Synthesis, Structure, and Reactivity of Thienyl-, Benzothienyl-, and Selenylcarbene Complexes of Rhenium: A New Mechanism for H/D Exchange during Hydrodesulfurization†

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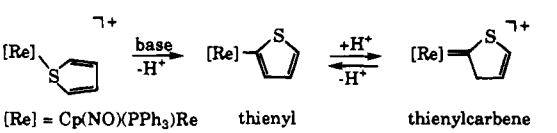
A series of $\eta^1(E)$-coordinated (E = S or Se) thiophene, benzo[b]thiophene and selenophene complexes $[Cp(NO)(PPh_3)Re(\eta^1(E)\text{-}L)]^+$, Cp = C_5H_5, L = thiophene (T), 2-methylthiophene (2-MeT), 2,5-dimethylthiophene (2,5-Me_2T), benzo[b]thiophene (BT), 3-methylbenzo[b]-thiophene (3-MeBT), selenophene (Sel), 2-methylselenophene (2-MeSel), and 2,5-dimethylselenophene (2,5-Me_2Sel) are prepared by the reaction of $[Cp(NO)(PPh_3)Re(ClC_6H_5)]^+$ with the appropriate ligand. The T, 2-MeT, BT, 3-MeBT, Sel, 2-MeSel complexes are deprotonated at C(2) by strong, non-nucleophilic bases to give the neutral $Cp(NO)(PPh_3)Re$(2-L-yl) complexes, where 2-L-yl = 2-thienyl (2-Tyl), 2-(5-methylthienyl) (2-(5-MeTyl)), 2−benzothienyl (2-BTyl), 2-(3-methylbenzothienyl) (2-(3-MeBTyl)), 2-selenyl (2−Selyl), and 2-(5-methylselenyl) (2-(5-MeSelyl)). The pK_a of the base required to effect this deprotonation increases with the L ligand in the complex in the following order: Sel < T < BT. The 2-Tyl, 2-BTyl and 2-Selyl complexes react with either $HBF_4{\cdot}Et_2O$ or HO_3SCF_3 at −42 °C to give the corresponding carbene complexes $[Cp(NO)(PPh_3)Re$(2-L-ylcarbene)$]^+$ resulting from protonation at C(3). The molecular structure of $[Cp(NO)(PPh_3)Re$(2-BTylcarbene)$]O_3SCF_3$, as determined by an X-ray diffraction study, exhibits a Re=C bond distance of 1.992(7) Å. The carbene complexes do not react with nucleophiles; however, those nucleophiles that are sufficiently basic deprotonate C(3) to give back the L-yl compound. The pK_a values of bases that are strong enough to cause deprotonation increase with the L-ylcarbene ligand in the order: Selylcarbene ~ Tylcarbene < BTylcarbene. The carbene complexes $[Cp(NO)(PPh_3)$-Re(2-(5-MeTylcarbene)$]^+$ and $[Cp(NO)(PPh_3)Re$(2-(5-MeSelylcarbene)$]^+$ are unstable and rearrange to their more stable isomers $[Cp(NO)(PPh_3)Re(\eta^1(S)\text{-}2\text{-}MeT)]^+$ and $[Cp(NO)(PPh_3)$-$Re(\eta^1(Se)\text{-}2\text{-}MeSel)]^+$. A new mechanism for H/D exchange of thiophene on hydrodesulfurization catalysts is proposed based on deuterium labeling studies of these thiophene complexes.

Introduction

Several different modes of thiophene adsorption to metal sites on catalyst surfaces have been proposed for the hydrodesulfurization (HDS) of thiophene. Of all the possible types of coordination in organometallic model complexes,[1–4] the $\eta^1(S)$ mode was one of the first proposed. It has also been the focus of several recent studies of thiophene, benzothiophene[5,6] and selenophene[7] complexes in this laboratory. The activation of C-S bonds in $\eta^1(S)$-bound thiophene complexes has yet to be demonstrated but has been proposed for the insertion of Rh into the C-S bond in the reaction of thiophene with $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)$.[8] Activation of C-H bonds in η^1-(*S*)-thiophene has been recently reported[6] in the complex $[Cp(NO)(PPh_3)Re(\eta^1(S)\text{-T})]^+$ which undergoes deprotonation (eq 1) by strong base (KOH/CH_3OH) to give the



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2-thienyl complex $Cp(NO)(PPh_3)Re$(2-thienyl). Re-protonation of $Cp(NO)(PPh_3)Re$(2-thienyl) with HO_3SCF_3 (triflic acid) does not give back the $\eta^1(S)$ thiophene complex; instead protonation occurs in the 3-position to form a thienylcarbene product. A similar series of reactions occurred with the analogous benzo[b]thiophene (BT) complex $Cp(NO)(PPh_3)Re(\eta^1(S)\text{-BT})^+$.[6]

In the present study, we report on an improved synthesis of the $[Cp(NO)(PPh_3)Re(\eta^1(S)$-thiophene$)]^+$ and $Cp(NO)(PPh_3)Re$(2-thienyl) complexes as well as their analogs with benzo[b]thiophene (BT) and selenophene (Seln) ligands. In addition, the thienylcarbene-type complexes of thiophene, benzothiophene and selenophene have been isolated, and their reactions have

† Dedicated to Professor William A. G. Graham, University of Alberta, on the occasion of his 65th birthday.

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been explored. The molecular structure of the benzothienylcarbene complex [Cp(NO)(PPh_3)Re(2-BTylcarbene)]O_3SCF_3 has been determined. These studies offer a new perspective on possible mechanisms for the deuterium exchange of thiophene with D_2 on HDS catalyst surfaces.

