

# Synthesis, Characterization, and Catalytic Properties of Gp 6 Metal Complexes of 1-N,N-dimethylaminomethyl-1',2-bis(diphenylphosphino)ferrocene (FcNPP). X-ray Crystal Structure of $W(CO)_4(\eta^2\text{-FcNPP(O)-P,N})$

Tae-Jeong Kim\*, Yong-Hoon Kim, Eun-Jin Kim,  
Sang-Ho Oh, Hong-Seok Kim\*, and Jong-Hwa Jeong†\*

Department of Industrial Chemistry, Kyungpook National University, Taegu 702-701

†Department of Chemistry, Kyungpook National University, Taegu 702-701

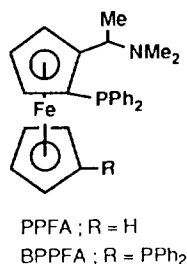
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Reactions of 1',2-bis(diphenylphosphino)-1-(N,N-dimethylaminomethyl)ferrocene (FcNPP) with  $M(CO)_6$  ( $M = Cr, Mo, W$ ) in the presence of TMNO (Trimethylamine oxide) in a stoichiometric ratio of 1:1.5:3.5 produced a series of Gp 6 metal carbonyl derivatives with a variety of coordination modes:  $M(CO)_4(\eta^2\text{-FcNPP-}P,P)$  ( $M = Cr, Mo, W$ ),  $M(CO)_5(\eta^1\text{-FcNPP-}P)$  ( $M = Mo, W$ ),  $M_2(CO)_9(\eta^1, \eta^2\text{-FcNPP-}P,P,N)$  ( $M = Cr, Mo$ ),  $M_2(CO)_{10}(\eta^1, \eta^1\text{-FcNPP-}P,P)$  ( $M = Cr, Mo, W$ ), and  $W(CO)_4(\eta^2\text{-FcNPP(O)-}P,N)$ . All these complexes were characterized by microanalytical and spectroscopic techniques. In one case, the structure of  $W(CO)_4(\eta^2\text{-FcNPP(O)-}P,N)$  was determined by X-ray crystallography. Crystals are monoclinic, space group  $P2_1/c$ , with  $a = 10.147(2)$ ,  $b = 19.902(3)$ ,  $c = 19.821(4)$  Å,  $\beta = 96.88(2)^\circ$ ,  $V = 3974(1)$  Å<sup>3</sup>,  $Z = 4$ , and  $D_{calc} = 1.64$  g cm<sup>-3</sup>. The geometry around the central tungsten metal is a distorted octahedron, with the nitrogen and phosphorus atoms being *cis* to each other. Some of these complexes exhibited catalytic activities in the allylic oxidation and epoxidation of cholesteryl acetate. Other oxidation products were also formed with the different chemical yields and product distribution depending upon the ligand and the central metal.

## Introduction

One of the most intriguing features of binary transition metal carbonyls such as  $M(CO)_6$  ( $M = Cr, Mo, W$ ) is their applications to the synthesis of carbonyl substitution products. Heat, UV, and other oxidants such as trimethylamine oxide (TMNO) have been employed to effect the nucleophilic substitution of CO by other ligand(s) incorporating group 15 donor atoms. There are now known a myriad of complexes of this sort, which have found wide applications as catalyst and reagent in a wide variety of homogeneous catalysis and in organic synthesis.<sup>1,2</sup>

In this connection, therefore, it is a little surprising to know that there have been few studies on the synthesis and applications of the derivatives of Gp 6 metal carbonyls incorporating such chiral organometallic ligands as 2-(diphenylphosphino)-1-(N,N-dimethylaminoethyl)ferrocene (PPFA) and 1',2-bis(diphenylphosphino)-1-(N,N-dimethylaminoethyl)ferrocene (BPPFA) that have so far been very efficiently used in a number of asymmetric catalytic reactions.<sup>3-12</sup>



In addition, according to our recent studies and others, these ligands form a number of complexes showing quite a variety of coordination modes upon complexation on metals

such as iron and cobalt.<sup>13-17</sup> For instance, a potential bidentate ligand BPPFA acts either as a monodentate through the phosphine  $\alpha$  to the  $-\text{CH}(\text{Me})\text{NMe}_2$ , a bidentate through two phosphines, or a bis(monodentate) through each phosphine leading to the formation of a bimetallic complex.

We have also shown that some iron complexes of BPPF (replacing the aminoethyl group in BPPFA with hydrogen) are very effective catalysts for the synthesis of carbamates from the reaction of propargyl alcohol with secondary amines in the presence of carbon dioxide.<sup>17</sup>

With these facts in mind it would be desirable to extend the studies on the synthesis and the coordination chemistry of this type of organometallic ligands with Gp 6 metal carbonyls and their potentiality as catalyst for the oxidation of cholesteryl acetate. In particular allylic and benzylic oxidations catalyzed by Gp 6 metal complexes have been the subject of many research groups in recent years in connection with obtaining some biologically important steroids.<sup>18-23</sup>

In this paper are described the synthesis, characterization, and catalytic application of a series of Gp 6 metal complexes incorporating FcNPP as ligand, where FcNPP = 1',2-bis(diphenylphosphino)-1-(N,N-dimethylaminomethyl)ferrocene.

## Experimental

### Reagents and Instrumentals

All manipulations were carried out under an argon atmosphere using a double manifold vacuum system and Schlenk techniques. All commercial reagents were used as received unless otherwise mentioned. Solvents were purified by standard methods,<sup>24</sup> and were freshly distilled prior to use. The ligand FcNPP was prepared as reported previously.<sup>13</sup> Melting points were determined using Yamato Model MP-21 melting

point apparatus and reported without correction. Microanalyses were obtained using a Carlo Erba Strum DP 200.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$ -NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 300.1, 75.5, and 121.5 MHz, respectively. IR spectra were recorded on a Mattson FT-IR Galaxy 6030E. GC-Mass spectra were obtained by using a Shimadzu QP-1000. X-ray diffraction was recorded on a Enraf-Nonius CAD4 diffractometer.

### Synthesis of group 6 metal carbonyl of FcNPP

**Reaction with  $\text{Cr}(\text{CO})_6$ .** Trimethylamine oxide (0.64 g, 5.7 mol) was dissolved in methanol (5 mL) in a 250 mL Schlenk tube. A solution of  $\text{Cr}(\text{CO})_6$  (0.54 g, 2.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL) was added. The solution was stirred at room temperature until the initial orange color turned to dark brown. To this solution was added FcNPP (1 g, 1.64 mmol) dissolved in  $\text{CH}_2\text{Cl}_2$  (20 mL). The color changed immediately to reddish orange. After stirring 5 h, the solution was taken to dryness in a rotatory evaporator to leave an orange solid. At this point, the composition of the reaction mixture, was analyzed by tlc or column chromatography and three major product bands were identified by visual inspection. Separation on a preparatory tlc was then effected and the major products isolated. The eluents used were mixtures of hexane and diethyl ether or  $\text{CH}_2\text{Cl}_2$  in increasing polarity throughout the separation. The first two bands of  $\text{Cr}_2(\text{CO})_9(\eta^1, \eta^2\text{-FcNPP-}P,P,N)$  (**2**) and  $\text{Cr}_2(\text{CO})_{10}(\eta^1, \eta^1\text{-FcNPP-}P,P)$  (**3**) were eluted using a mixture of hexanes/diethyl ether (4/1), and the third band of  $\text{Cr}(\text{CO})_4(\eta^2\text{-FcNPP-}P,P)$  (**1**) using mixture of hexanes/diethyl ether (1/1). All products crystallized from hexane/diethyl ether (**1**), diethyl ether (**2**), and diethyl ether/toluene (**3**). Yield of **1** (0.5 g, 40%); yield of **2** (0.05 g, 3%); yield of **3** (0.1 g, 6%).

