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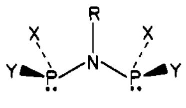
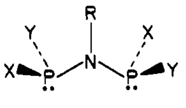
The Diastereomeric Selective Synthesis of a Diphosphinoamine: *meso*-i-$C_3H_7N[C_6H_5PNH(i\text{-}C_3H_7)]_2$

Sir:

Although several methods for formation of diphosphinoamines exist,[1-9] surprisingly little is known about forming compounds of type $RN(PXY)_2$ (**1a,b**) stereoselectively. Such reactions and the derived products could be of considerable interest to the continuing development of phosphorus–nitrogen synthetic chemistry. Recently, we undertook systematic studies of diphosphinoamine syntheses and now wish to report the unequivocal demonstration of the diastereomerically selective formation of the new diphosphinoamine *meso*-*i*-PrN[PhP(*i*-PrNH)]$_2$.



1a: meso



1b: *d*, *l*

Reaction of $PhPCl_2$ with *i*-$PrNH_2$ (1:2.2 mole ratio) in toluene in the presence of excess Et_3N at 0 °C results in precipitation of Et_3NHCl and formation of an approximately 1:1 mixture of PhP(*i*-PrNH)$_2$ (**2**)[10] and *i*-PrN[PhP(*i*-PrNH)]$_2$ (**3**). The reaction mixture exhibits ^{31}P NMR singlet resonances at δ 57.7 and 60.5 due to **2** and one diastereomer of **3**, respectively. Only a small quantity of a second diastereomer (7%) at δ 59.5 is seen. Recrystallization of **3** from toluene yields pure monodiastereomeric *meso*-**3** (**1a**, X = *i*-Pr, Y = Ph).[11] Compound **3** was obtained as a crystalline derivative suitable for X-ray analysis by its quantitative reaction with norbornadiene–tetracarbonylmolybdenum to form the diphosphinoamine complex *cis*-*meso*-*i*-PrN[PhP(*i*-PrNH)]$_2$Mo(CO)$_4$ (**4**).[12] The ^{31}P NMR spectrum of **4** in the initial reaction solution or after recrystallization from toluene showed only a single ^{31}P resonance at δ 90.3, consistent with a single diastereomeric product.

Characterization of **3** and **4** is based on spectral (^1H and ^{31}P NMR, IR, MS) and elemental analyses and is confirmed by a single-crystal X-ray analysis of **4**.[13] Crystals of **4**$\cdot{}^1/_2C_7H_8$ contain four molecules of two types (molecules A and B) per unit cell (Figure 1), which are related by an approximate (not crystallographic) mirror plane. The complex contains **3** cis coordinated to the Mo(CO)$_4$ moiety such that two *i*-PrNH groups and two Ph groups are located on opposite sides of the four-membered NP_2Mo ring. The molecule has approximate C_s point-group symmetry; **4A** and **4B** differ primarily in the rotation of the *i*-Pr group around the N(2)–C(54) bond. The four-membered NP_2Mo ring is bent slightly (5.5°) from planarity along the P···P axis. The cis-axial CO groups, especially CO(1), CO(2), and CO(3), are bent back from the ligand as expected if there exists substantial intragroup repulsions between CO(1–3) and the two bulky *i*-PrNH groups. Small differences in interatomic distances and angles between **4A** and **4B** are seen, but they do not appear chemically significant. Mean distances and angles agree, insofar as they can be compared, with those obtained for PhN[P(NHPh)$_2$]$_2$[14] and PhN[P(NHPh)$_2$]$_2$·Mo(CO)$_4$.[15]

Complex **4** and the diphosphinoamine **3** have either *S,R* or *R,S* configurations at phosphorus; hence, both are meso isomers. Only small quantities of the *d,l* diastereomer (*R,R* and *S,S*) of **3** were observed, and it could not be obtained free of the meso form. No evidence for presence of a second diastereomer of **4**, in the reaction of *meso*-**3** with norbornadiene–tetracarbonylmolybdenum was obtained. That the crystal of *meso*-**4** studied is representative of the bulk sample of **4** was shown when samples of **4** collected successively during the entire crystallization showed identical X-ray diffraction, mass spectral, and IR spectral data.

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(11) **3**: $^{31}P\{^1H\}$ NMR (C_7H_8) δ 60.5 (s); ^1H NMR ($CDCl_3$) δ 1.2 (m of d, $^3J_{HH}$ = 6.6 Hz, area 9, CH_3), 2.3 (m, area 1, NH), 3.4 (m of septets, $^3J_{HH}$ = 6.6 Hz, area 1.5, CH), 7.2 (m, area 5, C_6H_5); characteristic IR frequencies (cm^{-1}) 3337 w (N–H), 1380 m, 1361 m, 1168 vs, 1126 vs, 868 s, 853 s; mass spectrum, parent at *m/e* 389, $C_{21}H_{33}N_3P_2^+$. Anal. Calcd for $C_{21}H_{33}P_2N_3$: C, 64.76; H, 8.54; N, 10.79; P, 15.91. Found: C, 64.22; H, 8.59; N, 10.59; P, 15.91.