Experimental Section

General Procedures. All reactions and manipulations were carried out under an atmosphere of dry N_2 using standard Schlenk techniques unless otherwise stated.[9,10] All solvents were reagent grade or better and were dried and distilled under N_2 by the following methods. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from Na/benzophenone. Hexanes and dichloromethane (CH_2Cl_2) and acetonitrile (CH_3CN) were distilled from CaH_2. Acetone and chlorobenzene were dried with potassium carbonate (K_2CO_3) and distilled. The solvents were used immediately after distillation except for acetone and chlorobenzene which were stored over K_2CO_3 under N_2. The neutral alumina (Brockmann, Activity I, ~150 mesh) used for chromatography was deoxygenated at room temperature in high vacuum for 16 h, then deactivated with 5% w/w N_2-saturated deionized distilled water, and stored under N_2.

The ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 MHz spectrometer with deuterated solvents as the internal locks and referenced to tetramethylsilane (TMS δ = 0.00) or residual CH_2Cl_2 (δ = 5.33). The 2-D $^1H/^1H$ COSY, $^1H/^1H$ NOESY and $^1H/^{13}C$ HETCOR spectra were recorded on the same instrument using standard 2D pulse sequences on a non-spinning, thermostated sample. The $^{77}Se\{^1H\}$ NMR spectra were recorded on the Varian VXR-300 spectrometer at room temperature and referenced to selenophene (δ = 605.0 ppm) as the internal standard. Infrared spectra were obtained on a Nicolet 710 FTIR spectrophotometer using a solution cell with NaCl salt plates. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

The following compounds were prepared by literature methods: Cp(NO)(PPh_3)Re(CH_3),[11] selenophene (Sel),[12,13] 2-methylselenophene (2-MeSel),[14] and 2,5-dimethylselenophene (2,5-Me_2Sel).[15] All other reagents were used as received from commercial sources.

General Procedure for the Preparation of [Cp(NO)(PPh_3)Re(η^1(*E*)-L)](BF_4) (1–8). Compounds **1**–**8** containing an η^1(*E*)-bound ligand were prepared by a method similar to that previously reported by Gladysz and co-workers[16] for the synthesis of other Cp(NO)(PPh_3)Re(L)$^+$ complexes. To a solution of 0.155 g (0.277 mmol) of Cp(NO)(PPh_3)Re(CH_3) in 7.0 mL of chlorobenzene cooled to −42 °C in a CH_3CN/N_2(l) bath was added 46.0 μL of $HBF_4{\cdot}Et_2O$ (85%, 0.278 mmol). After stirring for 30 min, 1.00 mL (~40 fold excess) of the ligand (L) was added and the deep red solution was allowed to slowly warm to room temperature. Within 2 h a precipitate began to form; after 4 h, 40 mL of hexanes was added to give a light orange precipitate which was filtered and washed with 2 × 10 mL of hexanes followed by 2 × 10 mL of ether. The resulting yellow/orange solid was dried under a stream of N_2 for 10 min then under vacuum. Yield 94–85%.

Characterization of 1–8. [Cp(NO)(PPh_3)Re(η^1(*S*)-T)](BF_4) (1). ^1H NMR δ (CD_2Cl_2): 7.22(m, H(2)H(5)), 6.91(m, H(3)H(4)), 5.42(s, Cp), 7.59–7.35(m, Ph), 7.28–7.23(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 138.34(s, C(2) C(5)), 132.42(s, C(3)C(4)), 133.60(d, Ph), 133.53(d, Ph) 132.32(d, Ph), 129.90(d, Ph), 92.38-(s, Cp). IR cm^{-1} ν(NO) (CH_2Cl_2): 1724(s).

[Cp(NO)(PPh_3)Re(η^1(*S*)-2-MeT)](BF_4) (2). ^1H NMR δ (CD_2Cl_2): 7.05 (m, H(3)), 6.92(dd, H(4)), 6.13(d, H(5)), 2.50(s, Me), 5.39 (s, Cp), 7.59–7.35(m, Ph), 7.28–7.20(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 154.52 (s, C(2)), 132.85 (s, C(4)), 132.10 (s, C(5)), 132.42(s, C(3)), 14.43(s, CH_3), 93.37 (s, Cp), 133.60(d, Ph), 133.51(d, Ph) 132.32(d, Ph), 129.90(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1723(s). Anal. Calcd for $C_{28}H_{25}BF_4NOPReS$: C, 46.16; H, 3.10. Found: C, 45.96; H, 3.53.

[Cp(NO)(PPh_3)Re(η^1(*S*)-2,5-Me_2T)](BF_4) (3). ^1H NMR δ (CD_2Cl_2): 6.76(s, H(3)H(4)), 2.02 (s, CH_3), 5.37(s, Cp), 7.59–7.35(m, Ph), 7.28–7.20(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 149.74-(s, C(2)C(5)), 129.46(C(3)C(4)), 14.81(s, CH_3), 133.60(d, Ph), 133.50(d, Ph) 132.32(d, Ph), 129.90(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1723(s).

[Cp(NO)(PPh_3)Re(η^1(*S*)-BT)](BF_4) (4). ^1H NMR δ (CD_2Cl_2): 7.86 (m, 4H, BT), 6.25(d, 1H, BT), 5.22(s, Cp), 7.59–7.35(m, Ph), 7.28–7.20(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 148.3-(s, BT), 138.7(s, BT), 131.8(s, BT), 130.9(s, BT), 129.5(s, BT), 128.3(s, BT), 126.8(s, BT), 124.3(s, BT), 93.6(s, Cp), 133.6(d, Ph), 133.5(d, Ph), 132.3(d, Ph), 129.9(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1718(s). Anal. Calcd for $C_{31}H_{26}BF_4NOPReS{\cdot}1/4CH_2Cl_2$: C, 47.76; H, 3.01. Found: C, 47.75; H, 3.01.