**Reaction with  $\text{Mo}(\text{CO})_6$ .** The orange solid obtained from the similar procedure adopted for the chromium analogue was dissolved in a small amount of  $\text{CH}_2\text{Cl}_2$  and chromatographed on silica gel. Four major bands developed on elution with a mixture of hexane and  $\text{CH}_2\text{Cl}_2$  as increasing polarity. After eluting the first two orange bands of  $\text{Mo}_2(\text{CO})_9(\eta^1, \eta^2\text{-FcNPP-}P,P,N)$  (**6**) and  $\text{Mo}_2(\text{CO})_{10}(\eta^1, \eta^1\text{-FcNPP-}P,P)$  (**7**) with hexanes/ $\text{CH}_2\text{Cl}_2$  (4/1), the third and fourth bands of  $\text{Mo}(\text{CO})_5(\eta^1\text{-FcNPP-}P)$  (**5**) and  $\text{Mo}(\text{CO})_4(\eta^2\text{-FcNPP-}P,P)$  (**4**) were eluted with hexanes/ $\text{CH}_2\text{Cl}_2$  (3/7) and hexanes/ $\text{CH}_2\text{Cl}_2$  (7/3), respectively. All products crystallized from diethyl ether/ $\text{CH}_2\text{Cl}_2$  (**5**), pentane/ $\text{CH}_2\text{Cl}_2$  (**4**), hexane/diethyl ether (**7**), and hexanes/diethyl ether (**6**); Yield of **5** (0.5 g, 36%); yield of **4** (0.46 g, 17%); yield of **7** (0.21 g, 12%); yield of **6** (0.071 g, 4%).

**Reaction with  $\text{W}(\text{CO})_6$ .** The orange solid obtained from the reaction of FcNPP with  $\text{W}(\text{CO})_6$  after the similar work-up described above was chromatographed on silica gel. Three major product bands separated on elution with a mixture of hexanes and  $\text{CH}_2\text{Cl}_2$ . After separating the first two orange bands of  $\text{W}_2(\text{CO})_{10}(\eta^1, \eta^1\text{-FcNPP-}P,P)$  (**10**) and  $\text{W}(\text{CO})_5(\eta^1\text{-FcNPP-}P)$  (**9**) with a mixture of hexane/ $\text{CH}_2\text{Cl}_2$  (4/1), respectively, the third band of  $\text{W}(\text{CO})_4(\eta^2\text{-FcNPP-}P,P)$  (**8**) was eluted using  $\text{CH}_2\text{Cl}_2$  or diethyl ether. A small amount of  $\text{W}(\text{CO})_4(\eta^2\text{-FcNPP(O)-}P,N)$  (**11**) was finally separated. Each product crystallized from pentane/ $\text{CH}_2\text{Cl}_2$  (**8** and **9**), diethyl ether/hexanes (**10**) and hexanes/toluene (**11**); Yield of **8** (0.34 g, 23%); yield of **9** (0.29 g, 19%); yield of **10** (0.26 g, 13%); yield of **11** (0.08 g, 2%).

**Catalytic oxidation.** To a suspension of cholesteryl acetate (0.23 mmol) in acetonitrile (10 mL) was added the catalyst (0.012 mmol), followed by anhydrous *t*-butyl hydroperoxide (0.3 mL, 2.91 mmol). The reaction mixture was refluxed under  $\text{N}_2$  atmosphere for 15 h. The resulting solution was filtered, and the filtrate was concentrated to be subjected to column chromatography. Five bands developed on elution with mixtures of hexanes/ethyl acetate. The first two bands (**13** and **14**) were eluted with a 9/1 mixture, the third band (**12**) with a 4/1 mixture, and the last two unidentified bands with a 1/1 mixture.

$3\beta$ -Acetoxycholeste-5-en-7-one (**12**): white solid; mp. 154–155°C (lit.<sup>39</sup> 155–156°C); IR (KBr) 2949, 2868, 1730 (ester C=O), 1671 (conjugated C=O), 1464, 1379, 1248, 1040, 1039, 756  $\text{cm}^{-1}$ ; MS (relative intensity, %) 383 (32, M-HOAc), 368 (5, M-HOAc-Me), 270 (11, M-HOAc-Side chain), 187 (26), 174 (100), 159 (23),  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 201.8 (C-7), 170.1 (C=O), 163.8 (C-5), 126.7 (C-6), 72.2 (C-3), 54.8 (C-17), 50.0 (C-9), 49.9 (C-14), 45.4 (C-8), 43.1 (C-13), 39.5 (C-24), 38.7 (C-12), 38.3 (C-10), 37.7 (C-4), 36.2 (C-22), 36.0 (C-1), 35.7 (C-20), 28.5 (C-16), 27.9 (C-25), 27.4 (C-2), 26.3 (C-15), 23.8 (C-23), 22.7 (C-27), 22.5 (C-26), 21.3 ( $\text{CH}_3\text{C}=\text{O}$ ), 21.2 (C-11), 18.9 (C-21), 17.2 (C-19), 11.9 (C-18);  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 5.70 (d, 6-H, 1.2 Hz), 4.71 (m, 3 $\alpha$ -H), 1.21 (s, 19-H<sub>3</sub>), 0.92 (d, 21-H<sub>3</sub>, 6.5 Hz), 0.87 (d, 26, 27-H<sub>3</sub>, 6.8 Hz), 0.69 (s, 18-H<sub>3</sub>).

$3\beta$ -Acetoxy-cholest-5 $\zeta$ ,6 $\zeta$ -epoxycholestane (**13**): white solid; mp. 109–111°C (lit.<sup>40</sup> 110–112°C); IR (KBr) 2952, 2871, 1733 (C=O), 1466, 1374, 1266, 1243, 1046, 795  $\text{cm}^{-1}$ ; MS (relative intensity, %) 445 (3, M+1), 427 (M+1-H<sub>2</sub>O), 385 (44, M+1-HOAc), 370 (14, M+1-HOAc-Me), 272 (7, M-HOAc-Side chain), 248 (11), 212 (15), 185 (7), 163 (20);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 170.5 (C=O), 71.4 (C-3), 63.5 (C-5), 62.5 (C-6), 56.8 (C-17), 56.3 (C-9), 51.0 (C-14), 42.3 (C-13), 39.84 (C-8), 39.82 (C-12), 39.5 (C-24), 38.0 (C-10), 36.7 (C-22), 36.2 (C-1), 35.7 (C-4), 35.1 (C-20), 29.8 (C-7), 28.8 (C-23), 28.1 (C-16), 28.0 (C-25), 27.2 (C-2), 24.2 (C-15), 22.8 (C-27), 22.5 (C-26), 21.9 (C-11), 21.2 ( $\text{CH}_3\text{C}=\text{O}$ ), 18.7 (C-21), 17.0 (C-19), 11.8 (C-18),  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 4.78 (m, 3 $\alpha$ -H), 3.06 (d, 6-H, 1.9 Hz), 0.95 (s, 19-H<sub>3</sub>), 0.89 (d, 21-H<sub>3</sub>, 6.4 Hz), 0.86 (d, 26, 27-H<sub>3</sub>, 6.3 Hz), 0.66 (s, 18-H<sub>3</sub>).

