Bulk Susceptibility Measurements. The raw data (χ_{RT} = 3.58 × 10^{-4} emu/mol) were corrected for temperature-independent diamagnetism (χ^d = −4.90 × 10^{-4} emu/mol)[22] to afford the paramagnetic susceptibility χ^P_{RT} = 8.54 × 10^{-4} emu/mol. This value is significantly larger than that of $[Ni(tmp)]_2[ReO_4]$ (χ^P_{RT} = 2.49 × 10^{-4} emu/mol). The temperature dependence of the susceptibility (Figure 2) may be fit to the Curie-Weiss expression with an added constant (Q), which accounts for the temperature-independent contribution to the susceptibility.

$$\chi^P = \frac{C}{T - \Theta} + Q \qquad (2)$$

A least-squares fit of the data yields C = 3.18 (1) × 10^{-2} emu/mol K, Θ = −0.60 (1) K, and Q = 7.50 (1) 10^{-4} emu/mol. $[Ni(tmp)]_2[ReO_4]$ does not exhibit any Weiss constant, and the Curie constant (C = 3.04 (7) × 10^{-3} emu/mol K) is 1 order of magnitude smaller than that in $[Pd(tmp)]_2[ReO_4]$. Scatter in the data for $[Ni(tmp)]_2[ReO_4]$ could account for the different Weiss constants in the Ni and Pd complexes. The number of localized noninteracting spin sites per mole (N) can be calculated from the expression for the Curie constant

$$C = S(S + 1)(Ng^2\beta^2/3k_B) \qquad (3)$$

where β is the Bohr magneton, k is Boltzmann's constant, S is the spin, and g is the Lande factor. The measured Curie constant corresponds to N = 8.7 × 10^{-2} spins per Pd(tmp) molecule that are assigned to impurities or defect sites. The value of the temperature-independent paramagnetism (Q) is larger than that in $[Ni(tmp)]_2[ReO_4]$ but might still be attributed to Van Vleck paramagnetism that arises because the valence band is associated with the nearly degenerate a_{1u}, a_{2u} HOMO set of the macrocycles.

Conclusions

$[Pd(tmp)]_2[ReO_4]$ is isostructural with $[Ni(tmp)]_2[ReO_4]$ and $[Cu(tmp)]_2[ReO_4]$. All three of these semiconductors are ligand-oxidized and possess conduction bands formed from porphyrin p-π orbitals. The ESR measurements confirm the tmp ligand as the site of oxidation. Because the conduction band arises from overlap of the porphyrin orbitals, the room-temperature conductivity is comparable with that of the best Pt-spine conductors, despite the fact that the interplanar separation (≈3.38 Å) is considerably longer than the Pt-Pt distance (~2.95 Å) in the Pt-spine conductors.

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Registry No. $[Pd(tmp)]_2[ReO_4]$, 133042-93-0; Pd(tmp), 67159-01-7; $[N(n\text{-}Bu)_4]ReO_4$, 16385-59-4; Pt, 7440-06-4.

Supplementary Material Available: Complete crystallographic details (Table IS), intramolecular bond distances and angles (Table IIIS), and best-weighted least-squares planes (Table IVS) (5 pages); $10|F_o|$ vs $10|F_c|$ data (Table IIS) (10 pages). Ordering information is given on any current masthead page.

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Multiple Bonds between Main-Group Elements and Transition Metals. 91.[1] High-Oxidation-State Rhenium Complexes Containing the Hydridotris(1-pyrazolyl)borato Ligand

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The rhenium(VII) complex $[HB(pz)_3]ReO_3$ (**1**) is readily reduced by triphenylphosphine in the presence of excess $(CH_3)_3SiX$ (X = Br, Cl) to give the corresponding rhenium(V) complexes $[HB(pz)_3]ReOX_2$ (**2**, X = Cl; **3**, X = Br, pz = pyrazolyl ($C_3H_3N_2$)). $[HB(pz)_3]ReOCl_2$ (**2**), which seems to exist as two bond stretch isomers, reacts with 1 equiv of thiophenol in refluxing THF in the presence of a base [DBU or $N(C_2H_5)_3$] to give $[HB(pz)_3]ReO(Cl)(SC_6H_5)$ (**4**). Two equivalents of thiophenol reacts with **2** in refluxing THF, also in the presence of base, to give $[HB(pz)_3]ReO(SC_6H_5)_2$ (**5**). **2** will react with 1,2-ethanedithiol or 1,2-benzenedithiol under similar conditions to give $[HB(pz)_3]ReO(S_2C_6H_4)$ (**6**) and $[HB(pz)_3]ReO(S_2C_2H_4)$ (**7**), respectively. The solid-state structures of **4** and **5** have been determined by X-ray crystallography. Both were found to be monomeric with an approximately octahedral arrangement of ligands around the rhenium atoms. **4** crystallizes in the orthorhombic space group *Pbca* (No. 61) with cell parameters a = 13.159 (1) Å, b = 18.656 (1) Å, c = 15.902 (1) Å, V = 3904 (1) $Å^3$, Z = 8, R = 0.043, and R_w = 0.031 for 2713 reflections with $I > 2\sigma(I)$. **5** crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with cell parameters a = 15.594 (3) Å, b = 21.624 (1) Å, c = 15.931 (1) Å, β = 107.00 (1)°, V = 5137 (1) $Å^3$, Z = 4, R = 0.050, and R_w = 0.036 for 6683 reflections with $I > 2\sigma(I)$.

Introduction

Recently we reported the synthesis and solid-state structure of the complex $[HB(pz)_3]ReO_3$ (**1**).[2] This is a rare example of a rhenium(VII) compound containing the hydridotris(1-pyrazolyl)borato ligand. The only other rhenium(VII) example is the hexahydrido complex $[HB(pz)_3]ReH_6$.[3] Two rhenium(V) complexes have also been reported, $[HB(pz)_3]ReOCl_2$ and $[HB(pz)_3]ReSCl_2$.[4,5] **1** is particularly interesting, as it is an analogue of $(\eta^5\text{-}C_5Me_5)ReO_3$, which has been shown to have a wide and varied chemistry and has been used as a starting material in the preparation of a great many high-oxidation-state rhenium com-

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plexes containing the pentamethylcyclopentadienyl ligand.[6] In particular, it can be used to prepare the similarly useful compounds (η^5-C_5Me_5)$ReCl_4$ and (η^5-C_5Me_5)$ReOCl_2$.[7]

As part of our ongoing studies into high-oxidation-state organorhenium chemistry we thought it of interest for comparison purposes to study further the chemistry of rhenium oxo complexes containing the hydridotris(1-pyrazolyl)borato ligand. We now report an improved synthesis of the known[4] complex [HB(pz)$_3$]$ReOCl_2$ (**2**) as well as the synthesis of [HB(pz)$_3$]$ReOBr_2$ (**3**). Also reported are the syntheses of four novel thiolato derivatives of types [HB(pz)$_3$]ReOCl(SR) and [HB(pz)$_3$]ReO(SR)$_2$.

