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Synthesis and Characterization of $Tp^{iPr}MoO(S_2PR_2)$ (R = Pr^i, Ph, OEt, OPr^i, (−)-Mentholate) and $\{HB(OMe)(Pr^ipz)_2\}MoO(S_2PPr^i_2)$, Including Isomers of Known 1,2-Borotropically-Shifted Complexes

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Green/blue $Tp^{iPr}MoO(S_2PR_2)$ (Tp^{iPr} = hydrotris(3-isopropylpyrazolyl)borate; R = Pr^i, Ph, OEt, OPr^i, (−)-mentholate) complexes were synthesized and characterized by elemental analysis, mass spectrometry, IR and NMR spectroscopy, and X-ray crystallography. The diamagnetic, six-coordinate, oxo−Mo(IV) complexes possess distorted octahedral geometries defined by terminal oxo, bidentate dithio acid, and tridentate Tp^{iPr} ligands. The R = Pr^i and Ph derivatives are isomers of previously reported 1,2-borotropically shifted complexes, $Tp^{iPr*}MoO(S_2PR_2)$ (Tp^{iPr*} = hydrobis(3-isopropylpyrazolyl)(5-isopropylpyrazolyl)borate; ref: *Inorg. Chem.* **1996**, *35*, 5368). Conversion of $Tp^{iPr}MoO(S_2PPh_2)$ into $Tp^{iPr*}MoO(S_2PPh_2)$ at elevated temperatures (>80 °C) showed that the borotropically shifted isomer was thermodynamically more stable than the unshifted species. Reaction with methanol converts $Tp^{iPr}MoO(S_2PPr^i_2)$ into $\{HB(OMe)(Pr^ipz)_2\}MoO(S_2PPr^i_2)$ (Pr^ipz = 3-isopropylpyrazolyl), which was characterized by spectroscopic and crystallographic methods.

Introduction

The exchange of different substituents at the 3- and 5-positions in trispyrazolylborate ligands is generally referred to as a 1,2-borotropic shift, although the precise mechanisms of such rearrangements are obscure.[1,2] This phenomenon was first reported by Trofimenko and co-workers,[3] who observed the formation of $Co(Tp^{iPr*})_2$ and $Co(Tp^{iPr,4\text{-}Br*})_2$ in the reactions of Co^{2+}(aq) with KTp^{iPr} and $KTp^{iPr,4\text{-}Br}$, respectively (see Figure 1 for the structures of Tp^{iPr} and Tp^{iPr*}, etc.); similar rearrangements were proposed for related Ni(II), Cu(II) and Zn(II) complexes.[3] Indeed, 1,2-borotropic shifts are relatively common for ligands containing isopropylpyrazolyl groups and other examples involving chromium,[4] iron,[5,6] cobalt,[5−8] nickel,[5,6] zinc,[5,6] molybdenum,[5,6,9] rhodium,[10] and iridium[11] complexes have been reported. The

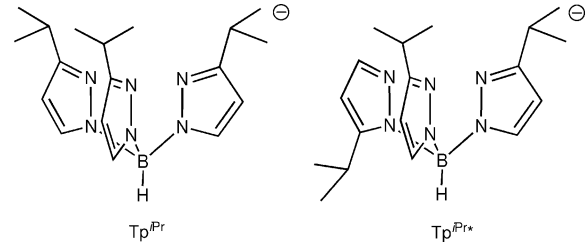

Figure 1. Structures of Tp^{iPr} and Tp^{iPr*} ($Tp^{iPr,4\text{-}Br}$ and $Tp^{iPr,4\text{-}Br*}$ are brominated at the ring 4-position). The ligand abbreviations used in this paper are based on the system introduced by Trofimenko.[1]

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reader is referred to the monographs, *Scorpionates*[1] and *Scorpionates II*,[2] for a complete coverage of 1,2-borotropic shifts in trispyrazolylborate ligands and their metal complexes.

The isolation of complexes related by a 1,2-borotropic shift is very uncommon; indeed, we are aware of only four examples in trispyrazolylborate chemistry. The first involved the independent synthesis of $AlEt_2(\kappa^2\text{-}Tp^{tBu})$ and $AlEt_2(\kappa^2\text{-}Tp^{tBu}*)$ and the conversion of the former into its borotropically shifted isomer at 60 °C in benzene.[12] The second involved the synthesis of $UCl_3Tp^{Mes}*$ and the serendipitous isolation of a few crystals of isomeric UCl_3Tp^{Mes} (Mes = mesityl) following attempts to grow single crystals of $UCl_2\{N(SiMe_3)_2\}Tp^{Mes}*$.[13] The two most recent examples have been reported by Wolowiec and co-workers, who reported the isolation of $Tp^{Ph,iPr}Co(NCS)(thf)$ and $Tp^{Ph,iPr}*Co(NCS)(thf)$ by fractional crystallization[8] and the independent synthesis of $Co(Tp^{Ph,Me})_2$ and $Co(Tp^{Ph,Me}*)_2$ from $Co^{2+}(aq)$ and the respective ligands.[14] To our knowledge, the independent synthesis of isomers related by a 1,2-bortropic shift is limited to the Al(III) and bis(ligand)-Co(II) complexes introduced above.

In 1996, Young et al.[9] reported the synthesis and characterization of $Tp^{iPr}*MoO(S_2PR_2)$ (R = Pr^i, Ph), formed in the reactions of $MoO(S_2PR_2)_2$ and KTp^{iPr} in *refluxing* toluene, and their conversion into the sulfido analogues, $Tp^{iPr}*MoS(S_2PR_2)$. A 1,2-borotropic shift in the pyrazole group *trans* to the terminal oxo or sulfido ligands was confirmed by X-ray crystallography. In this paper, we report the synthesis and characterization of related complexes, $Tp^{iPr}MoO(S_2PR_2)$ (R = Pr^i (**1**), Ph (**2**), OEt (**3**), OPr^i (**4**), (−)-mentholate (**5**)), that contain the unshifted Tp^{iPr} ligand. The isomeric pairs, $Tp^{iPr}MoO(S_2PR_2)$ and $Tp^{iPr}*MoO(S_2PR_2)$[9] (R = Pr^i, Ph), constitute additional examples of isomers related by a 1,2-borotropic shift that can be reliably accessed by independent syntheses. We also report the spectroscopic and crystallographic characterization of $\{HB(OMe)(Pr^ipz)_2\}MoO(S_2PPr^i_2)$ (**6**, Pr^{i}pz = 3-isopropylpyrazolyl), a product of the reaction of $Tp^{iPr}MoO(S_2PPr^i_2)$ with methanol.

