"Methyldiopium" and "Methylbinapium",
Chiral Phosphonium-Phosphine Ligands

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Abstract.

Monomethylphosphoniums derived from (R,R)-diop ("methyldiopium" 2•I) and (R)-binap ("methylbinapium" 7•I) are described. The crystal structure of 7•I is given, and 2•I is shown to act as a ligand of carbonyliron.
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Keywords: Asymmetry Phosphines Phosphoniums Carbonyl compounds

Many chiral ligands efficient in asymmetric catalysis retain two features of original Kagan's diop [1] and Noyori's and Takaya's binap [2]: a quite rigid chiral backbone and a C_2-symmetric dative-dative chelating ability. From a coordination chemistry viewpoint, we envisionned a disymmetrical dative-electrostatic chelation of anionic metal centers by chiral phosphinite-ammonium ligands, "ephosiums" and "valphosiums" [3,4]. We now describe related chiral phosphine-phosphonium ligands, lacking the C_2-symmetry but preserving the rigid backbones.

Owing to the C_2-symmetry, treatment of (R,R)-diop 1 with one equivalent of methylating reagent leads to a ternary mixture of unreacted 1, monomethylation product 2 ("methyl-diopium") and dimethylation product 3. In most of the conditions used, the ratio 1:2:3 is close to the statistical distribution 25:50:25, with the general trend: 2:3 < 50:25 (scheme 1). Attempts to protect one phosphorus atom of 1 in a BH_3 adduct resulted in a same lack of selectivity.
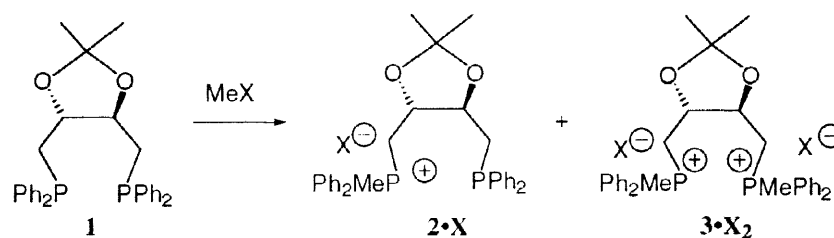

Scheme 1. From (R,R)-diop to "methyldiopium" 2 and "dimethyldiodium" 3: X = I, $Me_2O•BF_4$, OTf.

We found that when the reaction is conducted in a 5:6 $MeOH:CH_2Cl_2$ mixture, a default α = [MeI]/(2[diop]) = 1/4 enables the isolation of 2•I in more than 95% purity,[1] while excess

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[1] With α = 1/8, 100% pure 2•I is obtained. The theoretical statistical distribution is: 1 : 2 : 3 = $(1-\alpha)^2$: $2\alpha(1-\alpha)$: α^2.

diop is extracted and recycled in diethylether.[2] 2•I reacted with Fe(CO)$_5$ in the presence of Me$_3$NO, to give 4•I and 5•I$_2$:[3] to the best of our knowledge, they are first examples of complexes involving a chiral version of phosphonium-phosphine ligands, termed as "phophos" by Baird [5]. Metathesis of 2•I and KHFe(CO)$_4$ leads to 2•HFe(CO)$_4$,[4] but in accordance with a general trend [7], no selective CO-substitution by the phosphine enabled the detection of a zwitterionic hydride [3,4].[5]
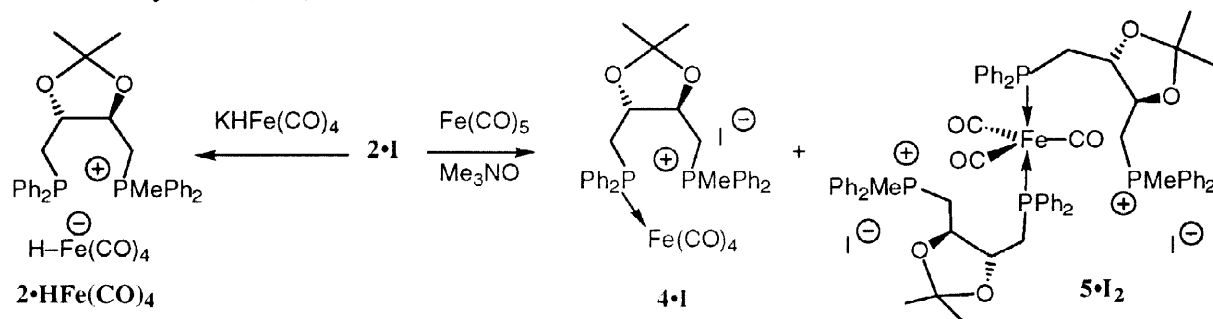
**Scheme 2.** Some coordination chemistry of methyldiopium 2•I.

