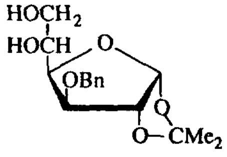
Table 2. Oxidative Cleavage of Vicinal Diols with NiO_2-Al_2O_3 in Benzence at 50℃

Diols	Products	Time, h	Yield, %[a,b]
trans-1,2-cyclohexanediol	1,6-hexanedial	5	75
1-phenyl-1,2-ethanediol	benzaldehyde + formaldehyde	5	98
1,2; 5,6-di-O-isopropylidene-D-glycer-	1,2-O-isopropylidene-D-glyceraldehyde	14	52
3	4+formaldehyde	10	(43)

[a] The yields were determined by GC. [b] The yields in parentheses are isolated ones.



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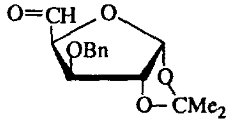

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indicates that NiO_2-Al_2O_3 system oxidizes benzylic and allylic alcohols to the corresponding aldehydes or ketones in shorter reaction time and in much higher yield than either activated MnO_2 or NiO_2 alone. For example, NiO_2-Al_2O_3 oxidizes geraniol to geranial in 85% in 6 h at room temperature wereas MnO_2 oxidizes geraniol to geranial in 50% in 90 h at 50℃.[12] Efficiency of NiO_2-Al_2O_3 system was more clearly shown in the oxidation of a carbohydrate allylic alcohol **1**. Oxidation of allylic alcohol **1** to ketone **2** was sluggish with activated MnO_2 or NiO_2 alone. Other various oxidizing agents such as PCC, PDC, and $KMnO_4$ under phase-transfer condition were not efficient and provided complex mixtures of products in certain cases. NiO_2-Al_2O_3 system efficiently oxidized compound **1** to its ketone **2** in 90% yield.

NiO_2-Al_2O_3 system also cleaved vicinal diols as shown in Table 2. 1-Phenyl-1,2-ethanediol was converted to benzaldehyde and formaldehyde in 98% yield in benzene at 50℃. At room temperature, however, quite long reaction time was required and the yield was substantially lowered. 1,2.5,6-Di-O-isopropylidene-D-mannitol and a carbohydrate diol **3** were also cleaved to the corresponding aldehydes in reasonable yields. The ease of using NiO_2-Al_2O_3 in organic solvents for cleavage of diols indicates that this solid oxidizing agent may prove to be a useful alternative to sodium metaperiodate or lead tetraacetate.

Acknowledgement. This work was supported by a grant from Yonsei University.

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9. NiO_2 was prepared as described in reference 8.
10. Al_2O_3 (W-200-B, Activity grade Super I) was purchased from ICN Pharmaceuticals, Inc. and used without futher activation.
11. The solid mixture was prepared by gentle grinding a mixture of NiO_2 and Al_2O_3 in a mortar for 2 min.
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Reaction and Coordination Chemistry of Ferrocenylphosphines with $(\eta^5\text{-}C_5H_5)Co(CO)_2$-Crystal Structures of Two Ferrocenylphosphine Oxides

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Received February 11, 1990

There has been considerable interest in reactions catalyzed by ferrocenylphosphine derivatives of metals such as Rh, Ni, Pd, Pt, and Au[1-10]. Of various chiral and achiral ferrocenylphosphine ligands those that have been most widely explored in connection with homogeneous catalysis are $(\eta^5\text{-}C_5H_4PPh_2)_2Fe$(BPPF), $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3(CHMeNMe_2)PPh_2\text{-}1,2)$(PPFA), and $(\eta^5\text{-}C_5H_4PPh_2)Fe(\eta^5\text{-}C_5H_3(CHMeNMe_2)PPh_2\text{-}1,2)$(BPPFA). We have recently been interested in the synthesis of rhodium and iron complexes incorporating these ligands principally for use as catalyst precursors in the catalytic hydrogenation of polynuclear heteroaromatic compounds[11] and in the CO_2 activation for the synthesis of carbamates[12,13], respectively. During the course of our investigations we have noticed that the above ligands form a wide range of complexes with various coordination modes: a typical chelating bidentate, a monodentate diphosphine, or a bridging ligand in dimeric and trimeric species.