Experimental Section

Materials and Methods. The dithio acids HS_2PR_2 (R = Pr^i,[15] Ph,[16] OEt,[17] OPr^i,[17] (−)-mentholate[18]), and $MoO_2\{S_2P((-)\text{-mentholate})_2\}_2$[19] were prepared according to literature methods or adaptations thereof. The ammonium salts of the dithio acids were prepared by bubbling ammonia gas through a solution of the free acid in toluene and were isolated by filtration and washing with toluene. All other reagents and solvents were analytical reagent grade or above. Solid-state (KBr disk) infrared spectra were recorded on a Biorad FTS 165 FTIR spectrophotometer. ^{1}H NMR spectra were recorded at room temperature on a Varian Unity-Plus 400 MHz spectrometer and referenced to residual protio-solvent ($CHCl_3$ δ_H 7.24), while ^{31}P and 2D ^{1}H NMR spectra were recorded on a stabilized Varian Inova-400 MHz spectrometer. ^{31}P NMR spectra were referenced to external 85% H_3PO_4 in D_2O. Electrospray ionization mass spectrometric (ESI-MS) experiments were carried out in positive-ion mode using a Micromass Quattro II mass spectrometer using samples dissolved in MeCN or MeCN/CH_2Cl_2 mixtures. Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA.

Syntheses. $NEt_4[Tp^{iPr}Mo(CO)_3]$. A mixture of KTp^{iPr} (10.08 g, 26.6 mmol) and $Mo(CO)_6$ (6.96 g, 26.4 mmol) in deoxygenated *N,N*-dimethylformamide (120 mL) was heated at 80 °C with stirring for 4 h under an atmosphere of dinitrogen. The volume of the reaction mixture was then reduced using a rotary evaporator to ca. 40 mL and the mixture was poured into a vigorously stirred solution of NEt_4Cl (9.60 g, 58 mmol) in cold water (150 mL). The resulting dirty-yellow precipitate was isolated by filtration, washed with water and partially dried at the pump. The crude compound was dissolved in acetone (ca. 200 mL) and the suspension was filtered to remove a small amount of insoluble material. Slow addition of water (400 mL) to the filtrate led to precipitation of a bone-brown/yellow colored material. This was isolated by filtration, washed with cold methanol and vaccuum-dried to give light yellow crystals of product. Yield: 11.4 g (86%).

Anal. Calcd for $C_{29}H_{48}BMoN_7O_3$: C, 53.63; H, 7.45; N, 15.10. Found: C, 53.37; H, 7.49; N, 14.94. IR (KBr, cm^{-1}): 2962 m, 2917 w, 2867 w, ν(BH) 2469 w and 2439 w, ν(CO) 1887 vs and 1756/1740 vs, 1508 m, 1483 m, 1459 m, 1394 m, 1384 m, 1360 m, 1191 s, 1102 w, 1066 w, 1039 m, 1000 w, 790 w, 774 m, 736 s. IR (MeCN, cm^{-1}): ν(CO) 1893 vs and 1756 vs. ^{1}H NMR (d_6-acetone): δ 1.21 (d, 18H, ^3J = 6.8 Hz, 6 CH_3 of Pr^i), 1.38 (tt, 12H, ^3J = 7.2 Hz, J_{NH} = 2 Hz, 4 CH_3 of NEt_4^+), 3.46 (q, 8H, ^3J = 7.2 Hz, 4 CH_2 of NEt_4^+), 4.21 (sept, 3H, ^3J = 6.8 Hz, 3 C*H* of Pr^i), 5.95 (d, 3H, ^3J = 2.4 Hz, 3 4-C*H*), 7.49 (d, 3H, ^3J = 2.4 Hz, 3 5-C*H*).

$Tp^{iPr}MoI(CO)_3$. A stirred solution of $NEt_4[Tp^{iPr}Mo(CO)_3]$ (5.00 g, 7.7 mmol) in deoxygenated MeCN (20 mL) under an atmosphere of dinitrogen was treated with solid iodine (2.05 g, 8.1 mmol). The mixture turned brown immediately and red-brown crystals of the product soon precipitated. The mixture was stirred for 1 h and then filtered in air. The red-brown crystals were washed with cold methanol and vaccuum-dried. Yield: 4.30 g (86%).

Anal. Calcd for $C_{21}H_{28}BIMoN_6O_3$: C, 39.04; H, 4.37; N, 13.01. Found: C, 39.27; H, 4.63; N, 12.82. IR (KBr, cm^{-1}): 2968 m, 2929 w, 2870 w, 2504 w, ν(CO) 2028 vs and 1936/1915 vs, 1509 s, 1490 m, 1460 w, 1446 w, 1386 s, 1364 s, 1289 w, 1202 s, 1181 s, 1104 w, 1079 w, 1067 m, 1045 s, 1022 w, 816 w, 793 w, 778 s, 735 s, 728 s, 661 w, 599 w, 547 w, 508 w, 483 w, 450 w, 418 w. IR (CH_2Cl_2, cm^{-1}) 2032 vs, 1947 vs, 1930 s(sh). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.19 (br s, 18H, 6 CH_3 of Pr^i), 2.62 and 3.00 (br s, total 3H, 3 C*H* of Pr^i), 6.13 (d, 3H, $^3J \sim$ 2 Hz, 3 4-C*H*), 7.62 (br s, 3H, 3 5-C*H*).

$Tp^{iPr}MoO(S_2PR_2)$. Except in the preparation of **5**, the following general procedure was adopted. A suspension of $Tp^{iPr}MoI(CO)_3$ (1.00 g, 1.55 mmol) and $NH_4S_2PR_2$ (1.60 mmol) in acetonitrile (30 mL) was stirred at room temperature for the stipulated time (vide

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infra). After stirring, the solvent was removed by rotary evaporation and the residue was triturated with methanol (15 mL) to produce green-blue crystals. The crystals were collected by filtration, washed with cold methanol (5 mL) and dried *in vacuo*. The compounds were recrystallized from dichloromethane/methanol.