$3\beta$ -Acetoxy-5 $\zeta$ ,6 $\zeta$ -epoxycholest-7-ene (**14**): colorless oil; IR ( $\text{CH}_2\text{Cl}_2$  solution) 2952, 2879, 1736 (ester C=O), 1466, 1365, 1243, 1196, 1034, 733  $\text{cm}^{-1}$ ; MS (relative intensity, %) 383 (16, M-HOAc), 368 (100, M-HOAc-Me), 270 (5, M-HOAc-Side chain), 248 (7), 174 (36), 159 (25);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 170.4 (C=O), 145.1 (C-8), 122.2 (C-7), 79.5 (C-5), 75.9 (C-6), 73.6 (C-3), 55.9 (C-17), 48.9 (C-9), 42.8 (C-14), 42.3 (C-13), 39.5 (C-24), 39.0 (C-12), 38.1 (C-4), 37.5 (C-10), 36.5 (C-1), 36.3 (C-22), 36.0 (C-20), 28.2 (C-16), 28.0 (C-25), 27.6 (C-2), 24.7 (C-15), 24.0 (C-23), 22.8 (C-27), 22.5 (C-26), 21.4 ( $\text{CH}_3\text{C}=\text{O}$ ), 20.8 (C-12), 18.8 (C-21), 18.0 (C-19), 11.3 (C-18);  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 5.70 (d, 7-H, 4.8 Hz), 4.66 (m, 3 $\alpha$ -H), 4.10 (bs, 6-H), 0.99 (s, 19-H<sub>3</sub>), 0.93 (d, 21-H<sub>3</sub>, 6.4 Hz), 0.87 (d, 26, 27-H<sub>3</sub>, 6.3 Hz), 0.65 (s, 18-H<sub>3</sub>).

### X-ray crystallographic analysis of **11**

Crystals of **11** were grown at room temperature from a hexane/toluene/ethanol solution of the compound. The crystal, 0.25 $\times$ 0.38 $\times$ 0.42 mm, was mounted in a capillary on an Enraf-Nonius CAD-4 diffractometer, and lattice parameters were determined by least-squares analysis of 25 reflections ( $18^\circ < 2\theta < 24^\circ$ ). Data were collected with the graphite-

**Table 1.** Crystal Data, Data Collection, and Refinement of the Structure for **11**

Formula	WFeP <sub>2</sub> O <sub>5</sub> NC <sub>42</sub> H <sub>35</sub> C <sub>2</sub> H <sub>5</sub> OH
fw	981.456
Space group	P2 <sub>1</sub> /c (No. 14)
<i>a</i> , Å	10.147(2)
<i>b</i> , Å	19.902(3)
<i>c</i> , Å	19.821(4)
β°,	96.88(2)
<i>V</i> , Å <sup>3</sup>	3974(1)
<i>Z</i>	4
ρ <sub>calcd</sub> , g/cm <sup>3</sup>	1.64
Crystal size, mm	0.25 × 0.38 × 0.42
μ(Mo Kα), cm <sup>-1</sup>	31.99
Scan method	ω/2θ
Data collected	7300
Range of data collection	<i>h</i> , <i>-h</i> , ± <i>l</i> ; 3 ≤ 2θ ≤ 50°
No. of unique data ≥ 3σ( <i>I</i> )	4338
No. of parameters refined	296
abs. corr. factor range	0.8821-0.9999
GOF	2.02
$R = \sum ( F_o  -  F_c ) / \sum  F_o $	0.037
$R_w = \sum \omega^{1/2} ( F_o  -  F_c ) / \sum \omega^{1/2}  F_o $	0.038

$$\omega = 1.7835/(\sigma^2(F) + 0.000228 F^2)$$

monochromated MoKα ( $\lambda = 0.71073$  Å) by using the ω/2θ scan mode. The intensity standard were monitored every 1 h during data collection. The data were modified for Lorentz-polarization effects and decay. Empirical absorption correction with 4Ψ scans was applied to the data. The structure was solved by use of the conventional heavy-atom method as well as Fourier difference techniques and refined on F by means of full-matrix least-squares procedures using SHELX-76.<sup>26</sup> The final cycle of refinement converted with  $R = 0.037$  and  $R_w = 0.038$ , where  $\omega$  is  $1.7835/(\sigma^2(F) + 0.000228 F^2)$ . The shift/esd ratio in the last cycle of least-squares is less than 0.06 for all parameters. The largest (1.0 e/Å<sup>3</sup>) was at 0.87 Å from W atom. Crystal data, details of the data collection, and refinement of the structure are listed in Table 1. Final positional parameters and temperature factors are listed in Table 2.

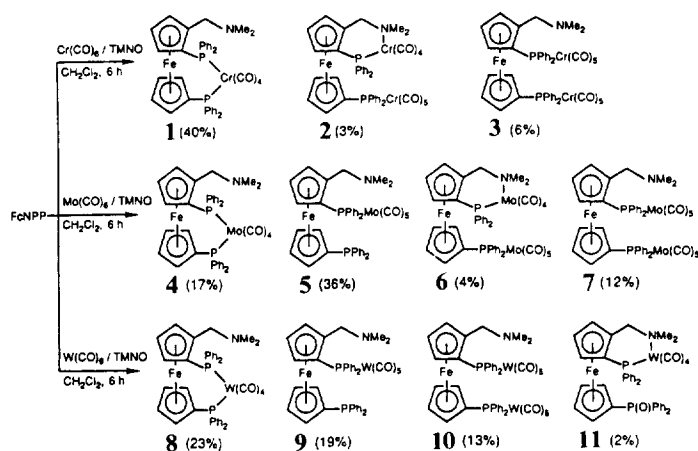
## Results and Discussion

**Synthesis and characterization.** Apart from their fascinating properties as chiral ligand in asymmetric catalysis,<sup>3-12</sup> the well-known organometallic ligands such as BPPF, PPFA, BPPFA, and FcNPP render rich chemistry from the structural viewpoint. For instance, these compounds possess both soft (phosphorus) and hard (nitrogen) donor sites, thus exhibiting in principle more than one possibility of coordination mode; a chelating bidentate through P-N or P-P, a bridging bidentate, or a monodentate through nitrogen or phosphorus. In fact, it has recently been shown<sup>27-35</sup> that they form a number of transition metal complexes with some unique coordination features including those coordination modes described above. The transition metal complexes which have