Experimental Section

All syntheses and sample manipulations were carried out by using standard Schlenk techniques. The solvents were dried by standard methods and distilled under nitrogen prior to use (hexane, toluene, and THF dried over Na/benzophenone; CH_2Cl_2 dried over P_2O_5 and distilled from CaH_2). Column chromatography was carried out with silylated silica gel (Kieselgel 60, 0.063–0.200 mm) as the stationary phase. IR spectra were recorded as KBr disks on a Nicolet DX 5 FT spectrophotometer. NMR spectra were recorded on a JEOL GX 400-MHz FT instrument using the chemical shift of the solvent as the internal standard. Mass spectra were obtained with Finnigan MAT 311 A and MAT 90 spectrometers. (Mass spectral data are referenced to ^{187}Re, ^{35}Cl, and ^{79}Br.) Elemental analyses were performed in the Microanalytical Laboratory of our institute (M. Barth and U. Graf). Na[HB(pz)$_3$] was prepared by the literature method.[8] 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was used as supplied by Aldrich Chemical Co.

Synthesis of [HB(pz)$_3$]ReOCl$_2$ (2). To a suspension of **1** (1.11 g; 2.48 mmol) in THF (40 mL) at −78 °C was added a solution of triphenylphosphine (0.65 g; 2.48 mmol) and trimethylsilyl chloride (3.1 mL; 25 mmol) in THF (20 mL). The resultant mixture was allowed to warm to room temperature and was left stirring at this temperature for 2 h, at the end of which time the solution appeared deep blue. The solvent was removed in vacuo, and the product was purified by column chromatography on silica gel, eluting with CH_2Cl_2. Removal of the solvent in vacuo and recrystallization from a THF/hexane mixture at −30 °C yielded a bright blue crystalline material, yield 0.95 g (79%) Anal. Calcd for $C_9H_{10}BCl_2N_6ORe$: C, 22.24; H, 2.07; N, 17.29; Re, 38.30; O, 3.29; Cl, 14.59. Found: C, 22.20; H, 2.09; N, 17.30; Re, 37.84; O, 3.20; Cl, 14.67. IR (KBr, cm^{-1}): 3151 (m), 3125 (m), 2528 (br, m) [ν(B–H)], 1504 (s), 1409 (s), 1387 (m), 1310 (s), 1212 (s), 1183 (m), 1124 (s), 1121 (s), 1073 (m), 1051 (s), 994 (m), 978 (s) [ν(Re=O)], 816 (w), 791 (m), 771 (s), 720 (m), 708 (s), 668 (w), 647 (m), 612 (m), 340 (sh), 331 (m), 309 (m) [ν(Re–Cl)]. FD MS (CH_2Cl_2 solution): *m/z* 486 (M$^+$). ^{1}H NMR ((CD_3)$_2$CO, 400 MHz): δ 8.28 (d, 2 H), 8.26 (d, 2 H), 7.66 (d, 1 H), 7.38 (d, 1 H), 6.73 (t, 2 H) 6.06 (t, 1 H).

Synthesis of [HB(pz)$_3$]ReOBr$_2$ (3). To a suspension of **1** (1.72 g; 3.8 mmol) in THF (140 mL) at −78 °C was added a solution of triphenylphosphine (1.01 g; 3.8 mmol) and trimethylsilyl bromide (5.1 mL; 39 mmol) in THF (10 mL). The resultant mixture was allowed to warm to room temperature and was left stirring at this temperature for 4 h, at the end of which time the solution appeared blue/green. The solvent was removed in vacuo, and the product was purified by colmn chromatography on silica gel, eluting with CH_2Cl_2. Removal of the solvent in vacuo and recrystallization from a THF/hexane mixture at −30 °C yielded a blue/green crystalline material that was analyzed to contain 0.5 mol of THF: yield 1.60 g (69%); mp >250 °C. Anal. Calcd for $C_9H_{10}BBr_2N_6ORe\cdot0.5C_4H_8O$: C, 21.62; H, 2.31; N, 13.75; Re, 30.47. Found: C, 21.88; H, 2.37; N, 14.15; Re, 30.64. After the solid was dried in vacuo for 1 h at 100 °C, the THF was removed. Anal. Calcd for $C_9H_{10}BBr_2N_6ORe$: C, 18.80; H, 1.88; N, 14.61; Br, 27.79. Found: C, 18.95; H, 1.92; N, 14.67; Br, 27.87. IR (KBr, cm^{-1}): 3149 (m), 3121 (m), 2521 (br, m) [ν(B–H)], 1502 (m), 1409 (s), 1386 (m), 1311 (s), 1213 (s), 1183 (m), 1125 (s), 1078 (m), 1050 (s), 995 (m), 981 (s) [ν(Re=O)], 791 (m), 772 (s), 712 (s), 649 (m), 613 (m). FD MS (CH_2Cl_2 solution): *m/z* 576 (M$^+$). ^{1}H NMR ((CD_3)$_2$CO, 400 MHz): δ 8.41 (d, 2 H), 8.28 (d, 2 H), 7.68 (d, 1 H), 7.43 (d, 1 H), 6.73 (t, 2 H) 6.04 (t, 1 H).