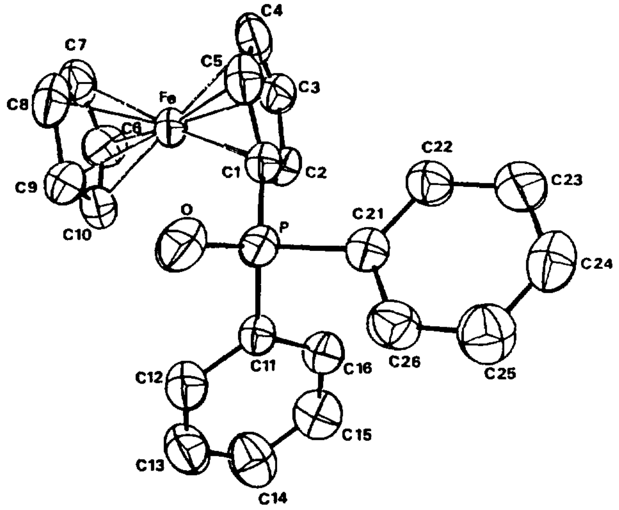


Figure 1. Molecular Structure of **2**. Selected bond lengths (Å) and angles (°) : Fe-C(1) 2.027(3), Fe-C(3) 2.058(4), Fe-C(5) 2.030 (4), Fe-C(6) 2.030(4), Fe-C(8) 2.048(4), Fe-C(10) 2.027(4), O-P 1.477(3), C(11)-P 1.808(4), C(21)-P 1.806(3), C(1)-P-O 114.6(2), C (11)-P-O 112.4(2), C(11)-P-C(1) 105.9(2), C(21)-P-O 112.5(2), C(21)-P-C(1) 105.8(2), C(21)-P-C(1) 104.8(2), C(2)-C(1)-P 128.2(3), C(5)-C(1)-P 124.9(3).

Thus, in order to extend the coordination chemistry of these ligands, we had available $(\eta^5\text{-}C_5H_5)Co(Co)_2$ (**1**) which is a much-studied compound in connection with cyclization of olefins and acetylenes[14-16]. This paper documents some preliminary work on the reactions of BPPF, PPFA, and BPPFA with **1** and the structure determination of two ferrocenylphosphine oxides derived serendipitously from BPPF and PPFA.

BPPF (2.27 g, 4.1 mmol) and **1** (0.53 m*l*, 5.3 mmol) in toluene (75 m*l*) were stirred under reflux for 30 h in an argon atmosphere. As the reaction proceeded, the solution became darkbrown with deposit of black precipitates. Toluene was evaporated and residue was extracted with CH_2Cl_2 (10 m*l*) to be chromatographed on silica gel. Two orange bands were collected on elution with CH_2Cl_2 / acetone (1/2) to give $(\eta^5\text{-}C_5H_5)Fe(C_5H_4P(=O)Ph_2)$ (**2**) (0.25 g, 25%) and $(\eta^5\text{-}C_5H_4PPh_2)Fe(\eta^5\text{-}C_5H_4P(=O)Ph_2)$ (**3**) (0.16 g, 11%) as orange crystals after usual workups.

The structures of **2** and **3** were established by analytical and spectroscopic methods[17*] and the X-ray crystal structure of **2** is shown in Figure 1[18].

The anticipated coordination products of the type CpCo $(BPPF)_n$ ($n=1,2$) have not been formed in an any observable amount.

The reaction of PPFA with **1** under the same reaction conditions as above has also led to the oxidation at phosphorus to give a chiral phosphine oxide $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3(CHMeNMe_2)P(=O)Ph_2\text{-}1,2)$ (**4**) (45%)[19*] as a sole product. Single crystals suitable for the X-ray study have been obtained by cooling an acetone solution of **4** at 0℃ and the crystal structure is shown in Figure 2[20].

One of characteristic features of **4** is that, unlike the parent PPFA, free rotation of the two N-methyl groups around the C-N axis seems to be prohibited due to increased steric congestion by introduction of oxygen on phosphorus. This is evidenced by the ^1H-NMR which gives rise to two resonances for the NMe_2 groups at δ 1.63 and 1.44 ppm. Other ^1H and ^{31}P-NMR patterns are as expected for the structure.