**Table 2.** Positional and Equivalent Thermal Parameters\* for **11**

Atoms	<i>x/a</i>	<i>b/y</i>	<i>c/z</i>	<i>U</i> <sub>eq</sub>
W	0.0358(<1)	0.2355(<1)	0.4753(<1)	0.048(<1)
Fe	0.3069(1)	0.4321(<1)	0.4026(1)	0.040(1)
P(1)	0.0888(2)	0.2942(1)	0.3704(1)	0.033(1)
P(2)	0.4118(2)	0.5616(1)	0.3122(1)	0.047(1)
O	0.5553(5)	0.5485(3)	0.3324(3)	0.066(5)
C(01)	0.0773(9)	0.1467(4)	0.4308(5)	0.068(7)
O(01)	0.0928(8)	0.0963(3)	0.4065(4)	0.104(6)
C(02)	-0.1486(10)	0.2243(5)	0.4369(5)	0.078(7)
O(02)	-0.2592(8)	0.2186(4)	0.4152(5)	0.128(8)
C(03)	-0.0194(10)	0.3195(5)	0.5216(4)	0.076(8)
C(03)	-0.0573(10)	0.3654(5)	0.5469(3)	0.134(10)
C(04)	-0.008(10)	0.1830(5)	0.5540(5)	0.085(7)
O(04)	-0.0425(8)	0.1512(4)	0.5968(4)	0.120(7)
C(11)	0.2500(6)	0.3359(3)	0.3807(3)	0.036(4)
C(12)	0.3192(6)	0.3623(3)	0.3284(4)	0.041(5)
C(13)	0.4498(7)	0.3804(3)	0.3585(4)	0.050(6)
C(14)	0.4584(7)	0.3650(3)	0.4287(4)	0.052(6)
C(15)	0.3359(7)	0.3390(3)	0.4434(3)	0.042(4)
C(1)	0.3079(8)	0.3222(4)	0.5136(4)	0.055(5)
N	0.2609(7)	0.2515(3)	0.5241(3)	0.051(4)
C(2)	0.2684(12)	0.2420(5)	0.5990(4)	0.075(8)
C(3)	0.3555(8)	0.2048(4)	0.4988(5)	0.095(6)
C(21)	0.3117(7)	0.5302(3)	0.3733(4)	0.041(5)
C(22)	0.1778(7)	0.5050(3)	0.3663(4)	0.040(4)
C(23)	0.1502(8)	0.4842(3)	0.4312(4)	0.054(6)
C(24)	0.2651(9)	0.4954(4)	0.4786(4)	0.062(7)
C(25)	0.3654(9)	0.5230(3)	0.4427(4)	0.054(6)
C(31)	0.1074(6)	0.2344(3)	0.3030(3)	0.035(4)
C(32)	-0.0044(7)	0.2105(4)	0.2621(3)	0.044(5)
C(33)	0.0077(7)	0.1607(3)	0.2154(4)	0.047(5)
C(34)	0.1272(8)	0.1327(3)	0.2093(4)	0.051(6)
C(35)	0.2376(8)	0.1547(4)	0.2481(4)	0.053(5)
C(36)	0.2292(7)	0.2058(3)	0.2940(4)	0.045(5)
C(41)	-0.0257(6)	0.3566(3)	0.3279(3)	0.034(4)
C(42)	0.0133(7)	0.3783(3)	0.2624(3)	0.041(4)
C(43)	-0.0924(7)	0.4284(4)	0.2326(4)	0.049(5)
C(44)	-0.1863(7)	0.4583(3)	0.2678(4)	0.051(5)
C(45)	-0.2021(7)	0.4365(3)	0.3317(4)	0.049(5)
C(46)	-0.1223(7)	0.3859(3)	0.3612(3)	0.043(4)
C(51)	0.3754(7)	0.6506(4)	0.3060(4)	0.050(6)
C(52)	0.3979(8)	0.6851(4)	0.2481(6)	0.070(8)
C(53)	0.3818(10)	0.7545(5)	0.2458(8)	0.092(12)
C(54)	0.3411(11)	0.7879(5)	0.3009(9)	0.107(17)
C(55)	0.3222(10)	0.7543(4)	0.3589(8)	0.089(11)
C(56)	0.3381(8)	0.6857(4)	0.3610(5)	0.061(7)
C(61)	0.3483(7)	0.5245(4)	0.2332(4)	0.051(5)
C(62)	0.2256(8)	0.5395(4)	0.1990(4)	0.064(6)
C(63)	0.1790(10)	0.5036(4)	0.1401(4)	0.072(7)
C(64)	0.2527(11)	0.4557(5)	0.1140(6)	0.077(8)
C(65)	0.3757(11)	0.4410(5)	0.1485(5)	0.081(8)
C(66)	0.4249(9)	0.4745(4)	0.2067(5)	0.063(7)
O(1S)	0.5587(18)	0.5263(10)	0.0446(8)	0.274(7)
C(1S)	0.6643(19)	0.4548(10)	0.0354(10)	0.189(7)
C(2S)	0.5672(25)	0.4383(11)	-0.0234(11)	0.227(9)

\*Equivalent isotropic  $U_{eq}$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Scheme 1.** Gp 6 metal complexes of FcNPP.

been employed for complexation with these ligands are  $M_3(CO)_{12}$  ( $M = Fe, Ru, Os$ ),  $Fe(CO)_5$ ,  $Fe_2(CO)_9$ ,  $CpCo(CO)_2$ , and so on.<sup>27-35</sup>

As one of the research objectives is to extend the coordination chemistry of some of these ligands, the group 6 metal carbonyls were chosen to react with the chiral ligand FcNPP. We have examined the carbonyl substitution reaction under various experimental conditions (*i.e.* UV, or heat) and found the use of stoichiometric amount of  $Me_3NO \cdot 2H_2O$  to be the effective way of achieving the carbonyl substitution under quite a mild condition such as room temperature. The role of this reagent is quite well documented in the literature.<sup>36</sup>

Scheme 1 shows the experimental conditions leading to the formation of various coordination compounds of FcNPP, **1-11**. The scheme demonstrates quite different and diversified reaction patterns as compared with our previous results obtained from the reactions of iron carbonyls and  $CpCo(CO)_2$  with analogous chiral ligands such as PPFA and BPPFA, in which the products with only one type of coordination through phosphorus in a monodentate manner were predominant regardless the reaction conditions (*vide supra*).<sup>15,16</sup>

In contrast, our present investigations show that the choice of preference in coordination is chelation through two phosphorus atoms giving the compounds of the type  $(\eta^2\text{-FcNPP-}P,P)M(CO)_4$  (**1**, **4**, and **8**) as major products. Other new class of complexes unobtainable with the case of iron carbonyls is the one with chelation through two neighboring P-N donors,  $(\eta^2\text{-FcNPP-}P,N)M(CO)_4$  (**2**, **6**, and **11**) although their yields were quite low (<4%).

It is also interesting to note that the products with a monodentate fashion through the phosphorus  $\alpha$  to the  $CH_2NMe_2$  group (compounds **5** and **9**) were obtained in a significant amount (a major product in the case of **5**), when considering the fact that iron carbonyls attack preferentially the other phosphorus as shown above.<sup>15</sup> The origin of these different behaviors between the group 6 metal carbonyls and iron carbonyls are yet uncertain. The yields of the expected bimetallic complexes of the type  $(\mu, \eta^1, \eta^1\text{-FcNPP-}P,P)[M(CO)_5]_2$  (**3**, **7**, and **10**) range 6-13%.