Preparation of [HB(pz)$_3$]ReO(Cl)(SC$_6$H$_5$) (4). To a solution of **2** (87 mg; 0.179 mmol) in THF (20 mL) were added DBU (67 μL; 0.448 mmol) and thiophenol (46 μL; 0.448 mmol). The solution was heated to 60 °C for 3 h. The resulting solution appeared dark green/black with a pale-colored precipitate. The precipitate was removed by filtration through a pad of silica gel, and the solvent was removed in vacuo. The product was purified by column chromatography on silica gel, eluting with CH_2Cl_2. The product (dark green band) was collected, and the solvent was removed in vacuo. Recrystallization from CH_2Cl_2/hexane at −30 °C gave a green/black crystalline material: yield 72 mg (71%); mp 212–216 °C. Anal. Calcd for $C_{15}H_{15}BClN_6OReS$: C, 32.18; H, 2.70; N, 15.01; Cl, 6.33; Re, 33.26. Found: C, 31.95; H, 2.68; N, 15.06; Cl, 6.28; Re, 32.88. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.23 (d), 7.90 (m), 7.58 (br), 7.45 (d), 7.33 (br), 7.14 (br), 6.50 (t), 6.34 (br), 6.00 (t). ^{13}C{^{1}H} NMR (400 MHz, CD_2Cl_2): δ 154.8, 148.0, 147.4, 145.4, 139.5, 137.9, 134.7, 133.2, 128.7, 126.9, 108.8, 108.2, 106.2. IR (KBr disk, cm^{-1}): 3141 (m), 3114 (m), 3050 (w), 2532 (m) [ν(BH)], 1500 (s), 1405 (s), 1387 (m), 1311 (s), 1212 (s), 1186 (m), 1120 (m), 1073 (m), 1050 (vs), 996 (m), 956 (vs) [ν(Re=O)], 773 (vs), 744 (m), 711 (m), 649 (m), 613 (m), 481 (m). MS FD (CH_2Cl_2): *m/z* 560 (M$^+$).

Preparation of [HB(pz)$_3$]ReO(SC$_6$H$_5$)$_2$ (5). To a solution of **2** (133 mg; 0.27 mmol) in toluene (20 mL) were added DBU (100 μL; 0.67 mmol) and thiophenol (56 μL; 0.54 mmol). The solution was heated to 100 °C for 24 h. Purification as for **2** (above) and recrystallization from a CH_2Cl_2/hexane mixture at −30 °C gave a brown crystalline material: yield 90 mg (46%); mp 142–144 °C. Anal. Calcd for $C_{21}H_{20}BN_6OReS_2\cdot CH_2Cl_2$: C, 37.47; H, 3.11; N, 12.05. Found: C, 36.28; H, 3.02; N, 12.05. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.92 (d, 1 H), 7.77 (d, 2 H), 7.53 (d, 1 H), 7.4–7.0 (m, 12 H), 6.22 (br, 2 H), 6.10 (t, 1 H). IR (KBr disk, cm^{-1}): 3125 (w), 3055 (w), 2521 (m) [ν(B–H)], 1577 (m), 1503 (m), 1436 (m), 1405 (s), 1390 (m), 1312 (s), 1214 (s), 1120 (m), 1051 (vs), 988 (m), 945 (vs) [ν(Re=O)], 792 (vs), 775 (m), 764 (m), 744 (m), 715 (m), 654 (m), 617 (m). MS FD (CH_2Cl_2): *m/z* 634 (M$^+$).

Preparation of [HB(pz)$_3$]ReO(S$_2$C$_6$H$_4$) (6). The method was analogous to that for **4**. A solution of **2** (178 mg; 0.366 mmol) in THF (20 mL) was reacted with DBU (120 μL; 0.808 mmol) and 1,3-benzenedithiol (46 μL; 0.401 mmol). Recrystallization of the product from THF/hexane at −30 °C gave a brown powder that was analyzed to contain 0.5 equiv of THF: yield 120 mg (55%); mp >250 °C. Anal. Calcd for $C_{15}H_{14}BN_6OS_2Re\cdot0.5C_4H_8O$: C, 34.51; H, 3.07; N, 14.21; Re, 31.47. Found: C, 34.24; H, 2.99; N, 14.40; Re, 31.99. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.37 (d, 2 H), 7.98 (d, 2 H), 7.88 (m, 2 H), 7.37 (d, 1 H), 7.11 (m, 2 H), 7.05 (d, 1 H), 6.54 (t, 2 H), 5.82 (t, 1 H). IR (KBr disk, cm^{-1}): 3114 (w), 3051 (w), 2518 (m) [ν(B–H)], 1501 (m), 1444 (w), 1406 (s), 1390 (m), 1311 (s), 1213 (s), 1189 (m), 1118 (m), 1074 (m), 1050 (vs), 985 (m), 952 (vs) [ν(Re=O)], 792 (m), 768 (s), 744 (m), 711 (m), 652 (m), 616 (m). MS FD (CH_2Cl_2): *m/z* 556 (M$^+$).

Preparation of [HB(pz)$_3$]ReO(S$_2$C$_2$H$_4$) (7). The method was analogues to that for **4**. A solution of **2** (111 mg; 0.23 mmol) in THF (20 mL) was reacted with DBU (75 μL; 0.50 mmol) and 1,2-ethanedithiol (20 μL; 0.23 mmol). The product was recrystallized from CH_2Cl_2/hexane and was obtained as a brown crystalline solid that was analyzed to contain 0.5 equiv of CH_2Cl_2: yield 75 mg (64%); mp >250 °C. Anal. Calcd for $C_{11}H_{14}BN_6OReS_2\cdot0.5CH_2Cl_2$: C, 25.12; H, 2.75; N, 15.28; Re, 33.86. Found: C, 25.41; H, 2.76; N, 15.88; Re, 34.41. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.41 (d, 2 H), 7.95 (d, 2 H), 7.31 (d, 1 H), 7.26 (d, 1 H), 6.50 (t, 2 H), 5.83 (t, 1 H), 3.94 (m, 2 H), 3.58 (m, 2 H). IR (KBr disk, cm^{-1}): 3123 (w), 3096 (w), 2906 (m), 2515 (m) [ν(B–H)], 1503 (m), 1407 (s), 1392 (m), 1312 (s), 1218 (s), 1120 (m), 1073 (m), 1050 (vs), 990 (m), 951 (vs) [ν(Re=O)], 923 (w), 789 (m), 775 (m), 766 (m), 713 (m), 656 (w), 617 (m). MS FD (CH_2Cl_2): *m/z* 508 (M$^+$).