[Cp(NO)(PPh_3)Re(η^1(*S*)-3-MeBT)](BF_4) (5). ^1H NMR δ (CD_2Cl_2): 7.87(m, 2H, BT), 7.81(m, 2H, BT), 5.79(s, H(2)), 2.30-(s, CH_3), 5.29(s, Cp), 7.59–7.35(m, Ph), 7.28–7.20(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 148.25(s, BT), 141.07(s, BT), 139.49(s, C(3)-BT), 129.41(s, BT), 128.22(s, BT), 124.62(s, BT), 124.52(s, BT), 124.58(s, C(2)BT), 14.80(s, CH_3), 93.65(s, Cp), 133.60(d, Ph), 133.50(d, Ph), 132.32(d, Ph), 129.90(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1720(s).

[Cp(NO)(PPh_3)Re(η^1(*Se*)-Sel)](BF_4) (6). ^1H NMR δ (CD_2Cl_2): 7.45(H(2),H(5)), 7.21(H(3),H(4)), 7.52–7.35(m, Ph), 7.28–7.20(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 141.86(s, C(2)C(5)), 134.37(s, C(3)C(4)), 92.52(s, Cp), 133.60(d, Ph), 133.52(d, Ph), 132.32(d, Ph), 129.90(d, Ph). ^{77}Se NMR δ (CD_2Cl_2): 368.2 (s, br). IR cm^{-1} ν(NO) (CH_2Cl_2): 1719(s). Anal. Calcd for $C_{27}H_{24}$-$BF_4NOPReSe$:C, 42.59; H, 3.18. Found: C, 42.37; H, 3.19.

[Cp(NO)(PPh_3)Re(η^1(*Se*)-2-MeSel)](BF_4) (7). ^1H NMR δ (CD_2Cl_2): 7.25(H(3)), 6.99(m, H(4)), 6.80(dd, H(5), $J_{H\text{-}Se}$ = 16 Hz), 5.30(s, Cp), 7.59–7.35(m, Ph), 7.28–7.20(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 159.10(s, C(2)), 136.33(s, C(4)), 135.52(s, C(3)), 130.17(s, C(5)), 16.74(s, CH_3), 92.71(s, Cp), 133.60(d, Ph), 133.5(d, Ph), 132.32(d, Ph), 129.90(d, Ph). ^{77}Se NMR δ (CD_2-Cl_2): 386.5(d, $J_{Se\text{-}P}$ = 13 Hz). IR cm^{-1} ν(NO) (CH_2Cl_2): 1716(s). Anal. Calcd for $C_{28}H_{25}BF_4NOPReSe$: C, 43.37; H, 3.38. Found: C, 43.28; H, 3.39.

[Cp(NO)(PPh_3)Re(η^1(*Se*)-2,5-Me_2Sel)](BF_4) (8). ^1H NMR δ (CD_2Cl_2): 6.64(s, H(3)H(4)), 2.05(s, CH_3), 5.22(s, Cp), 7.59–7.35(m, Ph), 7.28–7.20(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 155.42-(s, C(2)C(5)), 131.32(s, C(3)C(4)), 17.34(s, Me), 92.72(s, Cp), 133.60(d, Ph), 133.52(d, Ph), 132.32(d, Ph), 129.90(d, Ph). ^{77}-Se NMR δ (CD_2Cl_2): 384.2(d, $J_{Se\text{-}P}$ = 19.8 Hz). IR cm^{-1} ν(NO) (CH_2Cl_2): 1717(s).

General Procedure for the Preparation of Cp(NO)(PPh_3)Re(2-L-yl) (9, 10, 12–15). To a stirred solution of 0.250 mmol of [Cp(NO)(PPh_3)Re(η^1(*E*)-L)]BF_4, where η^1(*E*)-L = T, 2-MeT, BT, 3-MeBT, Sel, 2-MeSel, in 5.0 mL of CH_2Cl_2, 0.0290 g (0.258 mmol) of 1,4-diazabicyclo[2.2.2]octane (Dabco) was added. The yellow/orange solution turned a deep red/orange within five minutes. The reaction mixture was placed on an alumina/hexanes (1 × 20 cm) column and eluted with 1:1 hexanes:CH_2Cl_2. An orange red band was collected and the solvent was evaporated from it under vacuum to give an orange red solid. Yield: 90–95%.

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Characterization of 9, 10, 12–15. Cp(NO)(PPh$_3$)Re(2-Tyl) (9). ^{1}H NMR δ (CD_2Cl_2): 7.08(d, H(5)), 6.70(dd, H(4)), 6.38(d, H(3)), 5.19(s, Cp), 7.40–7.30(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 135.76(d, C(3)), 128.34 (s, C(5)), 127.53 (d, C(2)), 127.32 (s, C(4)), 91.41(s, Cp), 135.76(d, Ph), 134.10(d, Ph), 130.41(d, Ph), 128.48(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1653(s).

Cp(NO)(PPh$_3$)Re(2-(5-MeTyl)) (10). ^{1}H NMR δ (CD_2Cl_2): 6.27(dd, H(3), J_{H-P} = 1.2 Hz), 5.94(d, H(4)), 2.38(s, CH_3), 5.10(s, Cp), 7.39–7.32(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 142.35 (s, C(5)), 135.51 (s, C(4)), 125.28 (s, C(3)), 123.97 (d, C(2)), 14.56(s, Me), 90.80(s, Cp), 133.18(d, Ph), 134.76(d, Ph), 129.87-(d, Ph), 127.92(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1654(s). Anal. Calcd for $C_{28}H_{25}NOPReS$: C, 52.49; H, 3.93. Found: C, 52.52; H, 3.97.

Cp(NO)(PPh$_3$)Re(2-BTyl) (12). ^{1}H NMR δ (CD_2Cl_2): 7.57-(d, BT), 7.23(d, BT), 7.05(td, BT), 6.84 (t, BT), 6.45(s, br, H(3)), 5.27(s, Cp), 7.43–7.32(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 146.7(s, BT), 146.4(s, BT), 136.6(d, C(2)), 131.71(s, C(3)), 122.53(s, BT), 119.76(s, BT), 119.67(s, BT),119.09(s, BT), 91.78(s, Cp), 134.00-(d, Ph), 130.68(d, Ph) 132.32(d, Ph), 128.50(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1658(s).