Finally, in connection with the formation of the complex **11**, it is not unusual to find oxidation occurring on phosphorus during the work-ups such as chromatographic separation.<sup>15</sup>

The formations of all these products have been confirmed

**Table 3.** Bond Distances and Angles for **11**

W-P(1)	2.499(2)	W-C(01)	2.042(9)
W-C(02)	1.947(10)	W-C(03)	2.017(10)
W-C(04)	1.973(10)	W-N	2.393(6)
Fe-C(11)	2.030(6)	Fe-C(12)	2.037(7)
Fe-C(13)	2.056(8)	Fe-C(14)	2.055(7)
Fe-C(15)	2.028(7)	Fe-C(21)	2.040(6)
Fe-C(22)	2.029(6)	Fe-C(23)	2.035(8)
Fe-C(24)	2.048(8)	Fe-C(25)	2.036(7)
P(1)-C(11)	1.824(7)	P(1)-C(31)	1.816(6)
P(1)-C(41)	1.836(6)	P(2)-O	1.486(5)
P(2)-C(21)	1.784(8)	P(2)-C(51)	1.810(7)
P(2)-C(61)	1.781(8)	C(01)-O(01)	1.132(11)
C(02)-O(02)	1.158(13)	C(03)-O(03)	1.133(13)
C(04)-O(04)	1.144(13)	C(15)-C(1)	1.492(10)
C(1)-N	1.507(9)	N-C(2)	1.489(10)
N-C(3)	1.467(11)		
C(01)-W-P(1)	88.2(3)	C(02)-W-P(1)	91.2(3)
C(02)-W-C(01)	88.3(4)	C(03)-W-P(1)	95.2(3)
C(03)-W-C(01)	175.1(4)	C(03)-W-C(02)	88.1(4)
C(04)-W-P(1)	175.7(3)	C(04)-W-C(01)	87.8(4)
C(04)-W-C(02)	87.0(4)	C(04)-W-C(03)	88.7(4)
N-W-P(1)	89.1(1)	N-W-C(01)	93.1(3)
N-W-C(02)	178.6(3)	N-W-C(03)	90.6(3)
N-W-C(04)	92.8(3)	O(01)-C(01)-W	175.9(8)
O(02)-C(02)-W	178.4(9)	O(03)-C(03)-W	176.3(9)
O(04)-C(04)-W	175.1(9)	C(41)-P(1)-W	120.7(2)
C(41)-P(1)-C(11)	104.6(3)	C(31)-P(1)-C(11)	102.1(3)
C(41)-P(1)-C(31)	102.8(3)	C(21)-P(2)-O	112.0(3)
C(51)-P(2)-O	112.1(3)	C(51)-P(2)-C(21)	105.1(3)
C(61)-P(2)-O	113.8(4)	C(61)-P(2)-C(21)	106.0(3)
C(61)-P(2)-C(51)	107.3(4)		

by their analytical and spectroscopic data listed in Tables 4-6. In addition, the structure of **11** has been determined by X-ray crystallography.

The tetracarbonyl derivatives (**1**, **4**, and **8**) show three strong IR absorption bands, *viz.*, two sharp bands ( $2A_1$ ) around  $2000\text{ cm}^{-1}$  and  $1900\text{ cm}^{-1}$  and a broad band near  $1870\text{ cm}^{-1}$  ( $B_1+B_2$ ), which is typical of the *cis*- $[ML_2(CO)_4]$  geometry having the  $C_{2v}$  local symmetry.<sup>37</sup> Their  $^1H$ -NMR patterns are also supporting for this structure exhibiting a single resonance line for the uncoordinated  $NMe_2$  group (Figure 1). This suggests that the chelation is made through two phosphorus atoms. More conclusive evidence comes from the  $^{31}P$ -NMR pattern which shows a nice down field AB quartet in the region 16-50 ppm depending on the central metal. The coordination shift ( $\Delta\delta$ ) for the phosphines decreases as going down within the Gp 6 family of the periodic table, thus the phosphine resonances for the tungsten analogue (**8**) appear in the highest field (*cf.* Table 6). In the case of **8**, the AB resonances are accompanied by satellites due to the tungsten-phosphorus couplings ( $J_{PW} = 243\text{ Hz}$ ). The room temperature  $^{13}C$ -NMR patterns for the tetracarbonyl derivatives show four non-equivalent CO carbonyls (*i.e.*, AB-CDXY) which represent two triplets (overlapping doublets of doublets) due to the axial carbonyls and two doublets

**Table 4.** Physical and Analytical Data for Gp 6 Metal Carbonyls of FcNPP<sup>a</sup>

Compound	Color	mp. °C (decomp.)	Analysis		
			% C	% H	% N
Cr(CO) <sub>4</sub> (FcNPP) (1)	yellow	170	63.62 (63.49)	4.59 (4.55)	1.65 (1.81)
Cr <sub>2</sub> (CO) <sub>9</sub> (FcNPP) (2)	orange	193	56.50 (57.10)	3.56 (3.62)	1.52 (1.45)
Cr <sub>2</sub> (CO) <sub>10</sub> (FcNPP) (3)	yellow	156	57.86 (58.22)	3.98 (3.74)	1.35 (1.34) <sup>b</sup>
Mo(CO) <sub>4</sub> (FcNPP) (4)	yellow	205	59.91 (60.09)	4.27 (4.30)	1.78 (1.71)
Mo(CO) <sub>5</sub> (FcNPP) (5)	orange	160	59.20 (59.53)	4.08 (4.16)	1.73 (1.65)
Mo <sub>2</sub> (CO) <sub>9</sub> (FcNPP) (6)	yellow	163	52.50 (52.35)	3.43 (3.34)	1.25 (1.33)
Mo <sub>2</sub> (CO) <sub>10</sub> (FcNPP) (7)	yellow	97	52.50 (52.10)	3.21 (3.26)	1.39 (1.29)
W(CO) <sub>4</sub> (FcNPP) (8)	yellow	203	53.97 (54.27)	3.87 (3.88)	1.31 (1.54)
W(CO) <sub>5</sub> (FcNPP) (9)	orange	177	53.60 (53.93)	3.71 (3.77)	1.57 (1.49)
W <sub>2</sub> (CO) <sub>10</sub> (FcNPP) (10)	orange	105	45.40 (44.83)	2.70 (2.80)	1.15 (1.11)
W(CO) <sub>4</sub> (η <sup>2</sup> -FcNPP(O)) (11)	orange	181	55.49 (55.13)	3.87 (4.02)	1.35 (1.44) <sup>b</sup>

<sup>a</sup>Values in parentheses are calculated ones. <sup>b</sup>Calculated as containing 1/2 C<sub>7</sub>H<sub>8</sub> as confirmed by NMR.**Table 5.** Selected Infrared Data for the Gp 6 Metal Carbonyls of FcNPP<sup>a</sup>