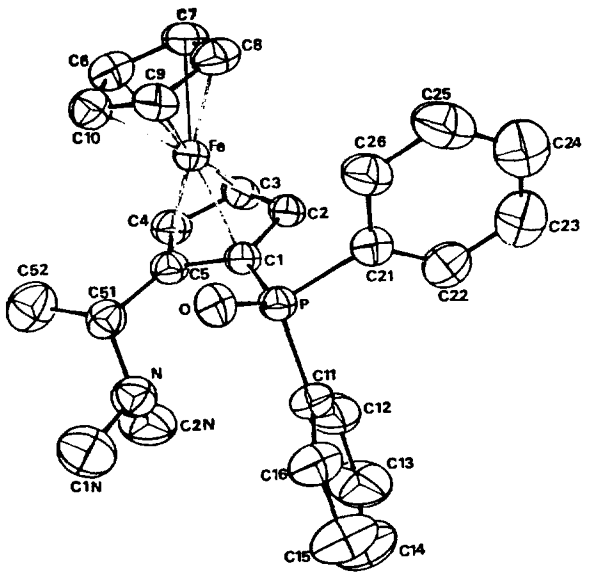
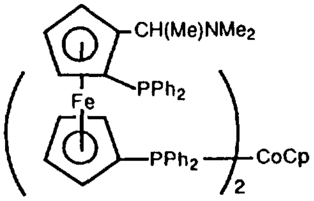


Figure 2. Molecular Structure of **4**. Selected bond lengths (Å) and angles (°) : Fe-C(1) 2.029(3), Fe-C(9) 2.064(5), O-P 1.491(3), C(1)-P 1.785(4), C(11)-P 1.806(4), C(21)-P 1.809(4), C(1N)-N 1.456 (8), C(2N)-N 1.433(8), C(5N)-N 1.454(5), C(2)-C(1) 1.437(6), C(5)-C(1) 1.431(6), C(8)-C(9) 1.422(8), C(21)-C(22) 1.367(6), C(22)-C(23) 1.391(8), C(1)-P-O 115.7(2), C(11)-P-O 112.8(2), C(21)-P-O 111.7 (2), C(11)-P-C(1) 106.7(2), C(21)-P-C(1) 104.3(2), C(21)-P-C(11) 104.8(2), C(2)-P-C(1) 126.0(3), C(5)-P-C(1) 126.2(4), C(51)-C(5)-C (4) 128.4(4), C(51)-C(5)-C(1) 123.6(4), C(5)-C(51)-N 108.0(4), C(52)-C(51)-N 115.7(4), C(51)-N-C(2N) 115.7(5), C(2N)-N-C(1N) 111.9(5).

The reaction of BPPFA with **1** is somewhat different from those of BPPF and PPFA, yielding mostly the cobalt-ferrocenylphosphine complex $CpCo(\eta^1\text{-}BPPFA\text{-}P)_2$ (**5**) (45%)[21*] as well as the oxidation product $(\eta^5\text{-}C_5H_4P(=O)Ph_2)Fe(\eta^5\text{-}C_5H_3(CHMeNMe_2)P(=O)Ph_2\text{-}1,2)$ (**6**) (10%)[22*].



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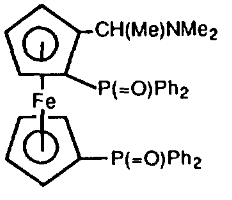

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The complex formation in **5** is best confirmed by the presence of a sharp singlet at δ 3.92 ppm due to the unsubstituted Cp ring protons. The ^{31}P-NMR is also supportive to give the different resonances at δ 26.84 (s) and −25.82 (s) ppm due to the coordinated and free phosphorus atoms, respectively. Remaining question concerning the site of coordination of BPPFA can be solved by assigning the high-field signal to the phosphine neighboring the $CHMeNMe_2$ group in the same ring. This can be achieved by comparing the ^{31}P NMR spectra of BPPFA, PPFA, and **5**. The ^1H NMR pattern of **6** is straightforward. Thus, for example, AB protons of the monosubstituted Cp ring protons appear as two singlets at δ 3.86 and 3.68 ppm while the disubstituted Cp ring gives rise to five broad signals expected for the ABC protons. The methine proton appears as a quartet at δ 4.26 ppm as usual.

Obviously, much work has yet to be done concerning the mechanisms for the formation of these unexpected phosphine oxides not alone their further uses as ligands for the preparation of other series of coordination compounds. The compound **5** is also interesting in that it may be used not only in the synthesis of heteronuclear metal clusters but also in homogeneous catalytic cyclization of some alkynes. These points are the subject of our future communication.

Acknowledgement. This work has been partially supported by the Ministry of Education through the Korea Research Foundation (1988) and the Korea Science and Engineering Foundation (Grant No. 88-0304-03). Dr. J. H. Cheong of Korea Institute of Science and Technology is gratefully acknowledged for the crystal structure determination.