Cp(NO)(PPh$_3$)Re(2-(3-MeBTyl)) (13). ^{1}H NMR δ (CD_2Cl_2): 7.45–7.32 (m of m, BT and Ph), 7.14(t, BT), 6.87 (t, BT), 2.51(s, CH_3), 5.25(s, Cp). ^{13}C NMR δ (CD_2Cl_2): 16.90(s, Me), 147.31(s, C(3)), 135.44(d, C(2)), 146.5(s, BT), 145.8(s, BT), 122.38(s, BT), 119.82(s, BT), 119.51(s, BT), 119.01(s, BT), 91.25(s, Cp), 134.04(d, Ph), 130.45(d, Ph), 132.32(d, Ph), 128.47(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1656(s).

Cp(NO)(PPh$_3$)Re(2-Selyl) (14). ^{1}H NMR δ (CD_2Cl_2): 7.76-(d, J_{H-Se} = 20.1 Hz, H(5)), 6.86(dd, H(4)), 6.54(d, H(3)), 5.20(s, Cp), 7.41–7.34(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 138.33(d, J_{C-P} = 2.5 Hz, C(3)), 136.54 (d, J_{C-P} = 11.5 Hz, C(2)), 132.42 (s, C(5)), 130.21(s, C(4)), 91.82(s, Cp), 135.64(d, Ph), 134.17(d, Ph), 130.50(d, Ph), 128.00(d, Ph). ^{77}Se NMR δ (CD_2Cl_2): 705.1 (s). IR cm^{-1} ν(NO) (CH_2Cl_2): 1653(s). Anal. Calcd for $C_{27}H_{23}$-NOPReSe:C, 48.14; H, 3.44. Found: C, 48.10; H, 3.41.

Cp(NO)(PPh$_3$)Re(2-(5-MeSelyl)) (15). ^{1}H NMR δ (CD_2Cl_2): 6.23(d, H(4)), 6.42(m, H(3)), 2.55(s, CH_3), 5.19(s, Cp), 7.42–7.35(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 148.45(s, C(5)), 138.74(s, C(4)), 133.74 (d, J_{C-P} = 9.7 Hz, C(2)), 128.91(s, C(3)), 18.11(s, Me), 91.66(s, Cp), 135.83(d, Ph), 134.15(d, Ph), 130.46-(d, Ph), 128.46(d, Ph). ^{77}Se NMR δ (CD_2Cl_2): 719.2 (s). IR cm^{-1} ν(NO) (CH_2Cl_2): 1653(s). Anal. Calcd for $C_{28}H_{25}$-NOPReSe: C, 48.91; H, 3.66. Found: C, 49.13; H, 3.58.

Preparation of Cp(NO)(PPh$_3$)Re(3-(2,5-Me$_2$Tyl)) (11). This compound was prepared as previously described using 0.100 g (0.135 mmol) of [Cp(NO)(PPh$_3$)Re(η^1(*S*)-2,5-Me$_2$T)]BF_4 and 0.011 g (0.200 mmol) KOH in methanol. Yield 0.028 g, 29% as an orange solid. ^{1}H NMR δ (CD_2Cl_2): 5.54 (s, H(4)), 2.43 (s, CH_3), 2.10 (s, CH_3), 5.15(s, Cp), 7.41–7.33(m, Ph). ^{13}C NMR δ (CD_2Cl_2): 142.32(d, C(4)), 133.24(s, C(2)), 132.59(s, C(5)), 126.07 (d, J_{C-P} = 9.6 Hz, C(3)), 19.03 (s, C(2)-CH_3), 14.82-(s, C(5)-CH_3)), 90.62(s, Cp), 136.22(d, Ph), 134.15(d, Ph), 130.22(d, Ph), 128.37(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1653-(s).

Preparation of Carbene Complexes. [Cp(NO)(PPh$_3$)-Re(2-Tylcarbene)]X (16a, X = BF_4; 16b, X = O_3SCF_3). To a stirred and cooled (−42 °C) solution of 0.100 g (0.131 mmol) of Cp(NO)(PPh$_3$)Re(2-Tyl) in 10.0 mL of Et_2O:CH_2Cl_2 (2:1), one equivalent (0.131 mmol) of acid (**16a,** 21.7 μL of HBF_4·Et_2O 85%; **16b**, 11.6 μL of HO_3SCF_3) was added. The orange-red solution immediately turned bright yellow and within 0.5 h a yellow precipitate began to form. After stirring for 1 h, 60 mL of ether:hexanes (1:1) was added and the resulting precipitate was filtered and washed with 2 × 10 mL of ether: hexanes (1:1). The bright yellow precipitate was dried under a stream of N_2 while being allowed to warm to room temperature. Then it was dried under vacuum to give **16a** (0.084 g, 90%) or **16b** (0.088 g, 86%). ^{1}H NMR δ (CD_2Cl_2): 7.32 (d, H(5)), 6.77(m, H(4)), 4.11(d, br, H(3)), 3.98 (d, br, H(3′)), 5.77(s, Cp), 7.50(s, br, Ph), 7.28–7.22 (m, Ph). ^{13}C NMR δ (CD_2Cl_2): 267.96 (d, J_{C-P} = 7.4 Hz, C(2)), 149.24(s, C(5)), 145.83 (s, C(4)), 55.93 (s, C(3)), 97.10(s, Cp), 134.41(d, Ph), 132.26(d, Ph), 131.64(d, Ph), 128.03(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1716(s). FAB (3-nitrobenzyl alcohol matrix): *m*/*z* 628 (M^+).