Compound	ν(CO)(cm <sup>-1</sup> )	Compound	ν(CO)(cm <sup>-1</sup> )
Cr(CO) <sub>4</sub> (η <sup>2</sup> -FcNPP- <i>P,P</i> ) (1)	1867 (vs), 1890 (vs), 2000 (s)	Cr <sub>2</sub> (CO) <sub>9</sub> (η <sup>1</sup> ,η <sup>2</sup> -FcNPP- <i>P,P,N</i> ) (2)	1826 (s), 1886 (s), 1901 (s) 1926 (vs), 1985 (w), 2010 (m) 2069 (m)
Mo(CO) <sub>4</sub> (η <sup>2</sup> -FcNPP- <i>P,P</i> ) (4)	1872 (vs), 1902 (vs), 2014 (s)		
W(CO) <sub>4</sub> (η <sup>2</sup> -FcNPP- <i>P,P</i> ) (8)	1869 (vs), 1900 (vs), 2010 (s)	Mo <sub>2</sub> (CO) <sub>9</sub> (η <sup>1</sup> ,η <sup>2</sup> -FcNPP- <i>P,P,N</i> ) (6)	1845 (s), 1902 (s), 1921 (s) 1941 (vs), 1995 (w), 2018(m) 2067 (m)
W(CO) <sub>4</sub> (η <sup>2</sup> -FcNPP(O)- <i>P,N</i> ) (11)	2068 (s), 1983 (sh), 1923 (vs)		
Mo(CO) <sub>5</sub> (η <sup>1</sup> -FcNPP- <i>P</i> ) (5)	1918 (vs), 1931 (vs), 1990 (m) 2069 (s)	[Cr(CO) <sub>5</sub> ] <sub>2</sub> (η <sup>1</sup> ,η <sup>1</sup> -FcNPP- <i>P,P</i> ) (3)	1927 (vs), 1985 (m), 2060 (s)
W(CO) <sub>5</sub> (η <sup>1</sup> -FcNPP- <i>P</i> ) (9)	1912 (vs), 1948 (vs), 1983 (m) 2068 (s)	[Mo(CO) <sub>5</sub> ] <sub>2</sub> (η <sup>1</sup> ,η <sup>1</sup> -FcNPP- <i>P,P</i> ) (7)	1931 (vs), 1989 (m), 2072 (s)
		[W(CO) <sub>5</sub> ] <sub>2</sub> (η <sup>1</sup> ,η <sup>1</sup> -FcNPP- <i>P,P</i> ) (10)	1927 (vs), 1981 (m), 2072 (s)

<sup>a</sup>Key: s=strong, vs=very strong, m=medium, w=weak.**Table 6.** NMR Data for the Gp 6 Metal Complexes of FcNPP<sup>a,b</sup>

Compound	<sup>1</sup> H	<sup>31</sup> P	<sup>13</sup> C
1	1.76 (s, NMe <sub>2</sub> ) 2.65 (q, CH <sub>2</sub> , <i>J</i> =13.2) 4.30-4.70 (m, Cp, 7H) 7.38-7.80 (m, Ph, 20H)	49.7 (q, <i>J</i> <sub>PP</sub> =35.1)	221.5 (t, <i>J</i> <sub>PC</sub> =14.8) 222.7 (t, <i>J</i> <sub>PC</sub> =14.8) 226.4 (dd, <i>J</i> <sub>PC</sub> =13.2) 226.5 (dd, <i>J</i> <sub>PC</sub> =13.2)
4	1.71 (s, NMe <sub>2</sub> ) 2.59 (q, CH <sub>2</sub> , <i>J</i> =13.2) 4.23-4.67 (m, Cp, 7H) 7.35-7.78 (m, Ph, 20H)	31.4 (q, <i>J</i> <sub>PP</sub> =27.8)	210.2 (t, <i>J</i> <sub>PC</sub> =9.3) 211.5 (t, <i>J</i> <sub>PC</sub> =9.3) 215.4 (dd, <i>J</i> <sub>PC</sub> =8.0) 215.7 (dd, <i>J</i> <sub>PC</sub> =8.0)
8	1.71 (s, NMe <sub>2</sub> ) 2.59 (q, CH <sub>2</sub> , <i>J</i> =13.5) 4.25-4.69 (m, Cp, 7H) 7.24-7.74 (m, Ph, 20H)	16.4 (q, <i>J</i> <sub>PP</sub> =26.7; <i>J</i> <sub>PW</sub> =243.0)	203.5 (t, <i>J</i> <sub>PC</sub> =7.3) 204.7 (t, <i>J</i> <sub>PC</sub> =7.7) 205.9 (dd, <i>J</i> <sub>PC</sub> =5.1) 206.4 (dd, <i>J</i> <sub>PC</sub> =4.5)
11	1.71 (s, NMe <sub>2</sub> ) 2.67 (q, CH <sub>2</sub> , <i>J</i> <sub>HH</sub> =13.2) 4.27-4.81 (m, Cp, 7H) 7.26-7.69 (m, Ph, 20H)	28.29 (s) 9.99 (s, <i>J</i> <sub>PW</sub> =248.2)	198.7 (d, 1CO, <i>J</i> <sub>PC</sub> =23.7) 197.7 (d, 2CO, <i>J</i> <sub>PC</sub> =7.3) 196.8 (d, 1CO, <i>J</i> <sub>PC</sub> =7.3)
5	1.73 (s, NMe <sub>2</sub> ) 2.79 (s, CH <sub>2</sub> ) 4.06-4.65 (m, Cp, 7H) 7.26-7.74 (m, Ph, 20H)	23.7 (s) -20.3 (s)	205.9 (d, 4CO, <i>J</i> <sub>PC</sub> =9.3) 210.5 (d, 1CO, <i>J</i> <sub>PC</sub> =24.4)
9	1.72 (s, NMe <sub>2</sub> ) 2.74 (s, CH <sub>2</sub> ) 4.05-4.65 (m, Cp, 7H) 7.24-7.77 (m, Ph, 20H)	7.20 (s, <i>J</i> <sub>PW</sub> =247.4) -20.3 (s)	197.8 (d, 4CO, <i>J</i> <sub>PC</sub> =7.2) 199.1 (d, 1CO, <i>J</i> <sub>PC</sub> =24.8)
2	2.04 (s, NMe) 2.71 (s, NMe) 2.49 (d, CH, <i>J</i> =13.2) 4.03 (d, CH, <i>J</i> =13.2) 3.66-4.24 (m, Cp, 7H) 7.02-7.50 (m, Ph, 20H)	38.1 (s) 44.6 (s)	214.8 (d, 1CO, <i>J</i> <sub>PC</sub> =12.8) 220.9 (d, 1CO, <i>J</i> <sub>PC</sub> =7.1) 224.3 (d, 1CO, <i>J</i> <sub>PC</sub> =1.9) 225.9 (d, 1CO, <i>J</i> <sub>PC</sub> =16.1) 216.6 (d, 4CO, <i>J</i> <sub>PC</sub> =13.8) 221.6 (d, 1CO, <i>J</i> <sub>PC</sub> =15.3)
6	2.09 (s, NMe) 2.81 (s, NMe) 2.61 (d, CH) 3.55-4.28 (m, Cp, 7H) 7.02-7.87 (m, Ph, 20H)	21.5 (s) 25.8 (s)	204.4 (d, 1CO, <i>J</i> <sub>PC</sub> =8.7) 211.3 (d, 1CO, <i>J</i> <sub>PC</sub> =10.4) 214.6 (d, 1CO, <i>J</i> <sub>PC</sub> =34.8) 219.9 (d, 1CO, <i>J</i> <sub>PC</sub> =9.4) 205.6 (d, 4CO, <i>J</i> <sub>PC</sub> =9.4) 209.6 (d, 1CO, <i>J</i> <sub>PC</sub> =24.6)
3	1.65 (s, NMe <sub>2</sub> ) 2.54 (q, CH <sub>2</sub> , <i>J</i> =13.5) 4.09-4.98 (m, Cp, 7H) 7.22-7.52 (m, Ph, 20H)	43.7 (s) 45.2 (s)	216.6 (d, 4CO, <i>J</i> <sub>PC</sub> =13.4) 221.2 (d, 1CO, <i>J</i> <sub>PC</sub> =12.1) 216.5 (d, 4CO, <i>J</i> <sub>PC</sub> =13.8) 221.1 (d, 1CO, <i>J</i> <sub>PC</sub> =12.3)