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[2] CH$_2$Cl$_2$ (6 mL) was added to a suspension of (−)-diop (0.930 g, 1.87 mmol), MeI (0.058 mL, 0.94 mmol) i n MeOH (10 mL), and the solution was stirred for 14 h, then evaporated. The residue was washed with Et$_2$O, giving 2•I (0.597g) more than 95 % pure. (the statistical ratio for α=1/4 is 1 : 2 : 3 = 56 : 38 : 6,[1] and has been thus improved to 2:3 > 95:5). NMR data in CD$_3$CN: ^{31}P{^{1}H} (81 MHz): δ = −18.0 (1 P; P:), + 28.7 (1 P; P$^+$). ^{1}H (250 MHz): δ =1.17, 1.20 (2 s, 6 H; C(CH$_3$)$_2$); 2.32 (ddd, $^2J_{HH}$ = 14 Hz, $^2J_{PH}$ = 7 Hz, $^3J_{HH}$ = 2 Hz, 1 H in CH$_2$P:); 2.55 (d, $^2J_{PH}$ = 14 Hz, 3 H, CH$_3$–P$^+$): 2.63 (ddd, $^2J_{HH}$ = 14 Hz, $^2J_{PH}$ = 2 Hz, $^3J_{HH}$ = 5 Hz, 1 H in CH$_2$P); 3.11 (ddd, $^2J_{HH}$ = 15 Hz, $^2J_{PH}$ = 12 Hz, $^3J_{HH}$ = 11 Hz, 1 H in CH$_2$P$^+$); 3.39 (ddd, $^2J_{HH}$ ≈ $^2J_{PH}$ ≈ 15 Hz, $^3J_{HH}$ = 3 Hz, 1 H in CH$_2$P$^+$); 3.86 (m, 1 H, $^+$PCH$_2$CHO); 3.98 (m, 1 H, :PCH$_2$CHO); 7.28-7.43 (m, 10 H, :P(C$_6$H$_5$)$_2$); 7.60-7.93 (m, 10 H; $^+$P(C$_6$H$_5$)$_2$). ^{13}C{^{1}H} (63 MHz): δ = 8.19 (d, $^1J_{PC}$ = 56 Hz, CH$_3$P$^+$); 26.68, 26.89 (2 s, (CH$_3$)$_2$C); 26.86 (dd, $^1J_{PC}$ = 54 Hz, $^4J_{PC}$ = 3 Hz, CH$_2$P$^+$); 30.47 (d, $^1J_{PC}$ = 15 Hz, CH$_2$P:); 75.96 (dd, $^2J_{PC}$ = 9 Hz, $^3J_{PC}$ = 7 Hz, $^+$PCH$_2$CHO); 80.62 (dd, $^2J_{PC}$ ≈ $^3J_{PC}$ ≈ 15 Hz, :PCH$_2$CHO); 110.66 (s, Me$_2$C); 119.95, 121.08 (2 d, $^1J_{PC}$ = 87Hz, (i-C)$_2$P$^+$); 129.17-129.83 (m, (m-C)$_2$P:, (p-C)$_2$P:); 130.54, 132.67 (2 d, $^2J_{PC}$ = 13 Hz, (o-C)$_2$P$^+$); 133.04-133.97 (m, (o-C)$_2$P:, (m-C)$_2$P$^+$); 134.52, 135.56 (2 d, $^4J_{PC}$ = 3 Hz, (p-C)$_2$P$^+$), 138.83, 139.36 (2 d, $^1J_{PC}$ = 13, 12 Hz, (i-C)$_2$P:). NMR data in CD$_3$CN for 3•I$_2$: ^{31}P{^{1}H} (81 MHz): δ = + 28.8 (P$^+$). ^{1}H (200 MHz): δ =1.15 (s, 6 H; C(CH$_3$)$_2$); 2.59 (d, $^2J_{PH}$ = 14 Hz, 6 H, CH$_3$–P$^+$): 3.19 (ddd, $^2J_{HH}$ = 16 Hz, $^2J_{PH}$ = 11 Hz, $^3J_{HH}$ = 10 Hz, 2 H in CH$_2$P$^+$); 4.04 (m, 2 H, $^+$PCH$_2$CHO); 4.43 (ddd, $^2J_{HH}$ ≈ $^2J_{PH}$ ≈ 15 Hz, $^3J_{HH}$ = 2 Hz, 2 H in CH$_2$P$^+$); 7.58-8.00 (m, 20 H; $^+$P(C$_6$H$_5$)$_2$). ^{13}C{^{1}H} (50 MHz): δ = 8.84 (d, $^1J_{PC}$ = 56 Hz, CH$_3$P$^+$); 25.50 (s, (CH$_3$)$_2$C); 26.67 (d, $^1J_{PC}$ = 54 Hz, CH$_2$P$^+$); 76.37 (dd, $^2J_{PC}$ = 7 Hz, $^3J_{PC}$ = 6 Hz, CHO); 112.17 (s, Me$_2$C); 119.85, 120.83 (2 d, $^1J_{PC}$ = 86, 87 Hz, (i-C)$_2$P$^+$); 130.61-130.98 (m, (o-C)$_2$P$^+$); 133.15-133.59 (m, (m-C)$_2$P$^+$); 135.69 (s, (p-C)$_2$P$^+$).