[Cp(NO)(PPh$_3$)Re(2-BTylcarbene)]X (17a, X = BF_4; 17b, X = O_3SCF_3). Compounds **17a** and **17b** were prepared in the same manner as **16a** and **16b** using 0.100 g (0.148 mmol) of Cp(NO)(PPh$_3$)Re(2-BTyl) and 24.5 μL of HBF_4·Et_2O (**17a**) or 13.1 μL HO_3SCF_3 (**17b**). These reactions yielded **17a** as an orange/yellow powder (0.105 g, 93%) or **17b** as a yellow powder (0.102 g, 83%). ^{1}H NMR δ (CD_2Cl_2): 7.42(BT), 7.35(BT), 7.17 (dd, BT), 7.43(d, BT), 4.78(d, H(3)), 3.53 (d, H(3′)), 5.86(s, Cp), 7.55(s, br, Ph), 7.42–7.22 (m, Ph). ^{13}C NMR δ (CD_2Cl_2): 277.71 (d, J_{C-P} = 7.9 Hz, C(2)), 66.21 (s, C(3)), 144.00 (s, BT), 142.42 (s, BT), 127.69 (s, BT), 126.28 (s, BT), 123.41(s, BT), 119.80 (s, BT), 98.01(s, Cp), 134.41(d, Ph), 132.41(d, Ph), 132.06(d, Ph), 129.25(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1720(s). FAB (3-nitrobenzyl alcohol matrix): *m*/*z* 677 (M^+). Anal. Calcd for $C_{31}H_{26}BF_4NOPReS$·1/2CH_2Cl_2: C, 46.88; H, 3.37. Found: C, 46.62; H, 3.59.

[Cp(NO)(PPh$_3$)Re(2-Selylcarbene)]X (18a, X = BF_4; 18b, X = O_3SCF_3). Compounds **18a** and **18b** were prepared in the same manner as **16a** and **16b** using 0.100 g (0.148 mmol) of Cp(NO)(PPh$_3$)Re(2-Selyl) (**14**) and 24.5 μL of HBF_4·Et_2O (**18a**) or 13.1 μL of HO_3SCF_3 (**18b**). From these reactions were isolated **18a** (0.992 g, 88%) or **18b** (0.106 g, 94%) as yellow powders. ^{1}H NMR δ (CD_2Cl_2): 7.68(d, J_{H-Se} = 17.4 Hz, H(5)), 6.78 (dd, H(4)), 4.25(d, H(3)), 4.15 (d, H(3′)), 5.81(s, Cp), 7.51(s, br, Ph), 7.29–7.18 (m, Ph). ^{13}C NMR δ (CD_2Cl_2): 274.83 (d, J_{C-P} = 6.8 Hz, C(2)), 49.59 (s, C(3)), 152.81-(s, C(5)), 146.73 (s, C(4)), 98.00(s, Cp), 132.34(d, Ph), 131.75-(d, Ph), 130.52 (d, Ph), 128.64(d, Ph). ^{77}Se NMR δ (CD_2Cl_2): 741.7 (s). IR cm^{-1} ν(NO) (CH_2Cl_2): 1716(s). FAB (3−nitrobenzyl alcohol matrix): *m*/*z* 674 (M^+).

[Cp(NO)(PPh$_3$)Re(2-(5-MeTylcarbene)]O_3SCF_3 (19). A 5-mm NMR tube was charged with 0.020 g (0.031 mmol) of Cp(NO)(PPh$_3$)Re(2-(5-MeTyl) (**10**) and 0.60 mL of CD_2Cl_2. After the tube was cooled to −42 °C, 2.8 μL (0.031 mmol) of HO_3SCF_3 was added and the red/orange solution became bright yellow. A ^{1}H NMR spectrum at −75 °C showed a quantitative conversion to **19**. ^{1}H NMR δ (CD_2Cl_2): 5.98(s, H(4)), 4.32(d, br, H(3)), 2.99 (d, br, H(3′)), 2.08 (s, Me), 5.75(s, Cp), 7.50(s, br, Ph), 7.31–7.22 (m, Ph). ^{13}C NMR δ (CD_2Cl_2): 280.34 (d, J_{C-P} = 7.1 Hz, C(2)), 146.88 (s, C(5)), 141.33 (s, C(4)), 68.72 (s, C(3)), 14.11(s, CH_3), 97.51(s, Cp), 134.41(d, Ph), 132.27(d, Ph), 131.64(d, Ph), 128.03(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1720-(s). Compound **19** is not stable and isomerizes to **2** above 0 °C as discussed in detail in the Results and Discussion section.

[Cp(NO)(PPh$_3$)Re(2-(5-MeSelylcarbene)]O_3SCF_3 (20). A 5-mm NMR tube was charged with 0.020 g (0.029 mmol) of Cp(NO)(PPh$_3$)Re(2-(5-MeSelyl) (**15**) and 0.60 mL of CD_2Cl_2. After the NMR tube was cooled to −42 °C, 2.6 μL (0.029 mmol) of HO_3SCF_3 was added and the red/orange solution became bright yellow. A ^{1}H NMR spectrum at −75 °C showed conversion to **20**. ^{1}H NMR δ (CD_2Cl_2): 5.98(s, H(4)), 4.32(d, br, H(3)), 2.99 (d, br, H(3′)), 2.08 (s, Me), 5.75(s, Cp), 7.50(s, br, Ph), 7.31–7.22 (m, Ph). ^{13}C NMR δ (CD_2Cl_2): 280.34 (d, J_{C-P} = 7.1Hz, C(2)), 146.88 (s, C(5)), 141.33 (s, C(4)), 68.72 (s, C(3)), 14.11(s, CH_3), 97.51(s, Cp), 134.41(d, Ph), 132.27(d, Ph), 131.64(d, Ph), 128.03(d, Ph). IR cm^{-1} ν(NO) (CH_2Cl_2): 1720-(s). Compound **20** is not stable and rapidly isomerizes to **7** above −30 °C as discussed in the Results and Discussion section.