7	1.66 (s, NMe <sub>2</sub> ) 2.59 (q, CH <sub>2</sub> , J=13.2)	24.1 (s)	205.8 (d, 4CO, J <sub>PC</sub> =9.2)	210.2 (d, 1CO, J <sub>PC</sub> =24.4)
	3.96-5.01 (m, Cp, 7H) 7.16-7.66 (m, Ph, 20H)	26.0 (s)	205.6 (d, 4CO, J <sub>PC</sub> =9.4)	209.8 (d, 1CO, J <sub>PC</sub> =24.6)
10	1.66 (s, NMe <sub>2</sub> ) 2.59 (q, CH <sub>2</sub> , J=13.1)	7.61 (s, J <sub>FW</sub> =260.0)	197.7 (d, 4CO, J <sub>PC</sub> =7.3)	198.7 (d, 1CO, J <sub>PC</sub> =23.5)
	4.03-5.03 (m, Cp, 7H) 7.17-7.66 (m, Ph, 20H)	8.74 (s, J <sub>FW</sub> =247.0)	197.2 (d, 4CO, J <sub>PC</sub> =7.3)	198.5 (d, 1CO, J <sub>PC</sub> =23.2)

<sup>a</sup>All spectra were obtained in CDCl<sub>3</sub>. <sup>b</sup>Coupling constants are in Hz: s=singlet, d=doublet, dd=doublet of doublets, m=multiplet, t=triplet, q=AB quartet. <sup>c</sup>The X portion of the AX pattern for the methylene protons are obscured by the Cp ring protons.

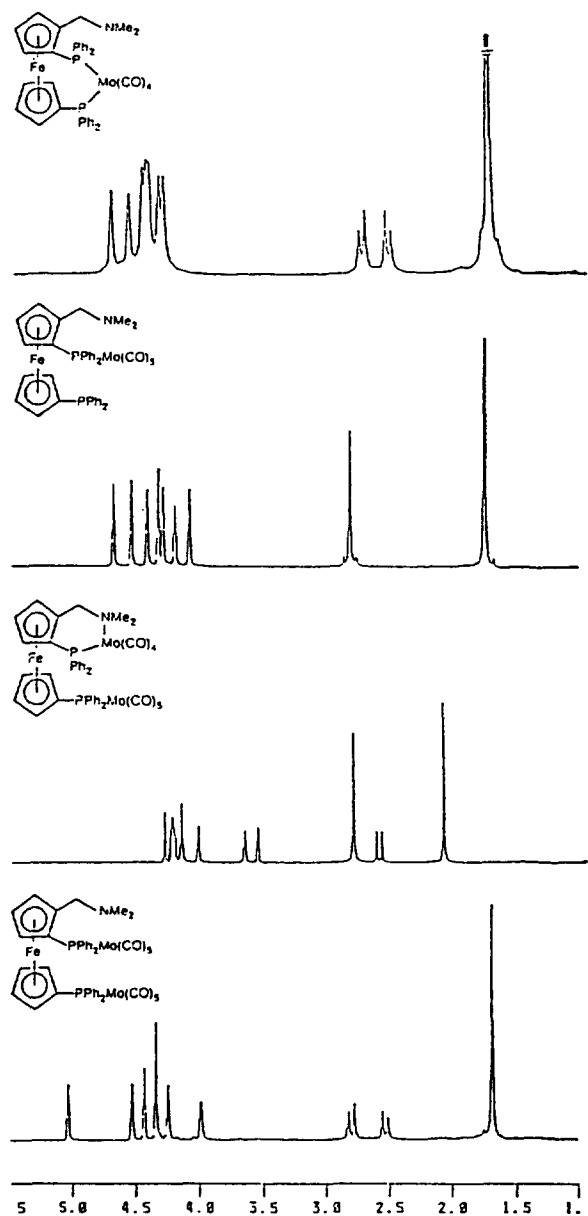


Figure 1. <sup>1</sup>H-NMR spectra of molybdenum complexes, 4, 5, 6, and 7.

of doublets at lower field for the equatorial carbonyls on two phosphorus atoms.

For the pentacarbonyl derivatives 5 and 9, coordination is made through the phosphorus adjacent to the methylamino group so that their <sup>31</sup>P-NMR spectra exhibit two signals with the high field shift arising due to free phosphine. Again, they show a single line for the two equivalent methyl protons in the free NMe<sub>2</sub> group in their <sup>1</sup>H-NMR spectra. The <sup>13</sup>C-

NMR shows a pair of doublets in an intensity of 1:4 representative of the AB<sub>4</sub>Y pattern of the five carbonyls.

The nonacarbonyl derivatives (2 and 6), along with the minor tetracarbonylphosphineoxide (11), have a common <sup>1</sup>H-NMR feature; that is, a chelation through P-N donors, resulting in a characteristic two-line pattern due to the methyl protons of the NMe<sub>2</sub> group which have now become diastereotopic upon complexation. This complexation affects the methylene protons as well, making one of the methylene protons appear much further downfield than usually found because in this type of complexes one proton is almost coplanar with a Cp ring and subjected to a ring current. The same observations have also been made with the rhodium (I) complex of the type [(NBD)Rh(PN)]ClO<sub>4</sub> (PN=Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>(P(CMe<sub>3</sub>)<sub>2</sub>-1,3)(η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(CHMeNMe<sub>2</sub>)(CMe<sub>3</sub>)<sub>2</sub>-1,2); NBD = norbornadiene).<sup>7</sup> A representative example is shown in Figure 1. Their <sup>13</sup>C-NMR patterns are also expected to give rise to six doublets with the intensity ratio of 1:1:1:1:4:1. The most intense line (I=4) must be due to the four *cis* carbonyls on the -PPh<sub>2</sub>M(CO)<sub>5</sub> moiety. These compounds show at least seven carbonyl stretching bands (Table 5).

The decacarbonyl derivatives (3, 7, and 10), consisting of two M(CO)<sub>5</sub> moieties bridged by two nonsymmetrical phosphines, exhibit spectral data perfectly consistent with the formulation. Thus, for example, their <sup>13</sup>C-NMR pattern for the carbonyls is that of a [AX<sub>4</sub>]<sub>2</sub>, comprising four pairs of doublets with the intensity ratio of 4:1:4:1. Again, as is the case for the nonacarbonyl derivatives, the two intense doublets (I=4) appearing at higher field are coming from the pair of four *cis* carbonyls. However, assignment of each doublet to the corresponding carbonyls was not possible. Based on the <sup>31</sup>P-NMR pattern, the two phosphorus atoms in the decacarbonyl derivative do not couple with each other unlike those in the tetracarbonyl complexes (η<sup>2</sup>-FcNPP-*P,P*)M(CO)<sub>4</sub>. The IR absorption pattern for the ν(CO) bands consists of three medium to very strong bands (2A<sub>1</sub>+E) as expected for the structure with the local symmetry of C<sub>4v</sub>.

Finally, a note should be made concerning the phosphine oxide derivative 11 that it gives a single resonance line for the -NMe<sub>2</sub> protons, the pattern of which is quite unusual as one looks at the crystal structure of this compound. Namely, according to the solid structure in Figure 2, a pair of singlets should arise due to the diastereotopic pair of methyl protons, thus indicating that its solution structure is a bit different from its solid structure; that is, the N-W bond strength becomes weakened significantly in solution, the two methyl groups now becoming equivalent on the NMR time scale due to the free rotation about the axis between the methine carbon and the nitrogen atom (*vide infra*). Cooling the temperature of the solution (-80°C) containing 11 did not alter the <sup>1</sup>H-NMR patterns significantly except a little line broadening.