[3] Fe(CO)$_5$ (0.1 mL, 0.74 mmol), 2•I (0.465 g, 0.73 mmol), Me$_3$NO (0.090 g, 0.81 mmol) and THF (10 mL) were stirred for 18 h between −78°C and 25°C, then filtered: the solid 5•I$_2$ was washed with THF and dried (0.418 g, 80%). IR (THF): ν$_{C≡O}$ (cm^{-1}) = 1875 (s). NMR data in CD$_3$CN: ^{31}P{^{1}H} NMR (81 MHz): δ = +80.5 (s, 1 P; FeP), +28.6 (s, 1 P; $^+$P). ^{1}H NMR: (200 MHz) δ = 1.11, 1.14 (2 s, 6 H, C(CH$_3$)$_2$), 2.51 (d, $^2J_{PH}$ = 14 Hz, 3 H, CH$_3$P$^+$); 2.59-2.90 (m, 2 H in CH$_2$PFe); 2.89, 3.17 (2 ddd, 2 H, CH$_2$P$^+$); 3.79 (m, 1 H, $^+$PCH$_2$CHO); 4.31 (m, 1 H, FePCH$_2$CHO); 7.41-7.80 (m, 20 H, (C$_6$H$_5$)$_4$). ^{13}C NMR: (63 MHz) δ = 8.01 (d, $^1J_{PC}$ = 55 Hz, CH$_3$P$^+$); 27.01, 26.47 (2 s, (CH$_3$)$_2$C); 25.36 (d, $^1J_{PC}$ = 55 Hz, CH$_2$P$^+$); 33.87 (broad, CH$_2$PFe); 75.83 (dd, $^2J_{PC}$ ≈ 9 Hz, $^3J_{PC}$ ≈ 7 Hz, $^+$PCH$_2$CHO); 79.18 (dd, $^2J_{PC}$ ≈ $^3J_{PC}$ ≈ 16 Hz, :PCH$_2$CHO); 110.39 (s, Me$_2$C); 120.07, 120.50 (2 d, $^1J_{PC}$ = 87 Hz, (i-C)$_2$P$^+$); 128.72-135.09 ((C$_6$H$_5$)$_4$); 214.03 (t, $^2J_{PC}$ = 26 Hz, Fe(CO)$_3$). 4•I was obtained from the THF filtrate: IR (THF): ν$_{C≡O}$(cm^{-1}) = 2046 (m), 1965 (m), 1940 (s). ^{31}P{^{1}H} NMR (81 MHz): δ = +71.1 (s, 1 P; FeP), +28.7 (s, 1 P; $^+$P).

[4] Solid KI was separated, and the removal of K$^+$ was evidenced by IR in THF, where the shoulder at 1858 cm^{-1} due to a C≡O···K$^+$ interaction had disappeared: ν$_{C≡O}$ (cm^{-1}) = 1998 (m), 1908 (m), 1878 (s, sharp)[6].

[5] Likewise reaction of 4•I and 5•I$_2$ with KOH or [Et$_4$N](OH) did not lead to any iron hydride [8], but to the disappearance of both the phosphonium group and the diop skeleton, most likely via an ylide destabilized by the adjacent dioxolane ring.