Crystallographic Data Collection and Refinement of the Structures

The data for the crystallographic studies of both **4** and **5** were collected on a CAD-4 diffractometer (Enraf-Nonius, κ geometry) with graphite-monochromated Cu Kα radiation (λ = 154.184 pm, 1° < θ < 65°) at ambient temperature (23 ± 1 °C). All computations were carried out on a VAX-3100 computer with the program systems STRUX-III[9] and SHELX-76. The structures were solved by using Patterson methods (SHELX-86)[10] and refined by subsequent least-squares and difference

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Table I. Details of X-ray Diffraction Studies for **4** and **5**

	4	**5**
mol formula	$C_{15}H_{15}BClN_6OReS$	$2 \times C_{21}H_{20}BN_6OReS_2 + 1.5 \times CH_2Cl = C_{43}H_{43}B_2Cl_3N_{12}O_2Re_2S_4$
M_r	559.2	1388.5
a, Å	13.159 (1)	15.594 (3)
b, Å	18.656 (1)	21.624 (1)
c, Å	15.902 (1)	15.931 (3)
β, deg		107.00 (1)
V, Å^3	3904 (1)	5137 (1)
Z	8	4
abs coeff, cm^{-1}	142.0	121.1
R^a	0.043	0.050
$R_w{}^b$	0.031	0.036
GOF^c	3.981	2.501
space group	*Pbca* (No. 61), orthorhombic	$P2_1/c$ (No. 14), monoclinic
transm coeff	0.13–0.59	0.21–0.57, 0.09–0.56
T, °C	23 ± 1	23 ± 1
ρ_{calc}, g cm^{-3}	1.903	1.795
ϵ^d	3.7×10^{-8}	2.9×10^{-8}

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] $GOF = [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$. [d] ϵ: $F_c(cor) = 1 + \epsilon F_c{}^2(Lp)$.

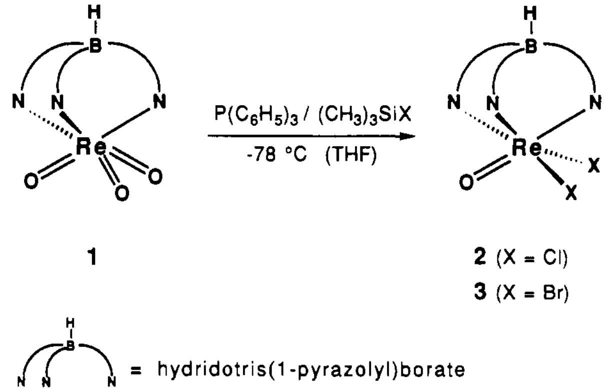
Table II. Non-Hydrogen Positional and Thermal Parameters for **4** with Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c	U(eq), Å^2
Re	0.14898 (3)	0.17511 (2)	0.11304 (2)	0.034
S	0.2755 (2)	0.1682 (1)	0.2126 (1)	0.049
Cl	0.1513 (2)	0.05136 (9)	0.0897 (1)	0.052
O	0.0445 (4)	0.1904 (3)	0.1722 (3)	0.049
N11	0.2774 (5)	0.1810 (3)	0.0193 (3)	0.040
N21	0.0695 (5)	0.1824 (3)	−0.0028 (3)	0.039
N31	0.1777 (5)	0.2860 (3)	0.1077 (4)	0.042
N12	0.2744 (5)	0.2288 (3)	−0.0464 (4)	0.040
N22	0.0868 (5)	0.2349 (3)	−0.0593 (4)	0.042
N32	0.1819 (5)	0.3223 (3)	0.0326 (4)	0.042
C1	0.2795 (6)	0.0841 (4)	0.2662 (5)	0.045
C2	0.3726 (7)	0.0567 (5)	0.2906 (6)	0.067
C3	0.3778 (9)	−0.0041 (5)	0.3371 (7)	0.089
C4	0.290 (1)	−0.0394 (5)	0.3592 (6)	0.084
C5	0.2010 (9)	−0.0145 (5)	0.3373 (6)	0.076
C6	0.1935 (7)	0.0470 (5)	0.2908 (5)	0.067
C13	0.3581 (7)	0.2210 (4)	−0.0936 (5)	0.050
C14	0.4157 (6)	0.1672 (5)	−0.0589 (5)	0.053
C15	0.3635 (6)	0.1437 (4)	0.0108 (5)	0.045
C23	0.0198 (7)	0.2301 (5)	−0.1220 (5)	0.056
C24	−0.0442 (7)	0.1755 (5)	−0.1044 (5)	0.063
C25	−0.0122 (6)	0.1461 (4)	−0.0300 (5)	0.051
C33	0.1922 (7)	0.3921 (4)	0.0481 (6)	0.055
C34	0.1921 (7)	0.4033 (4)	0.1339 (5)	0.059
C35	0.1831 (6)	0.3349 (4)	0.1694 (5)	0.052
B	0.1840 (9)	0.2811 (5)	−0.0519 (5)	0.052

Table III. Non-Hydrogen Positional and Thermal Parameters for **5** with Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c	U(eq), Å^2
ReA	0.36328 (2)	0.22674 (2)	0.01802 (2)	0.030
S1A	0.4651 (1)	0.2386 (1)	−0.0611 (2)	0.038
S2A	0.4146 (2)	0.1271 (1)	0.0536 (2)	0.049
O1A	0.2644 (4)	0.2175 (3)	−0.0566 (4)	0.044
N11A	0.4720 (4)	0.2582 (3)	0.1359 (5)	0.039
N21A	0.3048 (5)	0.2148 (4)	0.1243 (5)	0.042
N31A	0.3360 (4)	0.3231 (4)	0.0206 (5)	0.038
C41A	0.4870 (6)	0.3173 (4)	−0.0790 (6)	0.037
C51A	0.4717 (7)	0.0945 (4)	−0.0196 (7)	0.047
ReB	0.03904 (2)	0.77138 (2)	0.29404 (2)	0.029
S1B	0.1422 (1)	0.7701 (1)	0.2155 (1)	0.038
S2B	0.0802 (2)	0.8716 (1)	0.3378 (2)	0.043
O1B	−0.0606 (3)	0.7790 (3)	0.2183 (4)	0.041
N11B	0.1536 (4)	0.7413 (3)	0.4111 (4)	0.035
N21B	−0.0207 (4)	0.7737 (4)	0.3998 (4)	0.038
N31B	0.0200 (4)	0.6729 (3)	0.2885 (5)	0.038
C41B	0.1773 (6)	0.6945 (4)	0.1973 (6)	0.035
C51B	0.1438 (7)	0.9115 (4)	0.2789 (6)	0.043

Scheme I



Fourier techniques.[11] Corrections for Lorentz and polarization effects were applied. Hydrogen atoms were inserted for both structures at calculated positions but were not refined (d(C–H) and d(B–H) = 0.095 Å). Scattering factors were taken from ref 12, and anomalous scattering factors, from ref 13. Crystallographic details for **4** and **5** are summarized in Table I.