R = Pr^i (1). Reaction time: 16 h. Yield: 0.56 g (57%). Anal. Calcd for $C_{24}H_{42}BMoN_6OPS_2$: C, 45.58; H, 6.69; N, 13.29; S, 10.14. Found: C, 46.01; H, 6.73; N, 13.39; S, 10.14. IR (KBr, cm^{-1}): 2967 s, 2928 m, 2870 m, ν(BH) 2480 and 2452 m, 2007 w, 1923 w, 1870 w, 1720 w, 1629 w br, ν(CN) 1510 s, 1460 m, 1399 m, 1385 m, 1365 m, 1291 w, 1247 w, 1198 s, 1105 m, 1070 m, 1045 s, 1024 w, ν(Mo=O) 964 m, 880 w, 816 w, 793 m, 772 m, 734 s, 670 m, 645 m, 616 m, 500 w, 423 w. ^{1}H NMR ($CDCl_3$): δ 1.11 (d, 6H, ^3J = 6.8 Hz, 2 C*H*$_3$ of Pr^i), 1.23 (d, 12H, ^3J = 6.8 Hz, 4 C*H*$_3$ of Pr^i), 1.46 (dd, 6H, J_{PH} = 18.0 Hz, ^3J = 7.2 Hz, 2 C*H*$_3$ of $S_2PPr^i_2$), 1.47 (dd, 6H, J_{PH} = 18.0 Hz, ^3J = 7.2 Hz, 2 C*H*$_3$ of $S_2PPr^i_2$), 2.70 (dsept, 1H, J_{PH} = 7.6 Hz, ^3J = 7.2 Hz, C*H* of $S_2PPr^i_2$), 3.19 (dsept, 1H, J_{PH} = 10.8 Hz, ^3J = 7.2 Hz, C*H* of $S_2PPr^i_2$), 3.99 (sept, 1H, = 6.8 Hz, C*H* of Tp^{iPr}), 4.11 (sept, 2H, ^3J = 6.8 Hz, 2 C*H* of Tp^{iPr}), 5.83 (d, 1H, ^3J = 2.4 Hz, 4-C*H*), 6.16 (d, 2H, ^3J = 2.4 Hz, 2 4-C*H*), 7.30 (d, 1H, ^3J = 2.4 Hz, 5-C*H*), 7.68 (d, 2H, ^3J = 2.4 Hz, 2 5-C*H*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 162.6. ESI-MS: *m*/*z* 634.2 ([M]$^+$), 657.2 ([M + Na]$^+$).

R = Ph (2). Reaction time: 16 h. Yield: 1.00 g (92%). Anal. Calcd for $C_{30}H_{38}BMoN_6OPS_2$: C, 51.44; H, 5.47; N, 12.00; S, 9.15. Found: C, 51.39; H, 5.63; N, 11.76; S, 8.96. IR (KBr, cm^{-1}): 3055 w, 2966 s, 2924 m, 2867 m, ν(BH) 2475 w and 2446 m, ν(CN) 1509 s, 1494 m, 1460 m, 1436 m, 1396 m, 1384 m, 1363 m, 1308 w, 1290 w, 1280 w, 1230 w, 1195 s, 1161 w, 1100 m, 1075 m, 1067 m, 1047 m, 1041 m, ν(Mo=O) 960 s, 793 m, 776 m, 735 s, 706 m, 689 m, 628 m, 608 m, 566 s, 485 m, 475 w, 450 w, 423 w. ^{1}H NMR ($CDCl_3$): δ 0.60 (d, 6H, ^3J = 6.8 Hz, 2 C*H*$_3$ of Pr^i), 1.24 (d, 6H, ^3J = 6.8 Hz, 2 C*H*$_3$ of Pr^i), 1.25 (d, 6H, ^3J = 6.8 Hz, 2 C*H*$_3$ of Pr^i), 3.48 (sept, 1H, ^3J = 6.8 Hz, C*H* of Pr^i), 4.12 (sept, 2H, ^3J = 6.8 Hz, 2 C*H* of Pr^i), 5.72 (d, 1H, ^3J = 2.4 Hz, 4-C*H* of Tp^{iPr}), 6.18 (d, 2H, ^3J = 2.4 Hz, 2 4-C*H* of Tp^{iPr}), 7.29 (d, 1H, ^2J = 2.4 Hz, 5-C*H* of Tp^{iPr}), 7.68 (d, 2H, ^3J = 2.4 Hz, 2 5-C*H* of Tp^{iPr}), 7.46 and 7.59 (each m, 3H, 3−5-C*H* of Ph), 7.9−8.1 (m, 4H, 2- and 6-C*H* of Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 144.5. ESI-MS: *m*/*z* 702.2 ([M]$^+$), 725.1 ([M + Na]$^+$).

R = OEt (3). Reaction time: 6 h. Yield: 0.70 g (70%). Anal. Calcd for $C_{22}H_{38}BMoN_6O_3PS_2$: C, 41.52; H, 6.02; N, 13.21; S, 10.08. Found: C, 41.47; H, 6.00; N, 13.10; S, 10.03. IR (KBr, cm^{-1}): 2966 s, 2925 m, 2867 m, ν(BH) 2479 and 2451 m, ν(CN) 1509 s, 1489 m, 1460 w, 1398 m, 1384 m, 1361 m, 1293 w, 1278 w, 1195 s, 1106 w, 1066 m, 1045 m, 1010 m, ν(Mo=O) 967 s, 949 s, 932 s, 792 s, 761 m, 732 s, 669 w, 656 w, 568 w. ^{1}H NMR ($CDCl_3$): δ 1.01, 1.22 and 1.29 (each d, 6H, ^3J = 6.8 Hz, 2 C*H*$_3$ of Pr^i), 1.34 and 1.52 (each t, 3H, ^3J = 7.2 Hz, C*H*$_3$ of OEt), 3.31 (sept, 1H, ^3J = 6.8 Hz, C*H* of Pr^i), 4.09 (sept, 2H, ^3J = 6.8 Hz, 2 CH of Pr^i), 4.20 and 4.45 (each dq, 2H, J_{PH} = 8.0 Hz, ^3J = 7.2 Hz, C*H*$_2$), 5.74 (d, 1H, ^3J = 2.4 Hz, 4-C*H*), 6.23 (d, 2H, ^3J = 2.4 Hz, 2 4-C*H*), 7.26 (d, 1H, ^3J = 2.4 Hz, 5-C*H*), 7.71 (d, 2H, ^3J = 2.4 Hz, 2 5-C*H*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 137.6. ESI-MS: *m*/*z* 638.1 ([M]$^+$), 661.1 ([M + Na]$^+$).