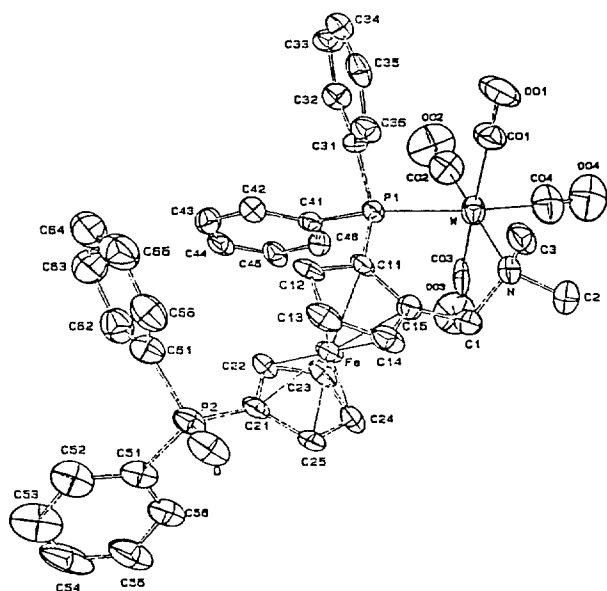
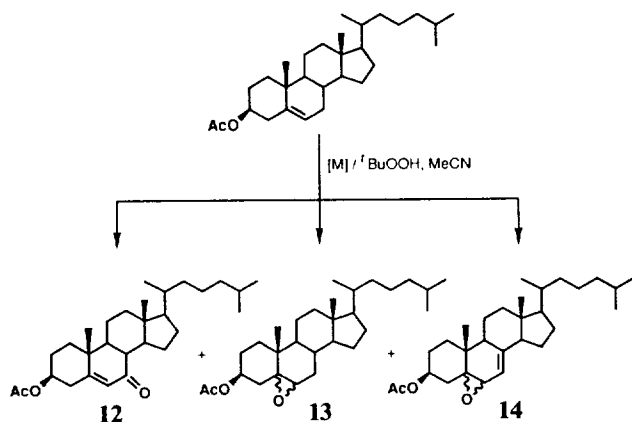


Figure 2. The X-ray crystal structure of 11.



Scheme 2. Catalytic oxidation of cholesteryl acetate.

**X-ray structure of 11.** A definitive characterization of 11, especially concerning the bonds of W with tertiary phosphine and amine and forming P=O bond, was confirmed by a single-crystal X-ray diffraction study. An ORTEP drawing of the molecule is shown in Figure 2. Positional parameters with equivalent isotropic thermal factors, and selected bond distances and angles are given in Tables 2 and 3, respectively. The molecular structure has the distorted octahedral geometry with *cis*-coordinating with P, N of substituted ferrocene at tungsten with formation of a six-membered ring. The W-N distance of 2.393(6) Å in the compound is somewhat longer than 2.37(1) Å in  $N_4P_4(NMe_2)_8W(CO)_4$ .<sup>38</sup> The single resonance of <sup>1</sup>H-NMR spectrum for the methyl groups in the  $NMe_2$  moiety may result from this fact; that is, the bond strength between the nitrogen atom and tungsten is weak enough to allow free rotation about the asymmetric carbon atom and nitrogen, and eventually making the two methyl groups equivalent in the NMR time scale. The bond distances of W-CO *trans* to P(1), 1.97(1) Å and W-CO *trans* to N, 1.95(1) Å are shorter than those of W-CO's at their *cis*-positions (W-C(O1); 2.042(9) Å and W-C(O3); 2.02(1) Å, showing the *trans*-effect, which is similar to the fact in  $N_4P_4$

Table 7. Catalytic Oxidation of Cholesteryl Acetate by Gp 6 Metal Carbonyl Derivatives<sup>a</sup>

Catalyst		Product yield(%) <sup>b</sup>		
		12	13	14
$M(CO)_6$	M = Cr	34	6	9
	Mo	13	23	15
(dppe) $M(CO)_4$	Cr	26	4	14
( $\eta^2$ -BPPF) $M(CO)_4$	Cr	51	8	5
$(\eta^2$ -FcNPP) $M(CO)_4$	Mo	12	27	4
	Cr (1)	36	7	9
	Mo (4)	12	40	6
	W (8)	4	9	2
( $\mu$ -BPPF)[ $M(CO)_5$ ] <sub>2</sub>	Cr	20	9	15
$(\mu$ -FcNPP)[ $M(CO)_5$ ] <sub>2</sub>	Cr (3)	50	2	0
	Mo (7)	10	45	4

<sup>a</sup>Recent conditions: [substrate]=0.23 mmol; [catalyst]=0.0115 mmol; [<sup>t</sup>BuOOH]=0.3 mL (anhy); Reaction temperature=70°C under  $N_2$ ; Time=15 h; Solvent=MeCN. <sup>b</sup>Isolated yield.

( $NMe_2$ )<sub>8</sub>W(CO)<sub>4</sub>.<sup>38</sup> The carbonyl groups are almost linear in the compound, and their W-C-O bond angles are in the range of 175.1(4)-178.4(9)°.

**Catalytic oxidation.** The allylic oxidation and epoxidation of cholesteryl acetate catalyzed by Gp 6 metal complexes are well-established.<sup>18-23</sup> In the present work the same substrate was used employing some of our new complexes 1, 3, 4, 7, and 8 as catalyst along with simple hexacarbonyls and other ferrocene-based carbonyl derivatives for the comparative purposes.

Scheme 2 illustrates the catalytic oxidation leading to the formation of the allylic oxidation product (12) and the epoxidation products (13 and 14) along with the formation of some other unidentified products in small amounts, which are also reported elsewhere.<sup>19</sup> The structures of these products were confirmed by their spectroscopic and physical (*i.e.*, melting point) data (see the experimental section.).

Table 7 presents the isolated yields of 12, 13, and 14. The over-all yields for the allylic oxidation and epoxidation are moderate and comparable with those reported by others.<sup>18a</sup> Of various complexes, the dichromium dodecacarbonyl derivative of FcNPP, 3, is the best catalyst in that it gives the highest yields and selectivity for the allylic oxidation. In our hands all of these new complexes show better efficiency than the simple unsubstituted hexacarbonyls,  $M(CO)_6$  and other derivative such as (dppe)Cr(CO)<sub>4</sub> (dppe=bis(diphenylphosphino)ethane). When the metal is switched from chromium to molybdenum epoxidation is favored as expected from the previous results observed in the literature.<sup>19c</sup> It can be seen that of the three metals, tungsten is the least effective both in allylic oxidation and in epoxidation. When the comparison is made between the two ferrocenylphosphine ligands FcNPP and BPPF the observations are a little mixing. Namely, for the cases of the tetracarbonyl derivatives the ligand BPPF shows higher efficiency than the ligand FcNPP for the allylic oxidation, yet the trend is reversed in the cases of bimetallic dodecacarbonyl derivatives. However, as far as epoxidation is concerned, BPPF can not beat FcNPP regardless the for-

mulation of the corresponding complexes.

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