6\text{-arene})\text{Mn(CO)}_3]^+ > [(\eta^6\text{-arene})\text{Mn(CO)}_2(\eta^1\text{-Ph}_2\text{P(CH}_2)_n\text{PPh}_2)]^+ > [(\eta^6\text{-arene})\text{Mn(CO)}(\eta^2\text{-Ph}_2\text{P(CH}_2)_n\text{PPh}_2)]^+$ , as expected for successive replacement of CO groups by the poorer  $\pi$ -accepting ditertiaryphosphine ligands.

The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  spectra show interesting features. For example, the  $^1\text{H}$  NMR spectrum of  $[(\text{C}_6\text{H}_6)\text{Mn(CO)}(\eta^2\text{-dppm})]\text{PF}_6$  shows a triplet at  $\delta$  5.58 ppm for the benzene protons due to coupling with  $^{31}\text{P}$  ( $J(\text{HP}) = 2.01$  Hz) and non-equivalence of the  $\text{CH}_2$  protons, which form an AB system, with one proton with  $\delta$  5.09 ppm as a sextet and the other as a sextet at  $\delta$  3.93, the two sets being split by coupling with each other with ( $J_{\text{AB}} = 16.3$  Hz) and with the two phosphorus atoms ( $J(\text{P-CH}_2) = 10.4$  Hz), as reported previously for the analogous  $[(\text{C}_7\text{H}_7)\text{Mo(CO)}(\eta^2\text{-dppm})]\text{PF}_6$  and  $[(\text{C}_5\text{H}_5)\text{Fe(CO)}(\eta^2\text{-dppm})]\text{PF}_6$  [4]. In the  $^{13}\text{C}$  NMR spectrum, the  $\text{CH}_2$  carbon

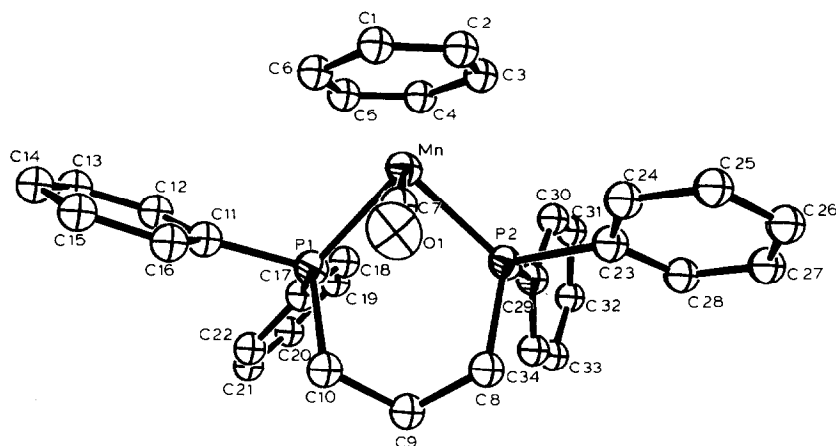


Fig. 1. ORTEP view of  $[(\eta^6\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})(\eta^2\text{-PPh}_2\text{C}_3\text{H}_6\text{PPh}_2)]^+$ .

resonance is observed as a triplet at  $\delta$  46.17 ppm due to coupling with the two phosphorus atoms.

The  $^{31}\text{P}$  NMR spectra of this series of complexes show only a single resonance at low field, as expected for the two equivalently-co-ordinated phosphorus atoms, e.g.  $[(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})(\eta^2\text{-dppm})]\text{PF}_6$  shows a singlet at  $\delta$  58.46 ppm. In this series of complexes, the chelate ring size has a large influence on the change in the  $^{31}\text{P}$  chemical shift on chelation. Thus the chelation shift (defined as the difference in  $^{31}\text{P}$  chemical shift between the coordinated phosphorus atom in the monodentate complex and that in the chelated complex ( $\delta_{\text{chelate}} - \delta_{\text{co-ord}}$ ) [7]) for the four-membered and six-membered rings is negative (considerably upfield from those for the monodentate complexes), whereas the five-membered ring complexes show positive chelation shifts (considerably downfield from those of the monodentate complexes). Similar behaviour has been observed for the complexes  $[(\text{C}_7\text{H}_7)\text{Mo}(\text{CO})\text{Ph}_2\text{-P}(\text{CH}_2)_n\text{PPh}_2]\text{PF}_6$ ,  $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]\text{PF}_6$  [4] and in the case of *fac-mer*- $[\text{Mo}(\text{CO})_3(\text{dppm})]$  [19] as well as  $[\text{W}(\text{CO})_4\text{dppm}]$  [20].