R = OPr^i (4). Reaction time: 4 h. Yield: 0.65 g (63%). Anal. Calcd for $C_{24}H_{42}BMoN_6O_3PS_2$: C, 43.38; H, 6.37; N, 12.65; S, 9.65. Found: C, 43.35; H, 6.34; N, 12.62; S, 9.40. IR (KBr, cm^{-1}): 2970 s, 2928 m, 2869 m, ν(BH) 2479 and 2450 m, ν(CN) 1510 s, 1385 m, 1364 m, 1293 w, 1196 s, 1102 m, 1066 m, 1045 m, 998 s, ν(Mo=O) 972 s, 770 m, 735 s, 646 m, 550 w. ^{1}H NMR ($CDCl_3$): δ 1.04, 1.23, 1.29, 1.34 and 1.56 (each d, 6H, ^3J ∼ 6.8 Hz, 6 C*H*$_3$ of Pr^i and 4 C*H*$_3$ of OPr^i), 3.36 (sept, 1H, ^3J = 6.8 Hz, C*H* of Pr^i), 4.12 (sept, 2H, ^3J = 6.8 Hz, 2 C*H* of Pr^i); 4.90 (dsept, 1H, J_{PH} ∼ 15 Hz, ^3J ∼ 7 Hz, C*H* of OPr^i), 5.13 (dsept, 1H, J_{PH} ∼ 10 Hz, ^3J ∼ 7 Hz, C*H* of OPr^i), 5.76 (d, 1H, ^3J = 2.4 Hz, 4-C*H*), 6.24 (d, 2H, ^3J = 2.4 Hz, 2 4-C*H*), 7.27 (d, 1H, ^3J = 2.4 Hz, 5-C*H*), 7.72 (d, 2H, ^3J = 2.4 Hz, 2 5-C*H*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 133.6. ESI-MS: *m*/*z* 666.1 ([M]$^+$), 689.1 ([M + Na]$^+$).

Tp^{iPr}MoO{S$_2$P((−)-mentholate)$_2$} (5). A solution of MoO_2-{S_2P((−)-mentholate)$_2$}$_2$ (2.33 g, 2.4 mmol) and PPh_3 (1.14 g, 4.3 mmol) in toluene (120 mL) was heated at 80 °C for one hour, cooled to room temperature and treated with KTp^{iPr} (1.57 g, 2.0 mmol) then refluxed for a further hour. The solution was filtered and the filtrate was reduced to dryness. The residue was column chromatographed on silica gel using dichloromethane/hexane as eluent. The main blue fraction was collected, reduced to dryness and recrystallized from dichloromethane/methanol to give a blue powder. Yield: 1.20 g (39%).

Anal. Calcd for $C_{38}H_{66}BMoN_6O_3PS_2$: C, 53.27; H, 7.76; N, 9.81; S, 7.20. Found: C, 53.09; H, 7.93; N, 9.80; S, 6.96. IR (KBr, cm^{-1}): 2960 s, 2926 s, 2868 s, ν(BH) 2485 m and 2479 m, ν(CN) 1511 s, 1494 s, 1485 s, 1456 s, 1401 s, 1384 s, 1362 s, 1347 w, 1335 w, 1313 m, 1296 m, 1261 m, 1237 m, 1192 s, 1159 w, 1136 m, 1106 m, 1084 m, 1066 m, 1048 s, 1018 s, 981 s, 971 s, ν(Mo=O) 960 s, 950 s, 884 m, 830 m, 807 m, 799 m, 772 m, 733 m, 718 w, 709 m, 664 w, 638 m, 617 w, 594 m, 575 m, 515 w, 496 w, 477 w, 426 w, 417 w. ^{1}H NMR ($CDCl_3$): For mentholate groups (all doublets have ^3J = 6.8 Hz): δ 0.86 (d, 3H) and 1.60 (m, 1H) (7-C*H*$_3$ and 5-C*H*); 0.90 (d, 3H), 0.94 (d, 3H) and 2.25 (sept, 1H) (9,10-(C*H*$_3$)$_2$ and 8-C*H* (*i*-Pr)); 0.91 (d, 3H), 0.98 (d, 3H) and 2.39 (sept, 1H) (9,10-(C*H*$_3$)$_2$ and 8-C*H* (Pr^i)); 0.95 (d, 3H) and 1.74 (m, 1H) (7-C*H*$_3$ and 5-C*H*); 0.6−1.6 (overlapping multiplets, 10H, all 2-C*H*, 3-C*H*$_2$ and 4-C*H*$_2$ protons); 1.14 and 2.53 (m, each 1H, 6-C*H*$_2$); 1.40 and 2.62 (m, each 1H, 6-C*H*$_2$); 4.48 (m, 1H, 1-C*H*); 4.64 (m, 1H, 1-C*H*). For Tp^{iPr} (Pr^i and ring CH $^3J_{HH}$ couplings are 6.8 and 2.4 Hz, respectively): 1.14 (d, 3H), 1.15 (d, 3H) and 3.18 (sept, 1H) (Pr^i); 1.20 (d, 3H), 1.27 (d, 3H) and 4.02 (sept, 1H) (Pr^i); 1.24, (d, 3H), 1.32 (d, 3H) and 4.08 (sept, 1H) (Pr^i); 5.68, 6.20, 6.22 (each d, 1H, 4-C*H*); 7.20, 7.68, 7.70 (each d, 1H, 5-C*H*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 132.0. ESI-MS: *m*/*z* 859.1 ([M + H]$^+$), 881.1 ([M + Na]$^+$).

{HB(OMe)(Pr^{i}pz)$_2$}MoO(S$_2$PPr$^i_2$) (6). A solution of **1** (100 mg) in 50:50 CH_2Cl_2:MeOH (10 mL) was allowed to stand in an uncapped vial for a week. Evaporation of the solution to dryness and column chromatography (silica gel/MeOH) yielded a blue band containing an inseparable mixture of **1** and **6** (typically 2:1 mol ratio, total yield 80 mg). The spectroscopic data presented below were extracted from spectra obtained from such mixtures (after accounting for features due to **1**).

IR (KBr, cm^{-1}): ν(Mo=O) 973 s. ^{1}H NMR ($CDCl_3$): δ 1.20 (d, 6H, ^3J = 6.8 Hz, 2 C*H*$_3$ of Pr^{i}pz), 1.28 (d, 6H, ^3J = 6.8 Hz, 2 C*H*$_3$ of Pr^{i}pz), 1.35 (dd, 6H, J_{PH} = 18.0 Hz, ^3J = 7.2 Hz, 2 C*H*$_3$ of $S_2PPr^i_2$), 1.51 (dd, 6H, J_{PH} = 18.0 Hz, ^3J = 7.2 Hz, 2 C*H*$_3$ of $S_2PPr^i_2$), 2.22 (dsept, 1H, J_{PH} ∼ 12 Hz, ^3J = 6.8 Hz, C*H* of $S_2PPr^i_2$), 2.65 (dsept, 1H, J_{PH} ∼ 12 Hz, ^3J = 6.8 Hz, C*H* of $S_2PPr^i_2$), 3.11 (s, 3H, OC*H*$_3$), 3.56 (sept, 2H, ^3J = 6.8 Hz, 2 C*H* of Pr^{i}pz), 6.17 (d, 2H, ^3J = 2.4 Hz, 2 4-C*H*), 7.58 (d, 2H, ^3J = 2.4 Hz, 2 5-C*H*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 193.0. ESI-MS: *m*/*z* 556.1 ([M]$^+$), 579.1 ([M + Na]$^+$).

