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PREPARATION OF $[(\eta^5 - MeC_5H_4)Mn(CO)(NO)(DMPP)]PF_6$, DMPP = 1-PHENYL-3,4-DIMETHYLPHOSPHOLE, AND ITS INTRAMOLECULAR [4+2] DIELS-ALDER CYCLOADDITION REACTION WITH Ph₂PCH=CH₂

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ABSTRACT

(η⁵-<u>Me</u>C₅H₄)Mn(CO)₃ reacts with NaNO₂, HCl and KPF₆ to form [(η⁵-<u>Me</u>C₅H₄)Mn(NO)(CO)₂]PF₆(1). Compound (1) reacts with 1-phenyl-3,4dimethylphosphole (DMPP) to form [(η⁵-MeC₅H₄)Mn(NO)(CO)(DMPP)]PF₆(2). Compound (2) reacts with Ph₂PCH=CH₂ (DPVP) to form [(η⁵-MeC₅H₄)Mn(NO) (DMPP)(DPVP)]PF₆(3), which undergoes an intramolecular [4+2] Diels-Alder cycloaddition reaction at 50°C to form [(η⁵-MeC₅H₄)Mn(NO)(2-diphenylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene)]PF₆(4a,b). The new complexes were characterized by elemental analyses, physical properties, infrared spectroscopy, and ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectroscopy. The structures of (2) and (4a) were confirmed by X-ray crystallography. They crystallize in the Pna2₁ and P2₁/n space groups, respectively, in unit cells of the following dimensions: (2): a = 19.333(3)Å, b = 11.011(1)Å, c = 10.562(2)Å, α = β = γ = 90°, ρ(calc) = 1.552 g cm⁻³, Z = 4. (4a): a = 10.932(2)Å, b = 19.220(2)Å, c = 16.957(2)Å, β = 104.62(1)°, ρ(calc) = 1.367 g cm⁻³, Z = 4. Refinements converged

395

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to R(F) = 0.0562 and 0.0752 for 2358 and 4504 independent observed (I $\ge 2\sigma$ (I)) reflections, respectively.

INTRODUCTION

A variety of conformationally rigid asymmetric bidentate ligands have been synthesized by metal promoted intramolecular [4+2] Diels-Alder cycloadditions of phospholes with various dieneophilic ligands.¹ The scope and diastereoselectivity of these reactions depends upon the nature of the metal and its ancillary ligands. Asymmetric synthetic modifications of some of these reactions using palladium complexes containing ortho-metallated chiral amines as a template have recently been reported.^{2,3} Complexes where the metal is a stereocenter⁴ have proven to be useful reagents for stereoselective syntheses.^{5,6} Among the earliest transition metal organometallic complexes containing metal stereocenters to be reported⁷ are complexes of the type $[(\eta^5-C_sH_s)Mn(CO)(NO) (R_3P)$]PF₆. Some of these complexes have been resolved into their configurationally stable optical isomers.^{8.9} In order to increase our understanding of the factors which influence the diastereoselectivity of these unique intramolecular [4+2] Diels-Alder cycloadditions with a goal of developing new synthetic methodology, we have prepared $[(\eta^5-MeC_sH_a)Mn(CO)(NO)(DMPP)]PF_6$ and studied its reaction with the dieneophilic phosphine, Ph₂PCH=CH₂ (DPVP).

RESULTS AND DISCUSSION

Compound (1), $[(\eta^5-\underline{MeC_5H_4})Mn(CO)_2(NO)]PF_6^{10}$, is readily prepared in good (~70%) yield by the method¹¹ used to prepare the $[(\eta^5-C_5H_5)Mn(CO)_2$ (NO)]PF₆ analog. Both of these compounds are pale yellow solids that are stable in the solid state. They are sparingly soluble in methanol or ethanol, quite soluble in acctone, but they decompose therein quickly with the liberation of CO.⁷⁻¹¹ The infrared spectra of both complexes exhibit two strong $\nu(C=O)$ and one strong





δ³¹P: 59.15 (DMPP), -144.77 (PF₆)



 δ^{31} P: 60.57d (DMPP), 57.62d (DPVP); ${}^2J_{PP} = 50.43$ Hz, - 144.77 (PF₆)



 $δ^{31}$ P: 170.99 d(P₂), 86.05 d(P₂) 168.32 d(P₂), 74.96 d(P₁) ²J_{PP} = 50.3 Hz, -144.97 (PF₆) ²J_{PP} = 53.65 Hz, -144.97 (PF₆)

Scheme 1

v(N=O) vibration at 2113, 2071, 1841 and 2119, 2080, and 1853 cm⁻¹, respectively. Thus, the better donor MeC₅H₄ increases slightly the Mn-CO and Mn-NO π -back bonding.