Determination of the Molecular Structure of [Cp(NO)-(PPh$_3$)Re(2−BTylcarbene)]O_3SCF_3 (17b). A single crystal of **17b** suitable for X-ray diffraction was obtained by layering a concentrated CH_2Cl_2 solution of **17b** with Et_2O and cooling at −78 °C for several days. A crystal of **17b** with the composition [Cp(NO)(PPh$_3$)Re(2-BTylcarbene)]O_3SCF_3·3CH_2Cl_2 was attached to the tip of a glass fiber and mounted on the Siemens P4RA diffractometer for data collection at 213 K. The cell constants for the data collection were determined from reflections found from a 360° rotation photograph. High angle

Table 1. Crystal and Data Collection Parameters for [Cp(NO)(PPh$_3$)Re(2-BTylcarbene)]O$_3$SCF$_3$ (17b)

formula	$C_{35}H_{32}Cl_6F_3NOPReS$
fw	1081.6
space group	$P\bar{1}$
a	10.4897(8) Å
b	12.554(2) Å
c	17.046(2) Å
α	79.73(1)°
β	73.95(1)°
γ	75.49(1)°
V, Å^3	2054.8(4)
Z	2
d_{calc}, mg/m^3	1.748
crystal size (mm)	0.32 × 0.18 × 0.08
μ(CuK$_\alpha$), cm^{-1}	111.45
diffractometer used	Siemens P4RA
radiation	CuKα (λ = 1.54178 Å)
orientation reflections: no., range	25, 2.00° plus Kα separation
temp (K)	213
scan method	$2\theta-\theta$
data collection range, 2θ, deg	4.0 to 115.0°
no. of data collected	5863
no. of unique data	5500 (R_{int} = 0.0274)
no. of data with ($F_o > 4.0\sigma(F_o^2)$)	4639
no. of parameters refined	511
transmission factors: min,max	0.3165/1.0000
R[a]	0.0437
R_w[b]	0.0470
goodness-of-fit[c]	1.58
largest peak e/Å	1.76
largest shift/eds. final cycle	0.009, 0.000

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \sum w[(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Goodness-of-fit = $[\sum w(|F_o| - |F_c|)^2/(N_{obs}-N_{params})]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Bond Angles in [Cp(NO)(PPh$_3$)Re(2-BTylcarbene)]O$_3$SCF$_3$ (17b)[a]

Re−N	1.762(8)	C(12)−C(13)	1.522(11)
Re−C(11)	1.992(7)	C(13)−C(14)	1.373(11)
Re−P	2.392(2)	C(13)−C(18)	1.365(13)
N−O	1.191(11)	C(14)−C(15)	1.374(13)
S−C(11)	1.712(9)	C(15)−C(16)	1.378(16)
S−C(18)	1.778(7)	C(16)−C(17)	1.368(12)
C(11)−C(12)	1.527(11)	C(17)−C(18)	1.393(12)
Re−C(11)−S	125.2(5)	C(14)−C(13)−C(18)	118.9(8)
Re−C(11)−C(12)	124.2(6)	C(13)−C(14)−C(15)	119.5(10)
S−C(11)−C(12)	110.3(5)	C(14)−C(15)−C(16)	120.7(9)
C(11)−S−C(18)	94.6(4)	C(15)−C(16)−C(17)	121.1(9)
S−C(18)−C(13)	112.4(6)	C(16)−C(17)−C(18)	116.8(9)
S−C(18)−C(17)	124.7(7)	C(13)−C(18)−C(17)	122.9(7)
C(11)−C(12)−C(13)	108.6(7)	N−Re−C(11)	94.3(3)
C(12)−C(13)−C(14)	127.6(9)	N−Re−P	90.2(2)
C(12)−C(13)−C(18)	113.5(7)	C(11)−Re−P	93.2(2)
		Re−N−O	174.7(6)

[a] Estimated standard deviations are given in parentheses.

cell constants were determined from a subset of intense reflections in the range of 35.0 to 50.0° 2θ. Pertinent data collection and reduction information is given in Table 1.

Lorentz and polarization corrections were applied. A non-linear correction based on the decay in the standard reflections was applied to the data. A series of azimuthal reflections was collected for this specimen. A semi-empirical absorption correction based on the azimuthal scans was applied to the data.[17]

The space group $P\bar{1}$ was chosen based on the lack of systematic absences and intensity statistics.[17] This assumption proved to be correct as indicated by a successful direct-methods solution and subsequent refinement.[17] All non-hydrogen atoms were placed directly from the E-map. All hydrogen atoms were refined as riding-atoms with C-H distance equal to 0.96 Å and with individual isotropic displacement parameters.

(17) SHELXTL-PLUS, Siemens Analytical X-ray, Inc., Madison, WI.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for [Cp(NO)(PPh$_3$)Re(2-BTylcarbene)]O$_3$SCF$_3$