Crystallography. Green crystals of **1** and **2**·0.25CH_2Cl_2 were grown by slow diffusion of methanol into dichloromethane solutions of the complexes. Blue crystals of **5** were grown by slow evaporation of a dichloromethane/hexane solution of the complex. Crystals of **6** were obtained fortuitously by slow evaporation of solutions of **1** in dichloromethane/methanol mixtures. Crystal-

Table 1. Crystallographic Data

compd	**1**	**2**	**5**	**6**
formula	$C_{24}H_{42}BMoN_6OPS_2$	$C_{60.5}H_{77}B_2ClMo_2N_{12}O_2P_2S_4$	$C_{38}H_{66}BMoN_6O_3PS_2$	$C_{19}H_{36}BMoN_4O_2PS_2$
fw	632.48	1443.47	856.81	554.36
space group	$P\bar{1}$	$P2_1/c$	$P2_1$	$Pbca$
a, Å	9.778(5)	21.2135(15)	10.3832(6)	10.6095(5)
b, Å	10.383(5)	15.1996(15)	17.4346(9)	14.9183(8)
c, Å	16.564(7)	21.5221(15)	12.1272(6)	34.4581(18)
α, deg	73.025(9)	90	90	90
β, deg	85.256(9)	90.3550(10)	94.5490(10)	90
γ, deg	74.028(9)	90	90	90
V, Å^3	1546.2(12)	6939.4(9)	2188.4(2)	5453.9(5)
Z	2	4	2	8
ρ, g cm^{-3}	1.359	1.382	1.300	1.350
μ, mm^{-1}	0.638	0.616	0.473	0.714
R^a	0.0531	0.0456	0.0271	0.0340
$R_w{}^b$	0.0888	0.1188	0.0631	0.0766

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2/\sum(w|F_o^2|)^2]\}^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg)

parameter	**1**	**2**	**2′**[a]	**5**	**6**
Mo−O(1)	1.667(3)	1.6647(18)	1.6664(17)	1.6768(16)	1.6645(16)
Mo−S(1)	2.4893(17)	2.4642(7)	2.4788(6)	2.4828(6)	2.4720(6)
Mo−S(2)	2.4856(15)	2.4896(7)	2.4869(6)	2.4765(6)	2.4625(6)
Mo−N(11)	2.450(4)	2.480(2)	2.454(2)	2.432(2)	2.1676(19)
Mo−N(21)	2.201(4)	2.183(2)	2.201(2)	2.191(2)	2.1994(18)
Mo−N(31)/O(2)[b]	2.201(4)	2.193(2)	2.2207(18)	2.178(2)	2.4236(17)
O(1)−Mo−S(1)	99.43(12)	99.42(7)	99.72(6)	99.71(6)	103.82(6)
O(1)−Mo−S(2)	102.39(12)	102.22(7)	101.43(6)	102.17(6)	104.66(6)
O(1)−Mo−N(11)	163.95(14)	167.45(8)	165.52(7)	166.14(7)	97.10(8)
O(1)−Mo−N(21)	90.60(15)	92.52(9)	92.51(8)	89.67(8)	95.10(8)
O(1)−Mo−N(31)/O(2)[b]	91.63(15)	92.95(9)	92.06(8)	91.51(8)	159.48(7)
S(1)−Mo−S(2)	79.03(5)	79.58(2)	79.36(2)	79.32(2)	80.17(2)
S(1)−Mo−N(11)	92.60(10)	88.73(5)	90.53(6)	90.47(5)	158.71(6)
S(1)−Mo−N(21)	168.51(10)	167.45(6)	166.79(6)	170.16(5)	93.97(5)
S(1)−Mo−N(31)/O(2)[b]	96.65(11)	94.88(6)	95.15(6)	96.32(6)	91.38(4)
S(2)−Mo−N(11)	90.25(10)	88.83(5)	90.44(5)	88.88(5)	90.84(5)
S(2)−Mo−N(21)	93.41(11)	94.20(6)	93.42(5)	95.88(6)	160.19(6)
S(2)−Mo−N(31)/O(2)[b]	165.81(11)	164.49(6)	166.09(6)	166.14(5)	91.31(4)
N(11)−Mo−N(21)	78.67(14)	80.20(8)	78.39(7)	80.79(7)	88.01(7)
N(11)−Mo−N(31)/O(2)[b]	76.36(14)	76.50(8)	76.75(7)	77.94(7)	69.41(7)
N(21)−Mo−N(31)/O(2)[b]	88.61(16)	88.31(9)	89.34(7)	86.32(8)	69.79(6)

[a] Corresponding values for the second molecule in the asymmetric unit in compound **2** (atoms numbers Mo(2), O(2), N(61), N(71), N(81), S(3), S(4)). [b] Atom is N(31) for **1**, **2** and **5**, and O(2) for **6**.

lographic data are summarized in Table 1. Selected bond distances and angles are listed in Table 2. Molecular diagrams were generated using ORTEP 3.[20]

Diffraction data were collected using a Bruker CCD diffractometer with a sealed tube Mo Kα (0.71073 Å) radiation source. Accurate cell parameters and crystal orientations were obtained by least-squares refinement of 1276, 7152, 9429 and 8481 reflections with θ values in the ranges 2.3−24.7°, 2.5−27.4°, 2.5−27.2°, and 2.3−28.3° for **1**, **2, 5** and **6**, respectively. Data for **1**, **2** and **5** were reduced using the program SAINT and corrected for absorption (ratio of max./min. transmission 0.64, 0.49 and 0.71 for **1**, **2**, and **5**, respectively).[21] The structures were solved by direct methods and difference Fourier synthesis.[21]

Hydrogen atoms were included in calculated positions. Full-matrix least-squares refinement on F^2, using all data, was carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Refinement details are included in the Supporting Information. For the structure of chiral **5**, the absolute structure (Flack) parameter was −0.059(18).[22]

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Results and Discussion

Synthesis and Characterization of Tp$^{i\mathrm{Pr}}$MoO(S$_2$PR$_2$) Complexes. The synthesis of the Tp$^{i\mathrm{Pr}}$MoO(S$_2$PR$_2$) complexes involved three steps. In the first, reaction of Mo(CO)$_6$ with KTp$^{i\mathrm{Pr}}$ in hot *N*,*N*-dimethylformamide, followed by cation exchange with aqueous NEt$_4$Cl, yielded yellow NEt$_4$[Tp$^{i\mathrm{Pr}}$Mo(CO)$_3$]. Initial attempts to isolate and purify the compound by repeated recrystallization led to persistent degradation, accompanied by a color change to black-brown and markedly diminished yields. The isolation of light yellow, analytically pure crystals requires rapid workup and effective washing with methanol. The complex appears to be air-stable but does decompose upon prolonged exposure to air; accordingly, it is most reliably stored under an atmosphere of dinitrogen.