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17. For **2**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.61-7.39(m, C_6H_5), 4.72(b, C_5H_4), 4.26(b, C_5H_5). ^{31}P-NMR (121.5 MHz, $CDCl_3$) δ 26.13 (s). Anal. Calcd for $C_{22}H_{19}POFe$: C, 68.42; H, 4.92. Found: C, 67.90; H, 4.70. For **3**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.64-7.37(m, P(O)Ph_2), 7.27(b, PPh_2), 4.57 and 4.36(b, $C_5H_4P(O)Ph_2$), 4.21 and 4.03(b, $C_5H_4PPh_2$). ^{31}P-NMR (121.5 MHz, $CDCl_3$) δ 6.72 (s, P(O)Ph_2), −19.37(s, PPh_2). Anal. Calcd for $C_{34}H_{28}P_2OFe$: C, 71.59; H, 4.91. Found: C, 70.70; H, 4.74.
18. Crystal data for **2**: Space group $P2_1/c$, a=14.172(2), b=10.434(1), c=11.894(2) Å, β=90.53(1)°, V=1758.7(5) Å^3, Z=4, D_{calcd}=1.494 gcm^{-1}, Mo-Kα radiation, λ=0.71073 Å, μ=2.29 cm^{-1}. An Enraf-Nonius CAD-4 diffractometer, 2047 unique absorption corrected reflections with 1>3σ (1) in the range 3° <2θ <50°. The structure was solved by Patterson and Fourier Methods. Final R=0.0317, R_w=0.0374.
19. For **4**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.65-7.32 (m, C_6H_5), 4.41-4.25(m, C_5H_3), 4.18(s, C_5H_5), 3.89(q, ^{3}J=6 Hz, CH), 1.63(s, NMe_2), 1.15(d, ^{3}J=6 Hz, CMe), ^{31}P-NMR (121.5 MHz, $CDCl_3$) δ 25.03 (s). Anal. Calcd for $C_{26}H_{28}NPOFe$: C, 68.29; H, 6.13; N, 3.06. Found: C, 68.10; H, 6.18; N, 3.15.
20. Crystal data for **4**: space group $P2_1$, a=9.3252(8), b=11.342(1), c=11.043(1) Å, β=102.631(8)°, V=1139.8(2) Å^3, Z=2, D_{calcd}1.331 gcm^{-1}, Mo-Kα radiation, λ=0.71073 Å, μ=2.29 cm^{-1}. An Enraf-Nonius CAD-4 diffractometer, 1797 unique absorption corrected reflections with 1>3σ (1) in the range 3° <2θ <50°. The structure was solved by Patterson and Fourier Methods. Final R=0.0311, R_w=0.0344.
21. For **5**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.59-7.14(m, C_6H_5), 4.36-4.13(m, C_5H_3), 3.92(s, C_5H_5), 3.84(q, ^{3}J=6 Hz, CH), 1.76(s, NMe_2), 1.23(d, ^{3}J=6 Hz, CMe). ^{31}P-NMR (121.5 MHz, $CDCl_3$) δ 26.64(s, PPh_2Co), -25.82(s, PPh_2). Anal. Calcd for $C_{81}H_{79}N_2P_4Fe_2Co$: C, 70.76; H. 5.75; N, 2.04. Found: C, 70.30; H, 5.51; N, 2.15.
22. For **6**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.55-7.32(m, C_6H_5), 4.81, 4.73, 4.59, 4.52 and 4.47(b, C_5H_3), 4.26(q, ^{3}J=9 Hz, CH), 3.86 and 3.68 (b, C_5H_4), 1.56(s, NMe_2), 1.01(d, ^{3}J=9 Hz, CMe), ^{31}P-NMR (121.5 MHz, $CDCl_3$) δ 26.17(s), 23.78 (s). Anal. Calcd for $C_{38}H_{37}NP_2O_2Fe$: C, 67.97; H, 5.51; N, 2.08. Found: C, 67.90; H, 5.61; N, 1.87.

Determination of Z-and E-2-Methylbut-1-en-1-ol

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Received December 10, 1990

Fast double bond migration of allylic alcohols with metal complexes is an unique way of generating simple enols in non-aqueous solvents.[1,2] The reaction of 2-ethylprop-2-en-1-ol with $[Rh(CO)(PPh_3)_3]\ ClO_4$ generates a simple and relatively stable enol, 2-methylbut-1-en-1-ol, **1** containing both **Z**- and **E**-isomers according to ^{1}H-NMR data (Eq. 1).[2] Unambiguous assignments of the ^{1}H-NMR signals of **1**, however,