#### *X-ray structure of $[(\eta^6\text{-arene})\text{Mn}(\text{CO})\text{Ph}_2\text{PC}_3\text{H}_6\text{PPh}_2]\text{PF}_6 \cdot 2\text{CH}_3\text{CN}$*

As shown both by the ORTEP view (Fig. 1) and the structural parameters (Table 5), the structure is normal. The Mn–C–O linkage is linear ( $178.2(7)^\circ$ ) and the bite angle ( $\text{P}_1\text{--Mn--P}_2$ ) is  $88.9(1)^\circ$ . The benzene ring carbons are planar. The Mn–C(ring) bond distances average  $2.174(9)$  Å and the Mn–P distances are  $2.276(2)$  Å, similar to those in  $(6\text{-exo-Ph,1-}\sigma,3\text{-5-}\eta\text{-C}_6\text{H}_7)\text{Mn}(\text{NO})\text{dppen}$  (where dppen = *cis*-1,2-bis(diphenylphosphino)ethylene)  $2.260(2)$  Å [21] but shorter than those in  $[\text{cis-Mn}(\text{CO})_2(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2]^+$   $2.423(2)$  Å and  $[\text{trans-Mn}(\text{CO})_2(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2]^+$   $2.317(2)$  Å [15].

#### Experimental

All solvents were dried prior to use. The  $\eta^6$ -arenetricarbonylmanganese cations were prepared by published methods [22,23]. Bis(diphenylphosphino)methane, bis(diphenylphosphino)ethane, and bis(diphenylphosphino)propane were used

Table 5

Selected bond distances (Å) and angles (deg.) for  $[(\eta^6\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})(\eta^2\text{-PPh}_2\text{C}_3\text{H}_6\text{PPh}_2)]\text{PF}_6$ 

| <i>Bond distances</i> |          |            |          |
|-----------------------|----------|------------|----------|
| Mn–P1                 | 2.275(2) | Mn–P2      | 2.276(2) |
| Mn–C7                 | 1.779(8) | O–C7       | 1.154(9) |
| P1–C10                | 1.812(8) | P2–C8      | 1.828(8) |
| C8–C9                 | 1.52(1)  | C9–C10     | 1.55(1)  |
| P1–C11                | 1.835(9) | P1–C17     | 1.840(8) |
| P2–C23                | 1.841(8) | P2–C29     | 1.829(8) |
| Mn–C1                 | 2.16(1)  | Mn–C2      | 2.161(9) |
| Mn–C3                 | 2.185(8) | Mn–C4      | 2.199(9) |
| Mn–C5                 | 2.176(8) | Mn–C6      | 2.146(9) |
| C1–C2                 | 1.38(1)  | C2–C3      | 1.41(1)  |
| C3–C4                 | 1.44(1)  | C4–C5      | 1.36(1)  |
| C5–C6                 | 1.40(1)  | C1–C6      | 1.44(1)  |
| <i>Bond angles</i>    |          |            |          |
| P1–Mn–P2              | 88.9(1)  | C23–P2–Mn  | 116.0(3) |
| C11–P1–Mn             | 111.3(3) | C17–P1–Mn  | 121.4(3) |
| C29–P2–Mn             | 120.1(3) | C10–P1–Mn  | 114.3(3) |
| C8–P2–Mn              | 114.4(3) | C9–C10–P1  | 113.2(6) |
| C10–C9–C8             | 113.0(7) | C9–C8–P2   | 118.8(6) |
| C23–P2–C8             | 98.2(3)  | C11–P1–C10 | 103.0(4) |
| C29–P2–C8             | 104.1(3) | C7–Mn–P1   | 86.1(3)  |
| C7–Mn–P2              | 86.6(3)  | C29–P2–C23 | 100.9(3) |
| C17–P1–C11            | 102.5(4) | O–C7–Mn    | 178.4(7) |
| C7–Mn–C1              | 83.4(4)  | C7–Mn–C2   | 93.3(3)  |
| C7–Mn–C3              | 126.3(3) | C7–Mn–C4   | 161.7(3) |
| C7–Mn–C5              | 141.3(3) | C7–Mn–C6   | 104.2(4) |
| C1–Mn–P1              | 125.3(3) | C1–Mn–P2   | 143.4(3) |
| C2–Mn–P1              | 162.2(2) | C2–Mn–P2   | 108.8(2) |
| C3–Mn–P1              | 147.5(2) | C3–Mn–P2   | 91.0(2)  |
| C4–Mn–P1              | 110.2(2) | C4–Mn–P2   | 101.4(2) |
| C5–Mn–P1              | 88.9(2)  | C5–Mn–P2   | 131.7(2) |
| C6–Mn–P1              | 93.8(3)  | C6–Mn–P2   | 169.0(3) |