In the second step, NEt$_4$[Tp$^{i\mathrm{Pr}}$Mo(CO)$_3$] was reacted with iodine to produce red-brown, seven-coordinate Tp$^{i\mathrm{Pr}}$MoI(CO)$_3$. This complex was only moderately air-stable and should be stored under an atmosphere of dinitrogen. The aforementioned carbonyl complexes have never been isolated but the tricarbonyl anion and its Tp$^{i\mathrm{Pr,Me}}$ analogue have been

generated in situ and used in the synthesis of nitrosyl-Mo(0) complexes.[3,5,6] The tungsten analogues, $NEt_4[Tp^{iPr}W(CO)_3]$ and $Tp^{iPr}WI(CO)_3$, are easier to handle and have been known for many years.[23,24] The IR and NMR data collected for $NEt_4[Tp^{iPr}Mo(CO)_3]$ are indicative of a *fac*-tricarbonyl anion possessing C_{3v} symmetry. Thus, solution IR spectroscopy revealed ν(CO) bands at 1893 and 1756 cm^{-1} that can be assigned to the A' and E stretching modes, respectively. The NMR spectrum exhibited resonances characteristic of the cation and four resonances from the Tp^{iPr} ligand, two doublets at δ 7.49 and 5.95, a septet at δ 4.21 and a doublet at δ 1.21; the Tp^{iPr} resonances are assigned to sets of equivalent 5-C*H*, 4-C*H*, isopropyl C*H* and isopropyl CH_3 protons, respectively. Infrared data for $Tp^{iPr}MoI(CO)_3$ are consistent with a 3:3:1 carbonyl-capped octahedral structure in the solution and solid states. Thus, three ν(CO) bands at 2032, 1947 and 1930s cm^{-1} were assigned to $A' + 2A''$ ν(CO) modes under C_s symmetry. The compound exhibits fluxional behavior at room temperature on the NMR time scale. The spectral properties of the above tricarbonyl complexes are similar to those of their Tp*-Mo, Tp*-W and Tp^{iPr}-W analogues (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate).[23−25]

In the third step of the synthesis, reaction of $Tp^{iPr}MoI(CO)_3$ with $NH_4S_2PR_2$ (R = Pr^i, Ph, OEt, OPr^i) in the presence of oxygen led to the formation of green/blue $Tp^{iPr}MoO(S_2PR_2)$. Synthesis of isomerically pure **1** required anaerobic reaction conditions, whereas isomerically pure **2** could be synthesized under aerobic or anaerobic conditions. Attempted synthesis of **2** from $MoO(S_2PPh_2)_2$ and KTp^{iPr} under aerobic rather than anaerobic conditions led to the isolation of a mixture of both isomers, viz., **2** and previously reported $Tp^{iPr}*MoO(S_2PPh_2)$.[9] The coordination of the dithiophosphinate ligands to a Tp^{iPr} complex using nonforcing conditions facilitates the isolation of **1** and **2**, whereas reaction of $MoO(S_2PR_2)_2$ with Tp^{iPr} under forcing conditions produces the 1,2-borotropically shifted isomers, $Tp^{iPr}*MoO(S_2PR_2)$.[9] Blue **5** can be successfully prepared by the high-valent route involving in situ generation of $MoO\{S_2P((-)\text{-mentholate})_2\}_2$ and its reaction with KTp^{iPr}. Compound **5** was also obtained using the low-valent route described for **1**−**4**. Indeed, the sterically unencumbered dithiophosphate complexes appear to be stable with respect to 1,2-borotropic shifts.

The diamagnetic, air-stable complexes were soluble and stable in chlorinated and aromatic solvents and insoluble in alcohols and alkanes. The mentholate complex appears to be unstable in chloroform (a color change from blue to green is observed with time).

Correct microanalyses were obtained and ESI mass spectrometry revealed the generation of parent ions consistent with the formulations, viz., $[M]^+$ and $[M + Na]^+$. Infrared spectra exhibited a single ν(Mo═O) band in the range 972−960 cm^{-1}. Bands associated with the dithio ligands and Tp^{iPr} were also present; in line with earlier observations,[26] the ν(BH) bands of the complexes (ca. 2450 cm^{-1}) were ca. 50 cm^{-1} lower in energy than those observed for the $Tp^{iPr}*$ analogues.[9] The ν(Mo═O) bands of the Tp^{iPr} and $Tp^{iPr}*$ complexes are relatively insensitive to the nature of the N-donor ligands, spanning a narrow 5 cm^{-1} range.

^{1}H NMR spectra of **1**−**4** exhibited resonance patterns indicative of molecular C_s symmetry. The Tp^{iPr} ligand was characterized by three doublet methyl resonances (6:6:6 integrated intensity), two septet methine resonances (1:2 intensity), two ring 4-C*H* resonances (1:2 intensity) and two ring 5-C*H* resonances (1:2 intensity). The dithio acid ligands exhibited two sets of resonances with discernible ^{31}P−^{1}H coupling from each of the inequivalent R groups attached to phosphorus. All the isopropyl CH protons of **1** are deshielded relative to those of $Tp^{iPr}*MoO(S_2PPr^i_2)$,[9] the most dramatic shift being ca. 0.8 ppm for the in-plane isopropylpyrazole unit. On the other hand, the 3(5)-CH protons in **1** are shielded relative to those of $Tp^{iPr}*MoO(S_2PPr^i_2)$, the unique proton being ca. 0.4 ppm higher in field. Similar, but less dramatic differences ($\Delta\delta$ < 0.3) are seen in the spectra of **2** and $Tp^{iPr}*MoO(S_2PPh_2)$, although a notable shielding ($\Delta\delta$ ca. 0.5) of a pair of methyl groups is observed in the former (δ 0.60) relative to the latter (δ 1.11). The presence of an unshifted Tp^{iPr} ligand in the dithiophosphate complexes **3**−**5** is supported by the observation of Tp^{iPr} chemical shifts that are very similar to those of **1** and **2** (structures confirmed by X-ray diffraction, vide infra).