X-ray Diffraction Study of [HB(pz)$_3$]ReO(Cl)(SC$_6$H$_5$) (4). A dark green, plate-shaped single crystal (approximately 0.02 × 0.16 × 0.07 mm) of compound **4** was grown from a dichloromethane/hexane mixture. Lattice constants were calculated by a least-squares fit of 25 reflections in the range 79.8° $< 2\theta \leq$ 88.6°. The diffraction data showed orthorhombic symmetry, and systematic absences uniquely determined the space group as *Pbca*. Intensities of three standard reflections were measured every hour, and a decay of 5.7% after 78.5 h of measurement was observed and corrected. A numerical absorption correction was carried out. A total of 3727 reflections were recorded. Of the 3296 unique reflections, of which 15 were suppressed because of insufficient absorption correction, 2713 (NO) with $I > 2\sigma(I)$ were used for structure refinement. A total of 236 (NV) parameters were full-matrix least-squares refined. All non-hydrogen atoms were refined anisotropically. The shift/error was smaller than 0.01 in the last cycle. The final atomic positional parameters are listed in Table II.

X-ray Diffraction Study of [HB(pz)$_3$]ReO(SC$_6$H$_5$)$_2$ (5). A dark brown, plate-shaped single crystal (approximately 0.08 × 0.11 × 0.02 mm) of **5**, crystallized from a dichloromethane/hexane mixture, was used for diffraction data collection. Crystallographic data for this compound appear in Table I. Lattice constants were calculated by a least-squares fit of 25 reflections in the range 79.8° $< 2\theta <$ 87.8°. The diffraction data showed monoclinic symmetry, and systematic absences uniquely determined the space group as $P2_1/c$. Because of technical reasons, the data collection was split into two parts. For the first collection 3999 peaks were measured (h(0/18), k(−25/0), l(0/18)). Intensities of three standard reflections were measured every hour. A decay of 5.7% after 85.3 h of measurement was determined and corrected. Numerical absorption correction was carried out, and 3331 reflections were used for scaling. For the second set, 5681 peaks were measured (h(−18/0), k(−25/0), l(0/18)). A decay of 9.9% after 125 h of measurement was determined and corrected. Numerical absorption correction was carried out, and 4663 reflections of this data set were used for scaling. The two data sets were scaled with 273 reflections ($I > 10\sigma(I)$), and 7994 corrected reflections were generated. Of the 7443 unique reflections (R = 0.0412, SHELX-76), 6683 reflections with $I > 2\sigma(I)$ were used for structure refinement. A total of 618 parameters were full-matrix least-squares refined. All non-hydrogen atoms except the disordered carbon atom C8 (of a CH_2Cl_2 molecule) were refined anisotropically. The shift/error did not exceed 0.001 in the last cycle. A final difference Fourier map was essentially featureless, with the largest peak −1.7 e/Å^3. The final atomic positional parameters are listed in Table III.

Results and Discussion

Preparation and Properties of [HB(pz)$_3$]ReOCl$_2$ and [HB(pz)$_3$]ReOBr$_2$. [HB(pz)$_3$]ReO$_3$ (**1**) reacts readily with 1 equiv of triphenylphosphine in THF to give a mixture of reduced rhenium products that could not be identified. However, when the same reaction is carried out at −78 °C in the presence of excess

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trimethylsilyl chloride or bromide, the rhenium(V) oxide dihalides $[HB(pz)_3]ReOCl_2$ (**2**) and $[HB(pz)_3]ReOBr_2$ (**3**) are formed in good yields (Scheme I). These reactions contrast with the analogous reduction of $(\eta^5\text{-}C_5Me_5)ReO_3$ with triphenylphosphine in the presence of excess trimethylsilyl halide, in which *all* of the oxygen atoms are replaced to give the tetrahalide compounds $(\eta^5\text{-}C_5Me_5)ReX_4$ (X = Cl, Br).[7] We found that the remaining oxo ligand in **2** cannot be removed with excess trimethylsilyl chloride even in refluxing toluene.

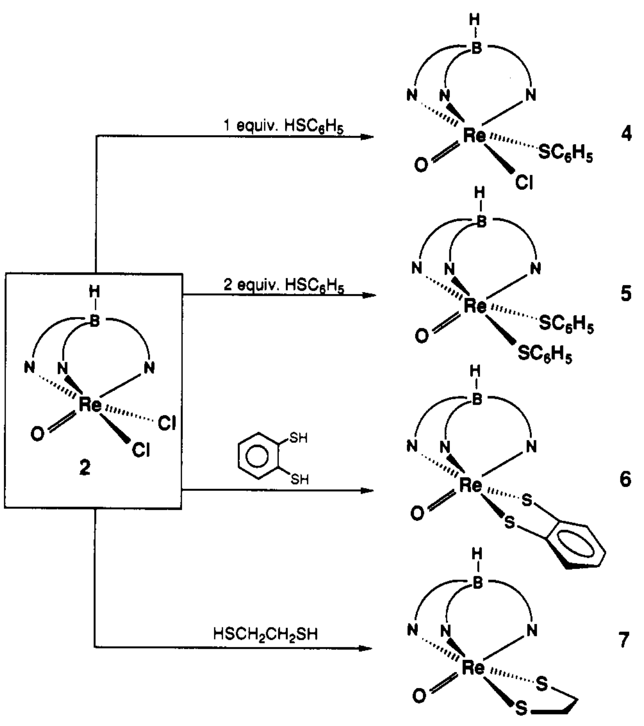
$[HB(pz)_3]ReOCl_2$ (**2**) can be prepared in yields of 62% by our method as a bright blue crystalline solid. A much lower yielding synthesis (40%) of **2** from sodium perrhenate and a large excess of potassium hydridotris(1-pyrazolyl)borate in ethanolic HCl has previously been reported.[4] This reaction also yielded a blue crystalline solid with the same spectroscopic characteristics. We have observed that heating **2** to ca. 200 °C causes the compound to change color from blue to green. The FD mass spectrum of this green compound shows only the molecular ion for **2**, indicating that the green compound is an isomer of **2**. The green compound has the same spectroscopic (IR, ^1H NMR) characteristics as **2**. Unfortunately, attempts to obtain an analytically pure sample have been unsuccessful. The similarity in the IR and ^1H NMR spectra implies that the isomers have essentially the same structure, and so we tentatively suggest that this green compound is a "bond stretch isomer"[14,15] of **2**. Such isomerism has been found in several d^1 and d^2 transition-metal complexes containing both oxo and chloride ligands. A well-documented example of this kind of isomerism is $[LWOCl_2][PF_6]$[16] (L = 1,4,7-triazacyclononane). Usually the only structural difference between the isomers is small differences in some metal–ligand bond lengths, particularly the M=O bond.[16]