An ethanol solution of (1) reacts slowly at ambient temperature with 1phenyl-3,4-dimethylphosphole (DMPP) to form $[(\eta^5-MeC_5H_4)Mn(CO)(NO)$ (DMPP)]PF₆(2) in high (~87%) yield. This golden-yellow crystalline compound is stable in the solid state and in acetone or nitromethane solutions. Its infrared spectrum displays strong $\upsilon(C=O)$ and $\upsilon(N=O)$ vibrations at 2042 and 1800 cm⁻¹. By way of comparison, these vibrations occur¹⁰ at 2039 and 1797 cm⁻¹ for $[(\eta^5-$ <u>MeC_5H_4)Mn(CO)(NO)(PPh_3)]PF_6</u>.

Compound (2) reacts slowly in acetone at 50°C with diphenylvinylphosphine (DPVP, Scheme 1) to form $[(\eta^5-MeC_sH_4)Mn(NO)(DMPP)(DPVP)]PF_4$ (3) which subsequently undergoes an intramolecular [4+2] Diels-Alder cycloaddition to form a 1:1 ratio of (4a) and (4b). The reaction was monitored by ${}^{31}P{}^{1}H{}$ NMR spectroscopy. The singlet for (2) was slowly replaced by an AB quartet for (3), which then diminished in intensity as two pairs of doublets appeared for (4a) and (4b). This is one of the few cases where the mixed ligand intermediate has been observed in these intramolecular [4+2] Diels-Alder cycloaddition reactions.¹² The diastereomer (4a) may be readily distinguished¹³ from the diastereomer (4b) on the basis of the difference in the chemical shifts of the resonances for P_1 and P_2 . The difference is always larger for diastercomers (b) than for diastereomers (a). Here the chemical shift differences are 84.94 (4a) and 93.36 (4b) ppm. Complexes (2) and (4a) were fully characterized by elemental analyses, infrared spectroscopy, and ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopy (see experimental section). Assignments were made by previously described techniques with the atom numbering schemes similar to those used previously.¹² These data show that these two complexes have three-legged piano stool structures as expected.

In order to confirm the structure of (4a) an X-ray crystal structure was obtained (Figure 1). A crystal structure of (2) was also obtained for comparison



Figure 1. Structure of the Cation of (4a) (top) (40% Probability Ellipsoids). Selected Distances (Å) and Angles (deg) are: Mn-P(1) = 2.292(1), Mn-P(2) = 2.243(2), Mn-N(1) = 1.632(8), N(1)-O(1) = 1.161(7), Mn-C(ave) = 2.150(10). P(1)-Mn-P(2) = 81.78(8), P(1)-Mn-N(1) = 94.5(2), P(2)-Mn-N(1) = 96.7(2), Mn-N(1)-O(1) = 176.0(7), C(21)-P(2)-C(24) = 80.6(3). A view of the cation normal to the MeC₅H₄ centroid (bottom).

purposes (Figure 2). Both structures consist of isolated cations and anions with no short contacts. Selected bond distances and angles are given in the figure captions. Both complexes contain linear NO groups. The Mn-N [1.632(8)Å, (4a); 1.752(9)Å, (2)] and N-O[1.161(7)Å, (4a); 1.137(11)Å, (2)] distances are consistent with more Mn-N π -back donation from the more electron rich Mn center in (4a). The Mn-P(2) distance in (4a) (2.243(2)Å) is shorter than the Mn-P(1) distance (2.278(2)Å) in (2) due to the chelate effect and also shorter than the Mn-P(1) distance $(2.292(1)\text{\AA})$ in (4a). The difference in the two Mn-P distances in (4a) is less than normally observed in complexes of this ligand.¹² For example in (5)(Figure 3) the Fe-P(2) distance (2.165(3)Å) is much shorter than the Fe-P(1) distance (2.258(3)Å). Note, however, that (5) contains the (b) diastereomer of the ligand which experiences a lesser degree of intramolecular steric interactions than does the (a) diastercomer present in (4a). These steric interactions have been the primary cause of the diastereoselectivity seen in all the previous reactions. With the manganese system, for reasons that are not clear to us, there is no diastereoselectivity in the intramolecular [4+2] Diels-Alder cycloaddition.