atom	x	y	z	U_{eq}[a]
Re	−1637(1)	312(1)	3399(1)	22(1)
C(1)	−2312(9)	−1349(7)	3861(5)	33(3)
C(2)	−863(8)	−1585(7)	3607(5)	34(3)
C(3)	−365(9)	−1123(7)	4121(5)	39(4)
C(4)	−1485(9)	−564(8)	4686(5)	38(4)
C(5)	−2684(9)	−725(8)	4533(5)	39(4)
N	−913(7)	1458(6)	3335(4)	30(3)
O	−334(6)	2172(6)	3308(4)	54(3)
S	−4819(2)	732(2)	3304(1)	33(1)
C(11)	−3457(8)	1234(7)	3326(5)	26(3)
C(12)	−3873(7)	2481(6)	3378(5)	26(3)
C(13)	−5411(8)	2830(7)	3526(5)	28(3)
C(14)	−6215(9)	3844(7)	3706(6)	43(4)
C(15)	−7596(9)	4011(8)	3821(7)	53(5)
C(16)	−8181(9)	3169(7)	3763(6)	41(4)
C(17)	−7406(8)	2151(8)	3582(5)	37(4)
C(18)	−6010(8)	2003(7)	3480(5)	26(3)
P	−851(2)	299(2)	1943(1)	23(1)
C(21)	−1714(8)	1480(7)	1351(5)	27(3)
C(22)	−2491(8)	1350(7)	849(5)	32(3)
C(23)	−3168(9)	2265(8)	443(6)	43(4)
C(24)	−3087(9)	3309(8)	526(6)	48(4)
C(25)	−2306(9)	3452(8)	1026(5)	38(4)
C(26)	−1608(8)	2529(7)	1432(5)	33(3)
C(31)	931(7)	333(7)	1570(5)	25(3)
C(32)	1448(8)	839(8)	795(5)	39(4)
C(33)	2822(9)	869(9)	521(6)	49(4)
C(34)	3688(9)	379(9)	1028(6)	52(5)
C(35)	3198(9)	−134(9)	1797(6)	49(4)
C(36)	1831(8)	−148(8)	2066(5)	37(4)
C(41)	−1063(8)	−930(7)	1611(4)	28(3)
C(42)	22(8)	−1639(7)	1163(5)	30(3)
C(43)	−172(9)	−2592(7)	966(5)	36(4)
C(44)	−1418(9)	−2842(8)	1188(5)	39(4)
C(45)	−2524(9)	−2147(8)	1641(5)	39(4)
C(46)	−2346(8)	−1196(7)	1840(5)	32(3)
S(50)	−3954(2)	1843(2)	−3996(1)	32(1)
O(51)	−2831(6)	995(5)	−3820(3)	39(2)
O(52)	−4953(6)	2219(6)	−3278(4)	52(3)
O(53)	−4484(6)	1663(5)	−4641(4)	48(3)
C(50)	−3190(10)	3023(8)	−4438(6)	44(4)
F(51)	−2651(6)	3330(5)	−3912(4)	67(3)
F(52)	−2203(5)	2815(5)	−5111(3)	56(2)
F(53)	−4092(7)	3905(5)	−4657(4)	76(3)
C(60)	7507(12)	5708(13)	3543(9)	79(7)
Cl(61)	9161(4)	5617(3)	3489(4)	154(3)
Cl(62)	7271(4)	4985(3)	2842(3)	101(2)
C(70)	1735(13)	3725(17)	1640(8)	98(8)
Cl(71)	3504(3)	3535(3)	1369(2)	93(2)
Cl(72)	1048(3)	4229(3)	781(2)	82(2)
C(80)	4267(11)	6119(12)	2000(7)	70(6)
Cl(81)	2544(3)	6569(3)	1959(2)	84(2)
Cl(82)	5353(3)	6320(2)	1020(2)	61(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Selected bond distances and angles are presented in Table 2 and a thermal ellipsoid drawing of **17** is given in Figure 1. The final positional and thermal parameters are listed in Table 3.

Deprotonation Studies of 1, 4, and 6. In a small test tube was placed ~0.010 g of the compound, and the tube was capped with a septum and degassed with N_2. The solid was dissolved by adding 0.5 mL of CH_2Cl_2; then a 10-fold excess of amine base was added. An infrared spectrum of each solution was taken after 2 min and then again after 1 h. Under the same conditions in the absence of base, complexes **1**, **4**, and **6** were stable for at least 1 h. In cases where reactions occurred, they were complete within 2 min; the only products of these reactions were **9**, **12**, and **14**. Displacement of the $\eta^1(E)$-bound ligand by the amine did not occur to an appreciable extent. The results of these studies along with the pK_a values for the amine bases are presented in Table 4.

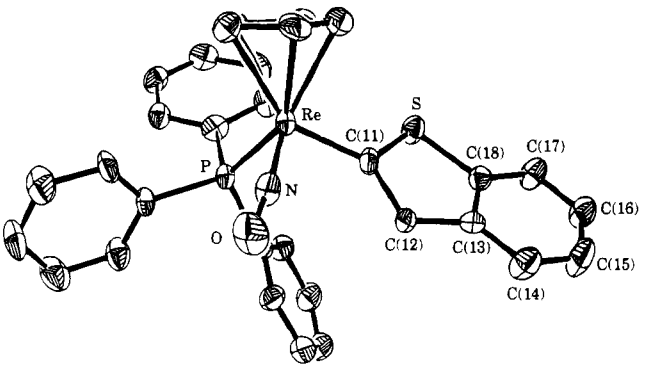

Figure 1. ORTEP Drawing of the cation $[Cp(NO)(PPh_3)Re(2\text{-}BTylcarbene)]^+$ in **17b**.

Table 4. Deprotonation of 1, 4, and 6 with Bases of Varying pK_a (Eq 3)

base	pK_a (aq)[a]	1 (T)	4 (BT)	6 (Sel)
pyridine (py)	5.25	no rxn	no rxn	no rxn
4-Mepy	6.02	no rxn	no rxn	rxn
2,6-Me_2py	6.99	no rxn	no rxn	rxn
morpholine	8.33	rxn	no rxn	rxn
Dabco	8.7	rxn	no rxn	rxn
(n-Pr)$_3$N	10.71	rxn	rxn	rxn
Proton Sponge	12.37	rxn	rxn	rxn
DBU	24.32[b]	rxn	rxn	rxn

[a] CRC Handbook of Chemistry and Physics; 66th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1985, pp D159–161. [b] Measured in CH_3CN, Schwesinger, R.; Schlemper, H. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1167.

Table 5. Deprotonation of Carbene Complexes 16–18 with Bases of Varying pK_a (eq 5)

base	pK_a (aq)	16	17	18
(p-ClC_6H_4)$_3$P	1.03[a]	no rxn	no rxn	no rxn
(p-FC_6H_4)$_3$P	1.97[a]	no rxn	no rxn	no rxn
Ph_3P	2.73[a]	no rxn	rxn	no rxn
(o-MeC_6H_4)$_3$P	3.08[a]	no rxn	rxn	no rxn
(m-MeC_5H_4)$_3$P	3.30[a]	no rxn	rxn	no rxn
(p-MeC_6H_4)$_3$P	3.84[a]	rxn	rxn	rxn
(p-$MeOC_6H_4$)$_3$P	4.57[a]	rxn	rxn	rxn
aniline	4.63[b]	rxn	rxn	rxn
pyridine	5.21[b]	rxn	rxn	rxn

[a] Bush, R. C., Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681. [b] CRC Handbook of Chemistry and Physics; 66th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1985, pp D159–161.