Complex **5** has C_1 symmetry by virtue of the (−)-mentholate moieties. Hence, all the protonic groups of Tp^{iPr} are inequivalent; this leads to an NMR spectrum exhibiting six double resonances for the methine groups and three resonances each for the methine (septet) and ring 4- and 5-CH (doublet) protons. The (−)-mentholate resonance patterns were consistent with two inequivalent (−)-mentholate groups. The assignments given in the Experimental Section were determined from COSY and HMQC spectra of (−)-menthol and **5**.

The ^{31}P chemical shifts of the $Tp^{iPr}MoO(S_2PR_2)$ complexes were shielded by ca. 10 ppm compared to the analogous $Tp^{iPr}*MoO(S_2PR_2)$ complexes.[9]

The partial conversion of **2** to $Tp^{iPr}*MoO(S_2PPh_2)$ in d_8-toluene can be conveniently followed by ^{1}H NMR spectroscopy, the growth of the resonance at δ 1.11 for $Tp^{iPr}*MoO(S_2PPh_2)$ at the expense of the δ 0.6 resonance of **2** being indicative of a borotropic shift. Conversion was initiated at ca. 80 °C and solutions held at 105 °C for 6 h showed around 50% conversion. However, substantial decomposition occurred over longer times and at higher temperatures. The conversion of **2** to $Tp^{iPr*}MoO(S_2PPh_2)$ at high temperatures shows that the 1,2-borotropically shifted isomer is thermodynamically favored over the unshifted analogue. Decomposition of **1** at moderately elevated temperatures prevented analogous studies of this complex.

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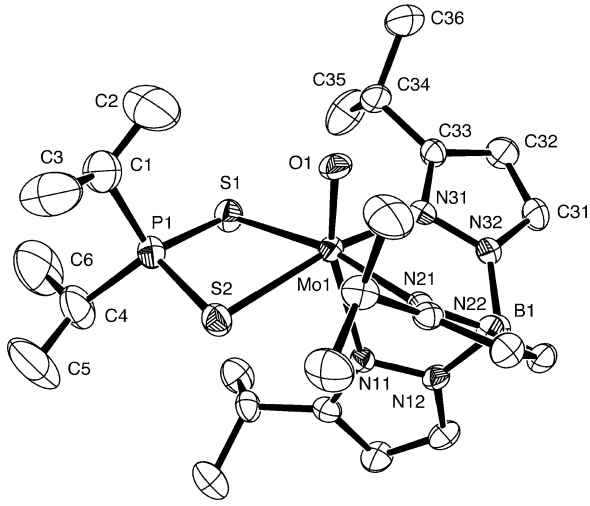

Figure 2. ORTEP projection of **1**. The numbering schemes for the pyrazole rings containing N(11) and N(21) parallel that shown for the ring containing N(31). Thermal ellipsoids are drawn at the 30% probability level and H atoms are excluded for clarity.

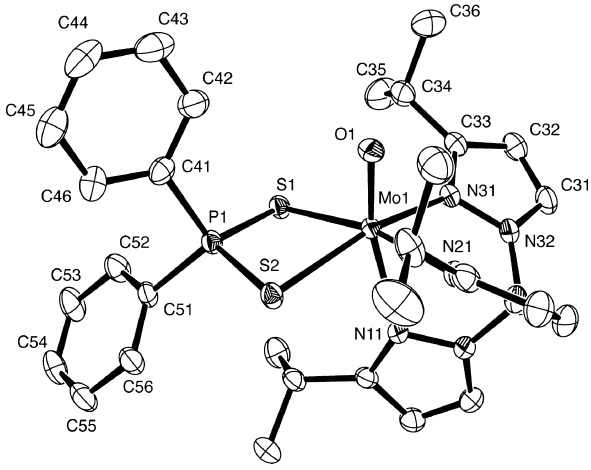

Figure 3. ORTEP projection of **2**. The numbering schemes for the pyrazole rings containing N(11) and N(21) parallel that shown for the ring containing N(31). Thermal ellipsoids are drawn at the 30% probability level and H atoms are excluded for clarity.

Crystal Structures of $Tp^{iPr}MoO(S_2PR_2)$ Complexes. The molecular structures of **1**, **2** and **5** are shown in Figures 2−4, respectively. There is only one molecule in the asymmetric unit of **1** and **5**, but there are two independent molecules in the asymmetric unit of **2**. All four molecules exhibit distorted octahedral geometries of local C_s symmetry, the coordination sphere comprising terminal oxo, bidentate $S_2PR_2^-$ and facially tridentate Tp^{iPr} ligands. The Mo═O bond lengths of 1.667(3) Å for **1**, 1.6647(18) Å and 1.6664(17) Å for **2**, and 1.6768(16) Å for **5** are typical of those in related oxo−Mo(IV) complexes.[27,28] The Mo−N(11) bond *trans* to the terminal oxo ligand is significantly lengthened, by 0.25 Å, 0.29/0.24 Å, and 0.25 Å for **1**, **2** and **5**, respectively, relative to the other Mo−N bonds due to the strong *trans* influence of the terminal oxo ligand.

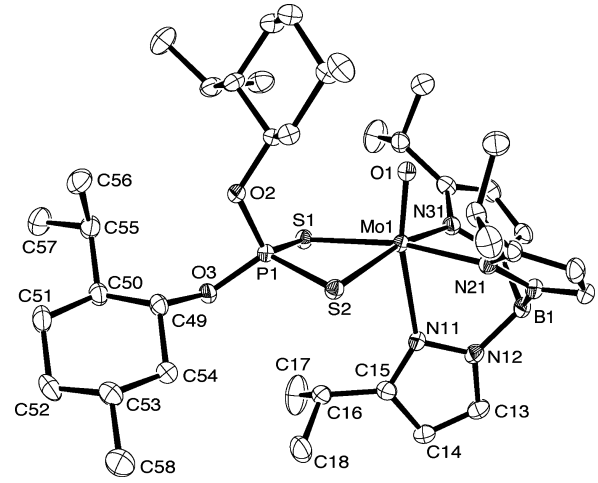

Figure 4. ORTEP projection of **5**. The numbering schemes for the pyrazole rings containing N(21) and N(31) parallel that shown for the ring containing N(11). Thermal ellipsoids are drawn at the 50% probability level and H atoms are excluded for clarity.