(12) **4**: $^{31}P\{^1H\}$ NMR (C_7H_8) δ 90.3 (s); ^1H NMR ($CDCl_3$) δ 1.2 (m of d, $^3J_{HH}$ = 6.6 Hz, area 9, CH_3), 2.2 (d, J_{PNH} = 10.0 Hz, area 1, NH), 3.6 (m of septets, $^3J_{HH}$ = 6.6 Hz, area 1.5, CH), 7.4 (m, area 5, C_6H_5); characteristic IR frequencies (cm^{-1}) 3370 w, 2013 vs, 1913 vs, 1893 vs, 1871 vs; 1385 m, 1365 m, 1162 m, 1414 s, 881 m, 857 m; mass spectrum, parent at *m/e* 597, $C_{25}H_{33}N_3O_4P_2Mo^+$. Anal. Calcd for $C_{25}H_{33}P_2N_3MoO_4$: C, 50.26; H, 5.57; N, 7.03; P, 10.37. Found: C, 51.28; H, 5.84; N, 7.22; P, 10.58.

(13) Crystal data for **4**: $MoP_2N_3O_4C_{25}H_{33}\cdot{}^1/_2C_7H_8$, formula wt 689.59, triclinic, $P\bar{1}$, a = 16.928 (6) Å, b = 19.118 (6) Å, c = 10.215 (3) Å, α = 97.52 (3)°, β = 96.78 (3)°, γ = 80.10 (3)°, V = 3213 (2) Å^3, Z = 4, D_{obsd} = 1.38 g cm^{-3}, D_{calcd} = 1.43 g cm^{-3}. Intensity data: Nicolet $P\bar{1}$ autodiffractometer, Mo Kα (λ = 0.710 69 Å), ω scan mode $3.0 \leq 2\theta \leq 42.5°$, 7106 reflections measured of which 3428 were observed ($Fo \geq 6\sigma(Fo)$). The structure was solved by direct methods and refined by blocked full-matrix least-squares calculations: R = 0.069, R_w = 0.085.

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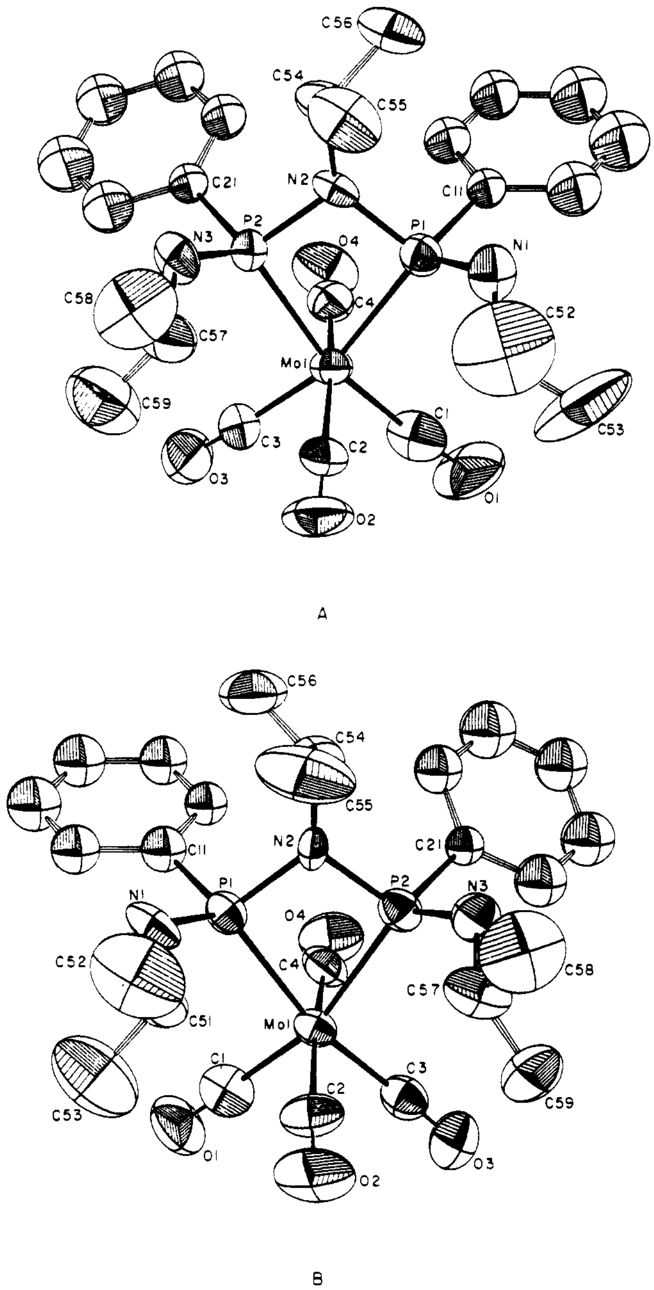