Reduction of **1** with triphenylphosphine in the presence of an excess of trimethylsilyl bromide in THF solution gives $[HB(pz)_3]ReOBr_2$ (**3**). This compound is a blue/green air- and water-stable crystalline material and is obtained in good yields. The IR spectrum shows two Re=O bands at 995 and 981 cm^{-1}. These bands are almost exactly the same as those found in the IR spectrum of **2**, suggesting that replacement of the chloride by bromide ligands does not significantly alter the strength of the Re=O bond.

Preparation and Properties of Thiolato Derivatives. Complex **2** was found to react readily with thiols in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) to give the corresponding thiolato derivatives according to Scheme II.

The reaction between 1 equiv of **2** and 2.5 equiv of thiophenol in refluxing THF gives **4** as a green/black crystalline solid. This compound can also be synthesized by treatment of **2** with 1 equiv of sodium thiophenolate. The spectroscopic data (^{13}C NMR, IR, and FD-MS) and elemental analyses for **4** are consistent with one chloride having been replaced with one thiophenolato group. The ^1H NMR spectrum, however, could not be properly interpreted due to broad and overlapping signals. The IR spectrum shows bands expected for the B—H bond (2532 cm^{-1}) and the terminal Re=O bond (996 and 956 cm^{-1}).

Scheme II



When 2 equiv of thiophenol is reacted with **2** in refluxing THF, both chloride ligands are exchanged for thiophenolato groups to give **5** (Scheme II). Recrystallization from CH_2Cl_2/hexane gives a brown, crystalline solid that contains 0.75 equiv of CH_2Cl_2. The spectroscopic data and analysis are consistent with this composition, and the presence of the CH_2Cl_2 was confirmed by the X-ray crystallographic study. The IR spectrum shows a band at 2521 cm^{-1} due to the B—H bond and bands at 988 and 945 cm^{-1} attributable to a terminal Re=O bond. The analogous compound $(\eta^5\text{-}C_5Me_5)ReO(SC_6H_5)_2$ has previously been reported. It can be prepared from $(\eta^5\text{-}C_5Me_5)ReO_3$ and excess thiophenol[17] or by treatment of $(\eta^5\text{-}C_5Me_5)ReOCl_2$ with 2 equiv of sodium thiophenolate.[18] The pentamethylcyclopentadienyl analogue of the monosubstituted thiophenolato derivative **4** has not been reported. However, it would seem probable that such a compound could be prepared from comparison with this present work. The related compound $(\eta^5\text{-}C_5Me_5)ReO(Cl)(S\text{-}t\text{-}C_4H_9)$ is known.[19] In this particular case, the steric bulk of the thiolato ligand made replacement of the second chloride slow, thus allowing the monosubstituted compound to be isolated.[19]

2 will react with aromatic dithiols with the replacement of both chloride ligands to give dithiolato-*S,S* chelate complexes. Thus one equivalent of 1,2-benzenedithiol reacts with **2** to give **6**, which after recrystallization from THF, is isolated as a brown microcrystalline solid containing 0.5 equiv of THF held in the solid but not coordinated to the rhenium (Scheme II). The IR spectrum exhibits the expected bands for the B—H bond (2518 cm^{-1}) and the terminal Re=O bond (985 and 952 cm^{-1}). The FD mass spectrum (CH_2Cl_2 solution) shows only the monomeric molecular ion. The ^1H NMR spectrum shows two types of pyrazolyl rings (ratio 1:2) consistent with a monomeric structure analogous to that of **5**.

Aliphatic dithiols behave in the same manner. Thus, 1,2-ethanedithiol reacts with **2** to give the brown microcrystalline solid **7**, which after recrystallization from CH_2Cl_2, yields a solid analyzing as $[HB(pz)_3]ReO(S_2C_2H_4)\cdot 0.5CH_2Cl_2$. Again, the IR spectrum exhibits bands attributable to the B—H bond (2515 cm^{-1}) and a terminal Re=O bond (990 and 951 cm^{-1}). The FD mass spectrum (CH_2Cl_2 solution) shows only the monomeric molecular ion. The ^1H NMR spectrum shows signals corresponding to two types of pyrazolyl rings (ratio 1:2), consistent with a monomeric, octahedral structure, and two octets (3.95 and 3.56 ppm) arising from the two methylene groups. It has recently been reported that $[HB(3,5\text{-}Me_2pz)_3]MoOCl_2$ will also react with thiols and diols in the presence of triethylamine to give products arising from substitution of both chlorides.[20] The ethanedithiol derivative $[HB(3,5\text{-}Me_2pz)_3]MoO(S_2C_2H_4)$ was reported and

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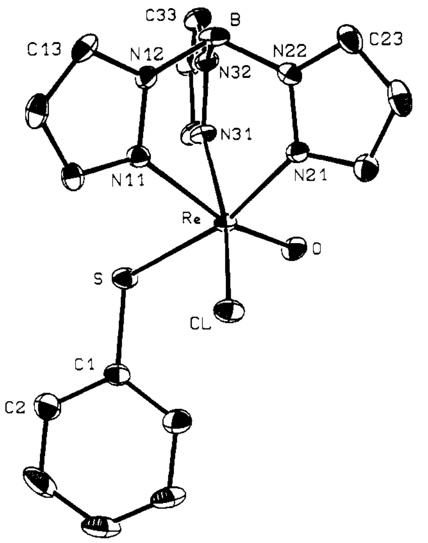

Figure 1. Crystal and molecular structure (ORTEP representation) of **4**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table IV. Interatomic Distances (Å) for **4** with Estimated Standard Deviations in Parentheses

Re–S	2.301 (2)	Re–Cl	2.339 (2)
Re–O	1.691 (5)	Re–N11	2.256 (6)
Re–N21	2.123 (6)	Re–N31	2.104 (5)
S–Cl1	1.785 (7)	N11–N12	1.374 (7)
N11–C15	1.337 (9)	N21–N22	1.348 (7)
N21–C25	1.341 (9)	N31–N32	1.375 (7)
N31–C35	1.342 (9)	N12–C13	1.341 (9)
N12–B	1.54 (1)	N22–C23	1.333 (9)
N22–B	1.55 (1)	N32–C33	1.332 (8)
N32–B	1.55 (1)	C1–C2	1.38 (1)
C1–C6	1.38 (1)	C2–C3	1.36 (1)
C3–C4	1.37 (1)	C4–C5	1.31 (1)
C5–C6	1.37 (1)	C13–C14	1.37 (1)
C14–C15	1.38 (1)	C23–C24	1.35 (1)
C24–C25	1.37 (1)	C33–C34	1.38 (1)
C34–C35	1.40 (1)		

found to have bands in its IR spectrum arising from a terminal Mo═O bond, consistent with a monomeric structure.