without further purification. Analytical results were obtained by the microanalytical laboratory of the Chemical Services Unit of University College, Dublin. Infrared spectra in the carbonyl region were recorded on a Perkin–Elmer 1720FT spectrometer linked to a Perkin–Elmer 3700 data station, using a 0.1 mm  $\text{CaF}_2$  cell.

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were recorded on the JEOL GX270 spectrometer by the Chemical Services Unit of University College, Dublin. Reactions were performed under nitrogen, except for in the case of the preparations of *cis*- and *trans*- $[\text{Mn}(\text{CO})_2(\eta^2\text{-dppm})_2]\text{PF}_6$  and *trans*- $[\text{Mn}(\text{CO})_2(\eta^2\text{-dppe})_2]\text{PF}_6$ .

#### *Preparation of $[(\eta^6\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})_2(\eta^1\text{-dppm})]\text{PF}_6$*

Bis(diphenylphosphino)methane (0.77 g, 2.01 mmol) was added to a stirred solution of  $\eta^6$ -arenetricarbonylmanganese hexafluorophosphate (0.73 g, 2.02 mmol) in acetone (100 ml) at room temperature. The reaction was monitored by IR spectroscopy in the carbonyl stretching region until complete removal of the starting material (ca. 4 h) was indicated. Addition of ether led to precipitation of the

product as yellow crystals which were filtered off and recrystallized from dichloromethane/hexane, yield (1.2 g, 83%). The product was stable for several months under  $N_2$  at  $0^\circ C$ .

$[(\eta^6-C_6H_6)Mn(CO)_2(\eta^1-dppe)]PF_6$ ,  $[(\eta^6-C_6H_6)Mn(CO)_2(\eta^1-dppp)]PF_6$  and  $[(\eta^6-C_6H_5CH_3)Mn(CO)_2PhP(CH_2)_nPPh_2]PF_6$  ( $n = 1-3$ ) were prepared similarly.

*Attempted preparation of  $[(\eta^6-C_6H_5Cl)Mn(CO)_2(\eta^1-dppe)]PF_6$*

Bis(diphenylphosphino)ethane (0.5 g, 1.26 mmol) was added to a solution of the  $\eta^6$ -chlorobenzenetricarbonylmanganese hexafluorophosphate (0.5 g, 1.26 mmol) in acetone (50 ml). The mixture was stirred for 10 mins and the reaction monitored by IR spectroscopy, which revealed three  $\nu(CO)$  peaks at 2021, 1950 and  $1915\text{ cm}^{-1}$  corresponding to *fac*- $Mn(CO)_3(\eta^2-dppe)Cl$  together with two other peaks at 2085 and  $2032\text{ cm}^{-1}$  due to the starting material. On completion of the reaction, removal of the solvent and recrystallization from *n*-pentane at  $-78^\circ C$  yielded the *fac*- $Mn(CO)_3(\eta^2-dppe)Cl$  as yellow crystals.