Figure 1. ORTEP drawing and numbering scheme for *cis-meso-i*-PrN-[PhP(*i*-PrNH)]$_2$Mo(CO)$_4$ (**4**) showing 50% probability ellipsoids of all atoms. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg), mean for molecules A and B: Mo-P(1), 2.497 (5); Mo-P(2), 2.492 (5); P(1)-N(2), 1.72 (1); P(2)-N(2), 1.69 (1); P(2)-N(3), 1.68 (2); P(1)-N(1), 1.68 (2); P(1)-C(11), 1.83 (1); P(2)-C(21), 1.82 (1); N(2)-C(54), 1.49 (2); P(1)-Mo-P(2), 65.1 (2); P(1)-N(2)-P(2), 104.3 (8); N(2)-P(1)-Mo, 94.9 (5); N(2)-P(2)-Mo, 95.8 (4); Mo-P(1)-N(1), 124.1 (6); Mo-P(2)-N(3), 126.5 (5); P(2)-Mo-C(3), 99.4 (7); P(2)-Mo-C(1), 165.5 (6); Mo-P(1)-C(11), 119.5 (4); Mo-P(2)-C(21), 118.7 (4); N(1)-P(1)-C(11), 100.5 (7); N(3)-P(2)-C(21), 106.3 (6); N(2)-P(1)-N(1), 111.4 (7); N(2)-P(2)-N(3), 110.5 (7); P(1)-Mo-C(1), 100.5 (6); P(1)-Mo-C(4), 92.0 (6); P(2)-Mo-C(2), 97.8 (6); P(2)-Mo-C(4), 88.7 (6); P(1)-Mo-C(2), 99.9 (6); P(1)-Mo-C(3), 163.5 (7).

The origin of diastereomer formation selectivity in the *i*-PrNH$_2$-PhPCl$_2$ reaction and the extent to which this is general in RNH$_2$-R'PCl$_2$ reactions or other diphosphinoamine formation reactions is unclear. Aniline and PhPCl$_2$ react at 25 °C to form both *d,l* and meso products.[16] Previous studies of MeN[P(NMe$_2$)$_2$]$_2$-PCl$_3$ and MeN(SiMe$_3$)$_2$-MePCl$_2$ reactions yield MeN[P(Cl)NMe$_2$]$_2$ and MeN[P(NMe)(Cl)SiMe$_3$]$_2$, respectively, which were suggested but not proved to be monodiastereomers.[6,10] In some cases, single-diastereomer product formation could have occurred but because the products were isolated by distillation at elevated temperatures product isomerization might be expected. *meso*-**3** does not form through *i*-PrNH$_2$ elimination between molecules of **2**; **3** forms only slowly as a *d,l*-meso mixture from **2** at 130 °C.

Diastereomer selection likely occurs because of conformation selection (excess population of one rotomer) in either intermediate or transition-state P-Cl bond-containing species. It is possible that, through variations in substitution and/or through use of other diphosphinoamine formation reactions, ways will be found to control diastereomer formation so that either meso or *d,l* isomers can be selectively formed. Such reactions are being studied currently in our laboratories.

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Registry No. **2**, 716-85-8; **3**, 98087-84-4; **4**, 98087-85-5; *i*-PrNH$_2$, 75-31-0; PhPCl$_2$, 644-97-3; (norbornadiene)tetracarbonylmolybdenum, 12146-37-1.

Supplementary Material Available: Listings of details of the crystal structure determination and crystal structure data, positional parameters, anisotropic thermal parameters, bond distances, and bond angles (10 pages). Ordering information is given on any current masthead page.

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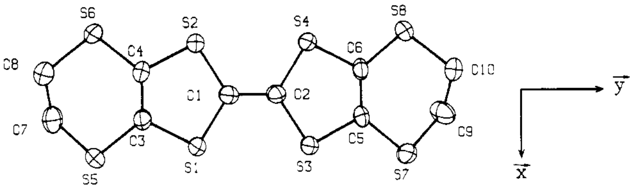
Role of the Intermolecular Interactions in the Two-Dimensional Ambient-Pressure Organic Superconductors β-(ET)$_2$I$_3$ and β-(ET)$_2$IBr$_2$

Sir:

Two ambient-pressure organic superconductors have recently been synthesized from the sulfur-containing organic donor bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET, **1**).[1-9]



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