The Mo−S(1) and Mo−S(2) bonds lie in the range 2.4642(7)−2.4893(17) Å and are slightly shorter than those observed in other bidentate 1,1-dithiophosphinate complexes.[9,27,29] The S(1), S(2), N(21), and N(31) atoms are approximately planar with mean deviations of 0.0441 Å, 0.0358/0.0146 Å, and 0.0442 Å and maximum deviations (for N(21)) of 0.0453, 0.0365/0.0149, and 0.0455 Å in **1**, **2** and **5**, respectively; the Mo atom is displaced from this plane (toward the terminal oxo group) by 0.237 Å for **1**, 0.268/0.255 Å for **2**, and 0.228 Å for **5**. The phosphorus atom is 0.369 Å, 0.297/0.215 Å, and 0.409 Å above the S(1), S(2), N(21), N(31) plane in **1**, **2** and **5**, respectively. A folding of the MoS_2P fragment along the S···S vector is also observed, the dihedral angles between the MoS_2 and S_2P planes being 24.1°, 21.8/17.6°, and 26.1° for **1**, **2** and **5**, respectively. Similar fold angles have been reported for $Tp^{iPr*}MoO(S_2PPr^i_2)$ (23.5°) and $Tp^{iPr*}MoS(S_2PPh_2)$ (25.0°).[9] Interestingly, essentially similar dithio ligand fold angles are observed in the 1,2-borotropically shifted and unshifted species, despite the disparity in the substituent (proton vs isopropyl) at the 3-position of the pyrazolyl group *trans* to the oxo ligand. Steric interactions between the oxo and 3-isopropylpyrazolyl groups on two of the pyrazolyl rings are reflected in a substantial increase in the N(21)−Mo−N(31) angles (88.61(16)° for **1**, 88.31(9)/89.34(7)° for **2**, and 86.32(8)° for **5**) compared to the remaining N−Mo−N angles of ca. 76−81°.

Characterization and Crystal Structure of Complex 6. Complex **1** reacts with methanol in dichloromethane to form blue $\{HB(OMe)(Pr^ipz)_2\}MoO(S_2PPr^i_2)$ (**6**) via methanolysis of the Tp^{iPr} ligand. Complex **6** is difficult to obtain in pure form as decomposition to purple and yellow scorpionate-free complexes is competitive with its formation. We have also failed to develop a separation protocol for **6** and its precursor **1**. Hence, spectral data have been derived from mixtures of **1** and **6**. The IR and NMR spectra of **6** are

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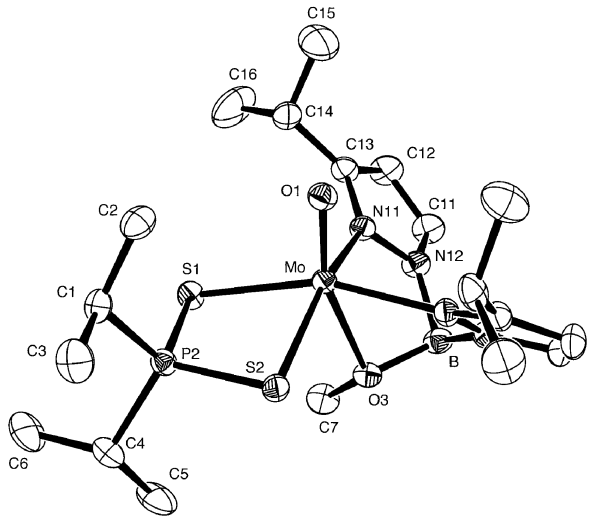

Figure 5. ORTEP projection of **6**. The numbering scheme for the second pyrazole ring (containing N(21)) parallels that shown for the ring containing N(11). Thermal ellipsoids are drawn at the 30% probability level, and H atoms are excluded for clarity.

consistent with the formulation and with rapid exchange of C_1 enantiomers (see crystal structure) to give effective C_s symmetry in solution. The B−OCH_3 resonance is observed at δ 3.11. The ^{31}P NMR spectrum of **6** exhibited a peak at 193 ppm, close to the value reported for {H_2B(3,5-$Me_2C_3HN_2)_2$}MoO(S_2PPr$^i{}_2$).[29] Complex **2** is stable toward methanol at room temperature but is also converted to purple and yellow scorpionate free-complexes upon reflux in dichoromethane/methanol (1:10). The dithiophosphate derivatives appear to be stable in the presence of methanol.

Complex **6** (Figure 5) exhibits a distorted octahedral geometry defined by terminal oxo, bidentate dithiophosphinate, and tridentate, bis(pyrazolyl)(methoxy)borate ligands. The methoxy oxygen is bound trans to the oxo group, both possible orientations for C(7) being present in the crystal lattice (the molecules are enantiomeric with C_1 symmetry but with effective C_s symmetry ignoring C(7) (and in solution, vide supra). The Mo−S(1) and Mo−S(2) bonds of **6** are slightly shorter than those observed in other dithiophosphinate complexes.[9,27,29] The S(1), S(2), N(11), and N(21) atoms are approximately planar with a mean deviation of 0.007 Å and maximum deviation of 0.0073 Å for N(21); the Mo atom is 0.403 Å above this plane in the direction of the oxo group, consistent with the weak coordination of the methoxy group *trans* to the oxo ligand. The phosphorus atom is 0.131 Å above the S(1), S(2), N(11), N(21) plane. The folding of the MoS_2P fragment along the S···S vector, as reported in **1**, **2** and **5** and the analogous borotropically shifted complexes,[9] is also observed in **6**, with a dihedral angle of 18.5° between the MoS_2 and S_2P planes. Again, steric interactions between the oxo ligand and 3-isopropylpyrazolyl groups in **6** are reflected in a substantial increase in the N(11)−Mo−N(21) angle (88.01(7)°) compared to other N−Mo−O angles of ca. 70°. Several related scorpionate ligand complexes, viz., {HB(OMe)(3-Bu^t-5-Pr^i$C_3HN_2)_2$}-ZnMe,[30] {HB(OEt)(3,5-$Me_2C_3HN_2)_2$}ReH_4(PPh_3)[31] and {HB(O-Pr^i)(3-Pr^i-5-Me$C_3HN_2)_2$}Mo($NO(CO)_2$,[32] have been structurally characterized.

Summary

The synthesis and characterization of the oxo−Mo(IV) complexes, Tp$^{i\mathrm{Pr}}$MoO(S_2PR_2) (R = Pr^i (**1**), Ph (**2**), OEt (**3**), OPr^i (**4**) (−)-mentholate (**5**)) and {HB(OMe)(Pr^{i}pz$)_2$}Mo-(S_2PPr$^i{}_2$) (**6**), are presented along with the X-ray crystal structures of **1**, **2**, **5** and **6**. Conversion of **2** into its 1,2-borotropically shifted isomer, Tp$^{i\mathrm{Pr}}$*MoO(S_2PPh_2), showed that this borotropically shifted isomer is thermodynamically favored relative to its unshifted analogue.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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