Both of the compounds **4** and **5**, containing the chelating dithiolato groups, are thermally very stable, neither melting nor decomposing below 250 °C.

X-ray Structural Study of [HB(pz)$_3$]ReO(Cl)(SC$_6$H$_5$). An ORTEP diagram of the structure is shown in Figure 1. The bond distances are listed in Table IV, and the bond angles, in Table V. Compound **4** is monomeric with an approximately octahedral arrangement of the coordination sphere around the rhenium atom. Within the crystal was found a racemic mixture of the two optical isomers. The Re═O bond has a length of 1.689 (5) Å, which is close to the values found in similar rhenium(V) complexes.[6a,21] It is slightly shorter than the average Re═O bond length found for **1** (1.712 (2) Å),[2] which is consistent with the increased bond order required to give an 18-electron system for **4**. The Re–Cl bond length of 2.339 (2) Å falls within the range expected for such bonds.[6a] The Re–N bond lengths are not equivalent. The bond trans to the oxo ligand is the longest (Re–N11 = 2.256 (6) Å), presumably a result of the trans influence of the multiply bonded oxo ligand. This value is also close to the value of 2.231 (3) Å previously found for Re–N bond lengths in **1**. The other two Re–N bonds are shorter, with values of 2.104 (5) Å (Re–N31, trans to Cl) and 2.123 (6) Å (Re–N21, trans to S). The bond lengths and angles within the [HB(pz)$_3$] unit show no unusual features and compare well to the values found for **1**.[2] The Re–S bond length is 2.301 (2) Å and is close to values found in other high-oxidation-state rhenium compounds with sulfur-containing ligands.[17,21,22]

Table V. Bond Angles (deg) for **4** with Estimated Standard Deviations in Parentheses

S–Re–Cl	92.5 (1)	S–Re–O	102.4 (2)
Cl–Re–O	105.4 (2)	S–Re–N11	85.1 (2)
Cl–Re–N11	86.2 (2)	O–Re–N11	165.7 (2)
S–Re–N21	163.2 (2)	Cl–Re–N21	86.1 (2)
O–Re–N21	94.1 (2)	N11–Re–N21	78.0 (2)
S–Re–N31	87.3 (2)	Cl–Re–N31	164.1 (2)
O–Re–N31	90.2 (2)	N11–Re–N31	77.9 (2)
N21–Re–N31	89.5 (2)	Re–S–C1	113.5 (3)
Re–N11–N12	120.8 (5)	Re–N11–C15	132.6 (5)
N12–N11–C15	106.6 (6)	Re–N21–N22	122.8 (5)
Re–N21–C25	129.9 (5)	N22–N21–C25	106.7 (6)
Re–N31–N32	121.8 (5)	Re–N31–C35	130.4 (5)
N32–N31–C35	107.3 (6)	N11–N12–C13	109.4 (6)
N11–N12–B	118.4 (6)	C13–N12–B	132.1 (7)
N21–N22–C23	109.7 (7)	N21–N22–B	119.6 (6)
C23–N22–B	129.9 (7)	N31–N32–C33	109.0 (6)
N31–N32–B	120.7 (6)	C33–N32–B	130.1 (7)
S–C1–C2	119.1 (7)	S–C1–C6	123.4 (7)
C2–C1–C6	117.3 (7)	C1–C2–C3	120.6 (9)
C2–C3–C4	119.9 (9)	C3–C4–C5	120.9 (9)
C4–C5–C6	120 (1)	C1–C6–C5	120.9 (9)
N12–C13–C14	107.9 (7)	C13–C14–C15	106.4 (7)
N11–C15–C14	109.8 (7)	N22–C23–C24	107.9 (7)
C23–C24–C25	106.8 (8)	N21–C25–C24	108.8 (7)
N32–C33–C34	109.3 (7)	C33–C34–C35	105.1 (7)
N31–C35–C34	109.2 (7)	N12–B–N22	106.8 (6)
N12–B–N32	106.2 (7)	N22–B–N32	109.2 (7)

Table VI. Selected Interatomic Distances (Å) for **5** with Estimated Standard Deviations in Parentheses

ReA–S1A	2.312 (2)	ReA–S2A	2.310 (2)
ReA–O1A	1.661 (5)	ReA–N11A	2.237 (7)
ReA–N21A	2.161 (8)	ReA–N31A	2.129 (8)
S1A–C41A	1.777 (9)	S2A–C51A	1.80 (1)
ReB–S1B	2.309 (2)	ReB–S2B	2.309 (2)
ReB–O1B	1.674 (5)	ReB–N11B	2.267 (6)
ReB–N21B	2.152 (7)	ReB–N31B	2.149 (7)
S1B–C41B	1.774 (9)	S2B–C51B	1.777 (9)

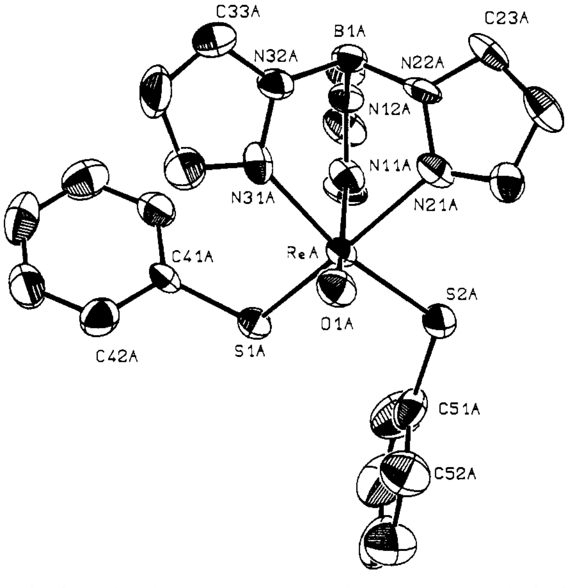

Figure 2. Crystal and molecular structure (ORTEP representation) of one of the molecules of **5**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