EXPERIMENTAL

Instruments

Physical and spectroscopic measurements were obtained as previously described.¹

<u>Synthesis</u>

 $[(\eta^{5}-MeC_{5}H_{4})Mn(CO)_{2}(NO)]PF_{6}(1)$. A solution containing 12.00 g (5.52 x 10⁻² mol) of $[(\eta^{5}-MeC_{5}H_{4})Mn(CO)_{3}]$ (Pressure Chemical Co.), 180 ml 95% ethanol and 36 ml of 12 M HCl was purged with nitrogen for twenty minutes and then heated to a gentle reflux. To this solution was slowly added a solution of 4.2 g (6.08 x 10⁻² mol) NaNO₂ in 10 ml of water with stirring over a period of 2 h. The reaction mixture was allowed to cool to ambient temperature and filtered by



Figure 2. Structure of the Cation of (2) (40% Probability Ellipsoids). Selected Distances (Å) and Angles (deg) are: Mn(1)-C(7) = 1.737(10), Mn(1)-N(1) = 1.752(9), Mn(1)-P(1) = 2.278(2), N(1)-O(2) = 1.137(11), C(7)-O(1) = 1.147(10), Mn(1)-C(ave) = 2.137(10). P(1)-Mn(1)-C(7) = 94.2(3), P(1)-Mn(1)-N(1) = 93.1(3), N(1)-Mn(1)-C(7) = 96.7(4), Mn(1)-C(7)-O(1) = 177.3(8), Mn(1)-N(1)-O(2) = 175.0(8), C(8)-P(1)-C(13) = 91.9(4).



Figure 3. A representation of the structure of (5).¹²

suction into a flask containing 12 g (6.85 x 10^{-2} mol) KPF₆ dissolved in 20 ml of water. After this mixture had remained at ambient temperature for 2 h, the bright yellow precipitate that formed was collected by filtration and washed with distilled water. The pure product was obtained by dissolving the crude product in a minimum volume of dry acetone and rapidly filtering this solution into a flask containing 40 ml of cold diethyl ether. Some product will decompose in acetone during the purification. The lemon yellow microcrystalline solid was isolated by filtration, washed with ether and vacuum dried to yield 8.43 g (69.6%) melting point 220-223°C. IR (Nujol) v(C=O), 2113, 2071 cm⁻¹, v(N=O), 1841 cm⁻¹. Anal. calcd. For C₈H₇F₆MnNO₃P (fw 365.0) C, 26.33, H, 1.92. Found (Galbraith): C, 26.07; H, 2.10.

 $[(\eta^{5}-MeC_{\xi}H_{4})Mn(CO)(NO)(DMPP)]PF_{\xi}(2)$. A solution containing 4.0 ml (2.12 x 10^{-2} mol) of DMPP¹⁴ and 6.00 g (1.65 x 10^{-2} mol) of (1) was stirred under nitrogen at ambient temperature for 48 h. The pale yellow solution became orange as an orange solid slowly precipitated. The solid was isolated by filtration and extracted with CH₂Cl₂. The CH₂Cl₂ was removed on a rotary evaporator to yield 9.05 g (86.5%) of golden-yellow microcrystals, melting point 170-172°C. Anal. calcd. for C₁₉H₂₀F₆MnNO₂P₂ (fw 525.2) C, 43.46; H, 3.81. Found: C, 43.27; H, 3.59. IR (Nujol) v(C=O) 2042 cm⁻¹, v(N=O) 1800 cm⁻¹. ³¹P{¹H} NMR (121.6 MHz, acetone-d₆) δ 59.15 (s, 1P, DMPP), -144.77 (sept. 1P, ¹J(PF) = 712.7 Hz, PF₆). ¹H NMR (500 MHz, acetone-d₆) δ 7.73 (m, 2H, PhH_m), 7.59 (m, 3H, PhH_{ove}), 7.08 (d, 1H, ${}^{2}J(PH) = 36.5 Hz$, H_{π}), 7.05 (d, 1H, ${}^{2}J(PH) = 36.5 Hz$, H_{π}), 5.75 (s, 1H, $C_{5}H_{4}$), 5.67 (s, 1H, C₅H₄), 5.58 (s, 1H, C₅H₄), 5.45 (s, 1H, C₅H₄), 2.29 (s, 3H, DMPP-CH₃), 2.28 (s, 3H, DMPP-CH₃), 2.09 (s, MeC₅H₄). ¹³C{¹H} NMR (125.7 MHz, acetone-d₆) δ 223.87 (d, ²J(PC) = 20.5 Hz, CO), 155.44 (d, ²J(PC) = 10.6 Hz, C_{β}), 154.55 (d, ²J(PC) = 10.4 Hz, C_{β}), 132.72 (d, ⁴J(PC) = 3.0 Hz, C_{ρ}), 132.22 (d, ${}^{2}J(PC) = 10.4 \text{ Hz}, C_{o}$, 130.49 (d, ${}^{3}J(PC) = 11.1 \text{ Hz}, C_{m}$), 128.82 (d, ${}^{1}J(PC) = 48.9$ Hz, C_i), 126.04 (d, ¹J(PC) = 50.8 Hz, C_a), 125.17 (d, ¹J(PC) = 50.4 Hz, C_a),