*Preparation of  $[cis-Mn(CO)_2(\eta^2-dppm)_2]PF_6$*

Bis(diphenylphosphino)methane (0.96 g, 2.5 mmol) was added to a solution of  $[(XYC_6H_4)Mn(CO)_3]PF_6$  ( $X = Y = H$ ;  $X = Me$ ,  $Y = H$ ) (0.3 g, 0.83 mmol) in acetone (50 ml). Refluxing for 2 h gave only the monosubstituted product, as indicated by its IR spectrum ( $\nu(CO)$  2003 and  $1958\text{ cm}^{-1}$ ). However, during prolonged refluxing (ca. 60 h) a crystalline material was formed, and after filtration was identified from its IR spectrum ( $\nu(CO)$   $1958\text{ cm}^{-1}$  and  $1904\text{ cm}^{-1}$ ) as  $[cis-Mn(CO)_2(\eta^2-dppm)_2]PF_6$ . Addition of ether to the filtrate gave more of the *cis* product as bright yellow crystals, although the crystals formed during the refluxing were of higher purity.

*Isomerization of  $[cis-Mn(CO)_2(\eta^2-dppm)_2]PF_6$  to  $trans-Mn(CO)_2(\eta^2-dppm)_2]PF_6$*

This *cis* complex  $[Mn(CO)_2(\eta^2-dppm)_2]PF_6$  is very stable in the solid state for several months. However, when a yellow acetonitrile solution was kept in daylight, isomerisation occurred, to give an orange solution showing a single  $\nu(CO)$  stretching frequency at  $1865\text{ cm}^{-1}$ . Removal of the solvent under reduced pressure and recrystallization of the orange residue from dichloromethane/hexane gave the pure product as orange crystals.

*Preparation of  $trans-[Mn(CO)_2(\eta^2-dppe)_2]PF_6$*

The same procedure described above was applied to bis(diphenylphosphino)ethane (0.66 g, 1.66 mmol). Again the monosubstituted product was formed initially, but after prolonged reflux the IR spectrum showed only a single band at  $1897\text{ cm}^{-1}$ . After complete conversion to the *trans* adduct, the solution was allowed to cool, and ether was added to precipitate the product as light orange crystals.

*Preparation of  $[(C_6H_6)Mn(CO)(\eta^2-dppm)]PF_6$*

Trimethylamine-*N*-oxide (TMNO) (0.079 g, 0.71 mmol) was added to a solution of  $\eta^6$ -benzenedicarbonyl-bis-(diphenylphosphino)methanemanganese hexafluorophosphate (0.5 g, 0.7 mmol) in acetone (60 ml) at room temperature. The orange solution was stirred for 6 h and then filtered to remove undissolved TMNO. Addition of ether precipitated the product as an orange powder. Recrystallization

Table 6

Crystal data for  $[(\eta^6\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})(\eta^2\text{-PPh}_2\text{C}_3\text{H}_6\text{PPh}_2)]\text{PF}_6 \cdot 2\text{CH}_3\text{CN}$ 

|                                           |                                                            |
|-------------------------------------------|------------------------------------------------------------|
| Crystal size (mm)                         | $0.25 \times 0.33 \times 0.3$                              |
| Formula                                   | $\text{C}_{38}\text{H}_{38}\text{F}_6\text{OP}_3\text{Mn}$ |
| M (a.m.u.)                                | 772.567                                                    |
| Monoclinic space group                    | $\text{P}2_1/\text{c}$                                     |
| $a$ (Å)                                   | 10.943(3)                                                  |
| $b$ (Å)                                   | 17.917(2)                                                  |
| $c$ (Å)                                   | 19.093(5)                                                  |
| $\beta$ (°)                               | 99.14(2)                                                   |
| $U$ (Å <sup>3</sup> )                     | 3696.29                                                    |
| $Z$                                       | 4                                                          |
| $D_c$ (g cm <sup>-3</sup> )               | 1.39                                                       |
| $\mu$ (cm <sup>-1</sup> )                 | 5.45                                                       |
| $F(000)$                                  | 1652                                                       |
| Radiation Mo- $K_\alpha$                  |                                                            |
| Graphite monochromator                    | $\lambda = 0.7093$ Å                                       |
| Diffractionmeter                          | Enraf-Nonius CAD4F                                         |
| Orienting reflections, Range              | $25, 13 < \theta < 20^\circ$                               |
| Temperature (°C)                          | 22                                                         |
| Scan method                               | $\omega - 2\theta$                                         |
| Data collection range                     | $2 < 2\theta < 48^\circ$                                   |
| No. unique data                           | 5770                                                       |
| Total $I > 3\sigma(I)$                    | 3698                                                       |
| No. of Parameters Fitted                  | 266                                                        |
| $R^a, R_w^b$                              | 9.13%, 10.45%                                              |
| Quality-of-fit indicator <sup>c</sup>     | 1.002                                                      |
| Largest shift/esd, final cycle            | < 0.01                                                     |
| Largest positive peak (e/Å <sup>3</sup> ) | 0.46                                                       |
| Largest negative peak (e/Å <sup>3</sup> ) | -0.48                                                      |