X-ray Structural Study of [HB(pz)$_3$]ReO(SC$_6$H$_5$)$_2$. An ORTEP diagram of the structure is shown in Figure 2. Selected bond distances are listed in Table VI, and selected bond angles and

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Table VII. Selected Bond Angles and Torsion Angles (deg) for **5** with Estimated Standard Deviations in Parentheses

S1A–ReA–S2A	89.6 (1)	S1A–ReA–O1A	105.4 (2)
S2A–ReA–O1A	104.3 (2)	S1A–ReA–N11A	87.2 (2)
S2A–ReA–N11A	87.4 (2)	O1A–ReA–N11A	162.7 (3)
S1A–ReA–N21A	162.7 (2)	S2A–ReA–N21A	83.8 (2)
O1A–ReA–N21A	91.7 (3)	N11A–ReA–N21A	76.6 (3)
S1A–ReA–N31A	94.3 (2)	S2A–ReA–N31A	164.7 (2)
O1A–ReA–N31A	89.0 (3)	N11A–ReA–N31A	78.0 (3)
N21A–ReA–N31A	88.2 (3)	ReA–S1A–C41A	112.9 (3)
ReA–S2A–C51A	114.0 (3)	S1B–ReB–S2B	89.9 (1)
S1B–ReB–O1B	105.0 (2)	S2B–ReB–O1B	104.0 (2)
S1B–ReB–N11B	86.3 (2)	S2B–ReB–N11B	86.4 (2)
O1B–ReB–N11B	164.4 (3)	S1B–ReB–N21B	162.7 (2)
S2B–ReB–N21B	83.5 (2)	O1B–ReB–N21B	92.2 (2)
N11B–ReB–N21B	77.3 (3)	S1B–ReB–N31B	94.3 (2)
S2B–ReB–N31B	164.9 (2)	O1B–ReB–N31B	88.9 (3)
N11B–ReB–N31B	79.4 (3)	N21B–ReB–N31B	88.2 (3)
ReB–S1B–C41B	113.4 (3)	ReB–S2B–C51B	116.4 (3)

O1A–ReA–S2A–C51A	−84.84
O1B–ReB–S2B–C51B	−98.87
O1A–ReA–S1A–C41A	−95.14
O1B–ReB–S1B–C41B	−90.52

torsion angles, in Table VII. The compound is monomeric with an approximately octahedral arrangement of the coordination sphere around the rhenium atom. Two distinct molecules of **5** (approximately mirror images of each other) were found in the unit cell as well as 1.5 equiv of CH_2Cl_2. One of the solvent molecules (CH_2Cl_2) was found to be disordered. For complex **5** the average Re═O bond length is 1.668 (5) Å, which is close to the value of 1.689 (5) Å found for complex **4**. The Re–S bonds have a mean length of 2.311 (2) Å, which is also close to the value of 2.301 (2) Å found for **4**. The Re–N bond trans to the oxo ligand has as expected the longest bond length (mean value 2.248 (6) Å), while the other two Re–N bond lengths are shorter, with a mean value of 2.147 (7) Å. All thiolate torsion angles are within 8° of a geometry causing maximal nonbonded repulsions between the filled p_π orbital on sulfur and π-electron density in the Re═O bond. Thus, the large S–Re–O angles (between 104.0 (2) and 105.4 (2)°) can be explained, as was first done for the molybdenum compound $[HB(pz)_3]MoO(SC_6H_5)_2$.[23] The bond lengths and angles found within the $[HB(pz)_3]$ unit show no unusual features and compare well to the values found previously for **1**[2] as well as the values found for **4**.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, Hoechst AG, and Degussa AG.

Supplementary Material Available: Anisotropic temperature factors and hydrogen atom coordinates for **4** and **5** (Tables SM1, SM2, SM4, and SM5), complete lists of atomic coordinates, bond distances, and bond angles for **5** (Tables SM7–SM9), an ORTEP diagram of the second molecule of **5** (Figure S2), and unit cell diagrams for **4** and **5** (Figures S1 and S3) (18 pages); listings of structure factors for **4** and **5** (Tables SM3 and SM6) (55 pages). Ordering information is given on any current masthead page.

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Primary Alkynylphosphines and Allenylphosphines

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Primary alkynyl- and allenylphosphines are prepared on a gram scale by a chemoselective reduction of the corresponding phosphonates. Their complexation at room temperature leads to the corresponding tungsten pentacarbonyl complexes. Characterization of the phosphines in the free or complexed state was performed by NMR (^1H, ^{31}P, ^{13}C) and infrared spectroscopy and high-resolution mass spectrometry.

Introduction

Compounds containing a divalent or trivalent heteroatom possessing a lone pair of electrons and bonded to one or two hydrogens and to an unsaturated system have been the subject of much interest.[1,2] In condensed phase, they are thermodynamically not stable because of rapid isomerization into the corresponding heteroalkenes or heterocumulenes. However, they are usually kinetically isolable at low temperature by using special techniques or equipment. Simple enols and enamines have been obtained by retro Diels–Alder cleavage under flash thermolytic conditions (FVT).[3,4] Recently, ethynamines were prepared from different precursors by FVT[5] and ethynols were identified by photodecarbonylation of hydroxycyclopropenones in an argon matrix.[6]

The corresponding phosphorus derivatives have been less studied compared to the oxygen or nitrogen analogues. The parent compound ethynylphosphine $H{-}C{\equiv}C{-}PH_2$ was analytically prepared for the first time in low yield (9%) by low-pressure electric discharge of an acetylene–phosphine mixture. It was described as a thermally unstable compound, which polymerizes above −20 °C as uncharacterized material.[7] So far only few derivatives stabilized by bulky substituents or complexation have been synthesized.[8] Interestingly, an alkynylphosphine/phospha-allene tautomerism was observed.[9] The potential interest of alkynylphosphines as phosphaallene precursors or ligands in organometallic chemistry prompted us to develop a general approach. As part of our recent interest in the preparation of reactive and unstable molecules containing phosphorus,[10] we recently syn-

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