(*R*)-binap **6** has a less fragile*C*₂-symmetric backbone, and was thus reacted with one equivalent of MeI to selectively afford "methylbinapium" **7•I** (scheme 3).[6]
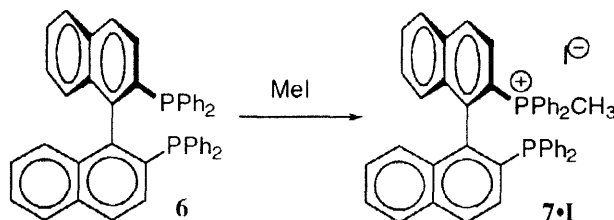
Scheme 3. Selective preparation of "methylbinapium" iodide **7•I** .

The high field P⁺–CH₃ resonance in the ¹H NMR spectrum of **7•I** in CD₂Cl₂ (1.8 ppm), suggests that the methyl group lyes inside the anisotropy cone of an aromatic ring. This feature is confirmed in the solid state by X-ray diffraction (Scheme 4). The geometry of the binap skeleton of **7** is superimposable to the crystal geometry of binap **6** [9,10], with perpendicular naphtylene planes and a ⁺P–Me axis tilted by *c.a.* 40° from the P–(lone pair) axis of binap.[7]
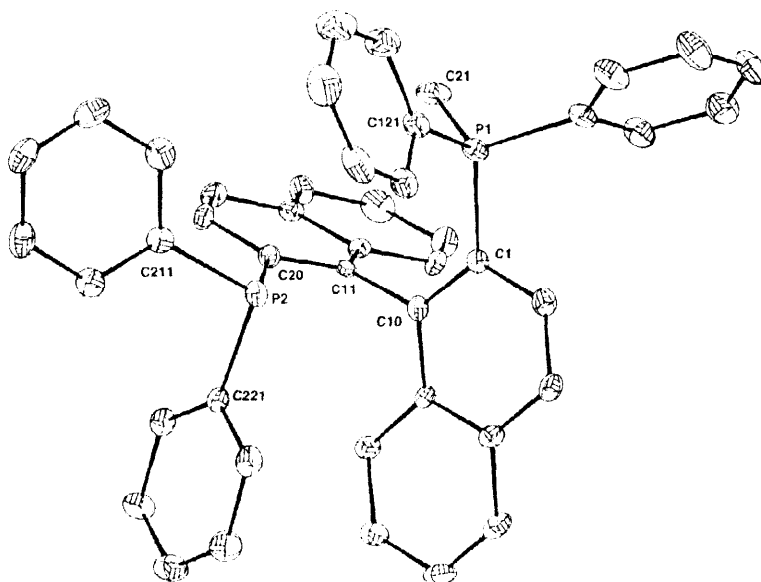
**Scheme 4.** CAMERON view of the X-ray crystal structure of methylbinapium iodide **7•I**.

Since steric hindrance protects **7•I** from a second methylation, it also prevents any reaction of **7•I** with carbonyliron precursors. However, **7•I** undergoes demethylation upon treatment by the reactive hydride KHCr(CO)₅ in refluxing THF [11]: binap **6** was obtained by air oxidation of an intermediate carbonyl chromium complex, whose spectral data are consistent with formula **8** (Scheme 5),[8] but not with the zwitterionic complex [HCr(CO)₅(methylbinapium)]. Finally, no iron nor chromium methylbinapium complex could be evidenced yet.
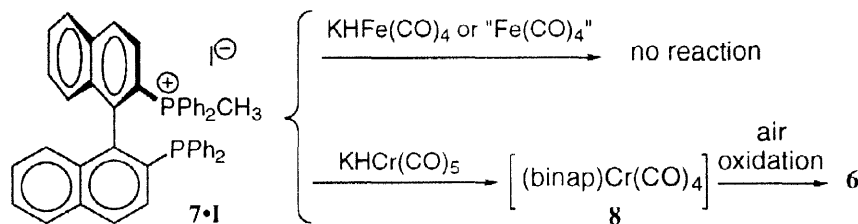
Scheme 5. Reactivity of methylbinapium **7** with hydride and carbonyl metals.

Cationic chiral phoshines were designed to perform asymmetric catalysis in aqueous media, but their structure precluded simultaneous interactions of metal centers with both the phosphine and peripheral ammonium ends [13]. Although no dative-electrostatic chelation of an anionic metal hydride by methyldiopium and methylbinapium could be revealed, looser interactions of the phosphonium end with substrates and formally neutral, but polar, catalytic transition metal centers (other than Fe, Cr) might highlight novel effects in asymmetric catalysis [14,15].

Acknowledgements.

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