114.83, 96.08, 95.66, 94.47, 93.45 (5 s's, C_5H_4), 17.67 (d, ³J(PC) = 13.8 Hz, DMPP-CH₃), 17.53 (d, ³J(PC) = 13.8 Hz, DMPP-CH₃), 12.90 (s, <u>Me</u>C₅H₄).

 $[(\eta^5-MeC_{c}H_{4})Mn(NO)(DMPP-DPVP-[4+2])]PF_{c}$ (4a). A solution containing 1.00 g (2.63 x 10^{-3} mol) of (2) and 0.60 ml (2.63 x 10^{-3} mol) of Ph₂PCH=CH₂ (Organometallics) in 125 ml of dry acetone was refluxed gently under nitrogen for 48 h. The deep red mixture was cooled to ambient temperature, sealed under nitrogen and left standing for one week. The solvent was removed on a rotary evaporator and the residue was recrystallized from CH₂Cl₂/hexane (1:4) to yield 0.59 g (44.0%) of dark red crystals, melting point 254-255°C. Anal. calcd. for C₁₂H₁₃F₆MnNOP₃ (fw 709.4) C, 54.19; H, 4.65. Found: C, 54.24; H, 4.53. IR (Nujol) v(N=O) 1848 cm⁻¹. ³¹P{¹H} NMR (202.3 MHz, acetone-d₆). (4a) δ 170.99 (d, 1P, P₁), 86.05 (d, 1P, P₂, ${}^{2}J(PP) = 50.3 \text{ Hz}$), -144.97 (sept. 1P, ${}^{1}J(PF) = 707.6$ Hz, PF_6). (4b) This compound was only characterized by ${}^{31}P{}^{1}H$ NMR spectroscopy of the crude reaction mixture. δ 168.32 (d, P₂), 74.96 (d, P₁, ²J(PP) = 53.65 Hz), -144.97 (sept, ${}^{1}J(PF) = 707.6$ Hz, PF₆). ${}^{1}H$ NMR (500 MHz, CD₃NO₂) (See Figure 4) δ 7.86-7.36 (m, 15H, Ph), 5.37, 4.58, 4.44, 4.34, (4s's, 4H, C,H₄), 3.91 (m, 1H, H_s), 3.68 (ddddd, ${}^{3}J(PH) = 37.0 \text{ Hz}$, ${}^{2}J(PH) = 9.0 \text{ Hz}$, ${}^{3}J(H_{2}H_{4}) = 9.0$ Hz, ${}^{2}J(H_{1}H_{2}) = 2.0 Hz$, ${}^{3}J(H_{2}H_{4}) = 2.0 Hz$, 1H, H_{2}), $3.67 (m, 1H, H_{1})$, $2.05 (m, 2H, 1H, 1H_{2})$, $3.67 (m, 1H, 1H_{1})$, $2.05 (m, 2H, 1H, 1H_{2})$, $3.67 (m, 1H, 1H_{1})$, $3.67 (m, 1H, 1H_{1})$, $3.67 (m, 2H, 1H, 1H_{2})$, 3.67 (m, 2H, 1HH₃₄), 2.02 (s, 3H, MeC₅H₄), 1.86 (s, 3H, DMPP-CH₃), 1.57 (s, 3H, DMPP-CH₃). $^{13}C{^{1}H}$ NMR (125.7 MHz, acetone-d₆). δ 139.44 (s, C₅ or C₆), 136.78 (s, C₆ or C_s), 135.13 (d, ²J(PC) = 10.3 Hz, C_o), 135.12 (d, ¹J(PC) = 50.3 Hz, C_i), 132.68 (d, ${}^{4}J(PC) = 2.4 \text{ Hz}, C_{p}, 132.50 \text{ (d, } {}^{2}J(PC) = 9.2 \text{ Hz}, C_{p}, 132.31 \text{ (d, } {}^{2}J(PC) = 8.9 \text{ Hz},$ C_o), 132.08 (d, ⁴J(PC) = 2.4 Hz, C_n), 131.88 (d, ¹J(PC) = 46.3 Hz, C_i), 131.83 (d, ${}^{4}J(PC) = 2.5 \text{ Hz}, C_{0}, 131.76 \text{ (d}, {}^{1}J(PC) = 46.6 \text{ Hz}, C_{0}, 130.32 \text{ (d}, {}^{3}J(PC) = 10.4 \text{ Hz}, C_{0}, 13$ Hz, C_m), 130.26 (d, ³J(PC) = 9.4 Hz, C_m), 130.04 (d, ³J(PC) = 9.8 Hz, C_m), 110.37, 96.15, 92.18, 91.57, 90.73, (5 s's, C_5H_4), 57.72 (dd, ¹J(PC) = 30.0 Hz, ²J(PC) = 10.8 Hz, C₁), 50.26 (dd, ${}^{1}J(PC) = 28.8$ Hz, ${}^{3}J(PC) = 1.6$ Hz, C₄), 33.74 (dd, ${}^{1}J(PC)$ $= 34.5 \text{ Hz}, {}^{2}\text{J}(\text{PC}) = 25.8 \text{ Hz}, \text{C}_{2}, 32.04 \text{ (dd}, {}^{2}\text{J}(\text{PC}) = 14.0 \text{ Hz}, {}^{2}\text{J}(\text{PC}) = 3.4 \text{ Hz},$ C₃), 15.34 (s, <u>Me</u>C₅H₄), 13.68 (d, ³J(PC) = 3.1 Hz, C₆-CH₃), 12.98 (s, C₅-CH₃).