<sup>a</sup>  $R = [\sum ||F_o| - |F_c||] / \sum |F_o|$ . <sup>b</sup>  $R_w = \{[\sum w(|F_o - F_c|)^2] / [\sum w(|F_o|)^2]\}^{1/2}$ ;  $w = 1 / [(\sigma F_o)^2 - 0.0017 \cdot F_o^2]$ .<sup>c</sup> Quality-of-fit =  $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{par}})]^{1/2}$ .

from acetonitrile/ether yielded fine orange crystals (0.39 g, 81%). This complex is stable at 0°C under N<sub>2</sub> for several months.

The analogous complexes  $[(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]\text{PF}_6$  and  $[(\text{C}_6\text{H}_5\text{CH}_3)\text{Mn}(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)]\text{PF}_6$  ( $n = 1-3$ ) were prepared similarly.

#### *X-Ray structure of $[(\eta^6\text{-arene})\text{Mn}(\text{CO})\text{Ph}_2\text{PC}_3\text{H}_6\text{PPh}_2]\text{PF}_6 \cdot 2\text{CH}_3\text{CN}$*

A suitable crystal was grown by slow diffusion of diethyl ether into a saturated acetonitrile solution of  $[(\eta^6\text{-benzene})\text{Mn}(\text{CO})\text{Ph}_2\text{PC}_3\text{H}_6\text{PPh}_2]\text{PF}_6$  at ambient temperature. It was mounted in a glass tube and kept in a refrigerator for several weeks.

Crystal data and some experimental details are shown in Table 6. The structure was solved by direct methods, SHELX86 [24], and refined by full-matrix least-squares using SHELX76 [25]. Data were corrected for Lorentz and polarization effects but not for absorption. Hydrogen atoms were included in calculated positions with fixed thermal parameters. The manganese, phosphorous, fluorine and oxygen atoms were refined anisotropically. The thermal terms  $U_{ij}$  were  $\exp(-2\pi^2(U_{11} \cdot h^2 a^{*2} + U_{22} \cdot k^2 b^{*2} + U_{33} \cdot l^2 c^{*2} + 2U_{12} \cdot hka^*b^* + 2U_{23} \cdot klb^*c^*))$ . The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction

Table 7

Atomic coordinates (Å) for  $[(\eta^6\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})(\eta^2\text{-PPh}_2\text{C}_3\text{H}_6\text{PPh}_2)]\text{PF}_6 \cdot 2\text{CH}_3\text{CN}$ 