Figure 4. Atom numbering scheme for (4a) and (4b).

Table I

Crystallographic Data

Compound

	(2)	(4a)
Formula	$C_{19}H_{20}F_6MnNOP_2$	$C_{32}H_{33}F_6MnNOP_3$
fw	525.24	709.44
cryst. syst.	orthorhombic	monoclinic
space group	Pna2 ₁	P2 ₁ /n
a(Å)	19.333(3)	10.932(2)
b(Å)	11.0113(10)	19.220(2)
c(Å)	10.562(2)	16.957(2)
$\beta(deg)$	90	104.62(1)
V(Å ³)	2248.5(5)	3447.6(8)
Z	4	4
pcalcd (Mg/m ³)	1.552	1.367
$\mu(\text{mm}^{-1})$	0.794	0.580
No data collected	2788	5724
Unique data	2358	4504
parameters	281	389
$R(I>2\sigma(I))$	0.0502	0.0752
R²ω	0.1383	0.1633
Goodness of fit	1.127	1.018

CRYSTALLOGRAPHY

Golden-yellow plates of (2) and deep red blocks of (4a) were grown from CH₂Cl₂/hexane (1:4). Crystal data are summarized in table I. Crystals of dimensions 0.08 x 0.42 x 0.60 and 0.22 x 0.40 x 0.42 mm, respectively, were mounted on glass fibers and placed on a Siemens P4 diffractometer. Intensity data were taken in the ω mode with graphite monochromated Mo-K_a radiation (λ = 0.71073 Å). Three check reflections, monitored every 100 reflections, showed random (< 2%) variation during the data collection. The data were corrected for Lorentz, polarization effects, and absorption (using an empirical model derived from azimuthal data collections). Scattering factors and corrections for anomalous dispersion were taken from a standard source.¹⁵ Calculations were performed with the Siemens SHELXTL plus (Version 5.03) software package on a PC. The structures were solved by Patterson methods. Anisotropic thermal parameters were assigned to all non-hydrogen atoms except C_{20} - C_{32} for (4a). Hydrogen atoms were refined at calculated positions with a riding model in which the C-H vector was fixed at 0.96 Å. The data were refined by the method of full-matrix leastsquares on F².

SUPPLEMENTARY MATERIAL

Tables of bond lengths and angles, aniostropic thermal parameters, atomic coordinates, and structure factors are available from the authors upon request.

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