| Atom   | x           | y           | z           |
|--------|-------------|-------------|-------------|
| Mn(1)  | 0.12035(10) | 0.44039(6)  | 0.23979(6)  |
| P(2)   | 0.10728(17) | 0.36412(11) | 0.14355(11) |
| P(1)   | 0.04013(18) | 0.34691(11) | 0.29915(11) |
| P(3)   | 0.5910(2)   | 0.5803(1)   | 0.2333(1)   |
| F(1)   | 0.4843(5)   | 0.5932(4)   | 0.1677(4)   |
| F(2)   | 0.5290(8)   | 0.5041(4)   | 0.2465(5)   |
| F(3)   | 0.6944(6)   | 0.5649(6)   | 0.2966(4)   |
| F(4)   | 0.6485(13)  | 0.6532(7)   | 0.2164(8)   |
| F(5)   | 0.5063(6)   | 0.6136(6)   | 0.2815(5)   |
| F(6)   | 0.6677(9)   | 0.5405(7)   | 0.1806(5)   |
| O(1)   | 0.3630(5)   | 0.3731(4)   | 0.2892(4)   |
| C(1)   | 0.2100(9)   | 0.5394(5)   | 0.2879(5)   |
| C(2)   | 0.2006(8)   | 0.5455(5)   | 0.2152(4)   |
| C(3)   | 0.0850(8)   | 0.5383(4)   | 0.1714(4)   |
| C(4)   | -0.0232(8)  | 0.5236(5)   | 0.2029(4)   |
| C(5)   | -0.0125(8)  | 0.5167(5)   | 0.2747(4)   |
| C(6)   | 0.1021(8)   | 0.5226(5)   | 0.3192(5)   |
| C(7)   | 0.2670(8)   | 0.3986(4)   | 0.2693(5)   |
| C(8)   | 0.1541(7)   | 0.2677(4)   | 0.1643(4)   |
| C(9)   | 0.0891(8)   | 0.2243(5)   | 0.2158(4)   |
| C(10)  | 0.1125(8)   | 0.2568(4)   | 0.2922(4)   |
| C(11)  | 0.0657(8)   | 0.3642(5)   | 0.3951(5)   |
| C(12)  | -0.0310(10) | 0.3892(5)   | 0.4290(5)   |
| C(13)  | -0.0089(11) | 0.4044(6)   | 0.5007(6)   |
| C(14)  | 0.1035(12)  | 0.3981(7)   | 0.5383(6)   |
| C(15)  | 0.2019(13)  | 0.3733(7)   | 0.5083(7)   |
| C(16)  | 0.1817(10)  | 0.3546(6)   | 0.4348(6)   |
| C(17)  | -0.1256(7)  | 0.3234(4)   | 0.2809(4)   |
| C(18)  | -0.2048(8)  | 0.3618(5)   | 0.2305(4)   |
| C(19)  | -0.3280(11) | 0.3424(6)   | 0.2175(6)   |
| C(20)  | -0.3723(11) | 0.2857(6)   | 0.2535(5)   |
| C(21)  | -0.2955(10) | 0.2472(6)   | 0.3020(5)   |
| C(22)  | -0.1697(9)  | 0.2675(5)   | 0.3187(5)   |
| C(23)  | 0.2148(7)   | 0.3846(4)   | 0.0811(4)   |
| C(24)  | 0.3301(7)   | 0.4163(4)   | 0.1048(4)   |
| C(25)  | 0.4156(9)   | 0.4272(5)   | 0.0595(5)   |
| C(26)  | 0.3873(9)   | 0.4049(5)   | -0.0095(5)  |
| C(27)  | 0.2728(9)   | 0.3748(5)   | -0.0358(5)  |
| C(28)  | 0.1883(9)   | 0.3632(5)   | 0.0099(5)   |
| C(29)  | -0.0389(7)  | 0.3554(4)   | 0.0826(4)   |
| C(30)  | -0.0953(9)  | 0.4189(5)   | 0.0519(5)   |
| C(31)  | -0.2046(10) | 0.4138(6)   | 0.0044(5)   |
| C(32)  | -0.2612(10) | 0.3449(6)   | -0.0132(5)  |
| C(33)  | -0.2017(11) | 0.2819(7)   | 0.0161(6)   |
| C(34)  | -0.0940(9)  | 0.2866(5)   | 0.0634(5)   |
| C(101) | 0.5957(18)  | 0.0607(10)  | -0.0939(9)  |
| C(102) | 0.6361(18)  | 0.0599(10)  | -0.0240(13) |
| N(101) | 0.6745(21)  | 0.0658(11)  | 0.0323(15)  |
| C(103) | 0.5078(19)  | 0.2240(12)  | 0.0830(9)   |
| C(104) | 0.4835(20)  | 0.2212(12)  | 0.0066(14)  |
| N(102) | 0.4778(19)  | 0.2155(11)  | -0.0527(13) |

factors for non-hydrogen atoms were taken from the literature [26–28]. All calculation were performed on a VAX 8700 computer. The ORTEP program was used to obtain the drawings [29]. The atom coordinates are shown in Table 7. A complete Table of bond lengths and angles and lists of thermal parameters and structure factors are available from the authors.

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