Deprotonation Studies of 16–18. The complex (~ 0.010 g) was put into a small test tube and capped with a septum. After degassing the tube with N_2, 0.5 mL of CH_2Cl_2 was added to dissolve the complex; then a 10-fold excess of the phosphine was added. An infrared spectrum of each solution was taken after 2 min and again after 1 h. In the cases where reaction occurred, the starting complexes **16**, **17**, and **18** disappeared completely and IR bands for the deprotonated products **9**, **12**, and **14** appeared. In all cases, the reactions were complete within 2 min and no other product formed. Results of these studies along with pK_a values of the phosphine bases are given in Table 5.

Results and Discussion

Synthesis and Characterization of $[Cp(NO)(PPh_3)Re(\eta^1(E)\text{-}L)]^+$ Complexes (1–8). The compounds $[Cp(NO)(PPh_3)Re(\eta^1(s)\text{-}Th)]BF_4$, where Th = thiophene (T), 2,5-dimethylthiophene (2,5-Me_2T), benzothiophene (BT), and 2-methylbenzothiophene (2-MeBT), were recently[6] synthesized utilizing a method similar to that used for the preparations of $[Cp(NO)(PPh_3)Re(L')]^+$ complexes, where L' can be one of several two-electron donor ligands including dialkyl sulfides.[18] The yields (78–39%) were highly dependent on the purity of the reactants and solvents and the temperature sensitive nature of the intermediate $[Cp(NO)(PPh3)Re(Cl\text{-}CH_2Cl)]^+$. Changing the solvent from CH_2Cl_2 to chlorobenzene[16] allows milder conditions, a smoother reaction and higher yields of product. The application of this route (eq 2) to a variety of thiophenes,

$$Cp(NO)(PPh_3)Re(ClPh)^+ + L \longrightarrow [Cp(NO)(PPh_3)Re(\eta^1(E)\text{-}L)]^+ \quad (2)$$

E = S	E = Se
1, L = T	6, L = Sel
2, L = 2-MeT	7, L = 2-MeSel
3, L = 2,5-Me_2T	8, L = 2,5-Me_2Sel
4, L = BT	
5, L = 3-MeBT	

benzothiophenes, and selenophenes gives the $\eta^1(E)$-complexes as tan-yellow powders in yields of 94–85%. The compounds **1**–**8** were characterized by elemental analysis and IR, ^1H and ^{13}C NMR spectrometry; ^{77}Se NMR data were obtained for compounds **6**–**8**. The slightly lower ν(NO) value for the selenophene complex **6** (1719 cm^{-1}) as compared with that for the thiophene complex **1** (1724 cm^{-1}) indicates that selenophene is a better σ-donor ligand than thiophene; the same trend is observed in the ν(CO) values of the sulfur-selenium pairs in the isoelectronic complexes $[Cp(CO)(PPh_3)Ru(\eta^1(E)\text{-}L)]^+$.[7] The ^1H NMR resonances of Sel in **6** are not distinguishable in the spectrum because they overlap with those of the PPh_3. The 2-D $^1H/^{13}C$ HETCOR spectrum, however, clearly shows peaks for H(2)H(5) (δ 7.45) and H(3)H(4) (δ 7.21) which are upfield of the corresponding resonances for the free selenophene ligand (H(2)H(5) (δ 7.88), H(3)H(4) (δ 7.23)). $\eta^1(S)$ coordination of thiophene in **1** and $\eta^1(Se)$ coordination of selenophene in $[Cp(CO)(PPh_3)Ru(\eta^1(E)\text{-}L)]^+$ result in a similar upfield shift.[7,19] The ^{13}C NMR spectra of **1** (C(2)C(5) (δ 138.34), C(3)C(4) (δ 132.42)) and **6** (C(2)C(5) (δ 141.86), C(3)C(4) (δ 134.37)) exhibit resonances downfield from those of the free ligand.[7] A similar downfield shift upon $\eta^1(E)$-coordination has been reported in the complexes: $[Cp(CO)(PPh_3)Ru(\eta^1(E)\text{-}L)]^+$,[7,19] $Cp(CO)_2Re(\eta^1(E)\text{-}L)$,[20] $[Cp(CO)_2Fe(\eta^1(S)\text{-}T)]^+$,[21] and $[Cp(CO)_2Ru(\eta^1(S)\text{-}T)]^+$.[22]

Despite the asymmetry at Re, the H(2) and H(5) protons in **1** (T) and **6** (Sel) and the methyl groups in **3** (2,5-Me_2T) and **8** (2,5-Me_2Sel) occur as single resonances in their room temperature ^1H NMR spectra. At low temperature (183 K), the ^1H NMR spectra of **3** and **8** in CD_2Cl_2 each show two resonances at δ 2.45, δ 1.59 and δ 2.35, δ 1.91, respectively, for the diastereotopic methyl groups. The free energy of activation for the coalescence of these peaks was calculated to be 37(1) kJ/mol (T_c = 195 K) for **3** and 42(1) kJ/mol (T_c = 215K) for **8** at their coalescence temperatures (T_c).[23] Coalescence of the methyl group signals has been observed in the related complexes $[CpRu(CO)(PPh_3)(\eta^1(E)\text{-}L)]^+$; the 2,5-$Me_2$T complex has a free energy of activation of 40 kJ/mol (T_c

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(19) Benson, J. W.; Angelici, R. J. *Organometallics* **1992**, *11*, 922.
(20) (a) Choi, M. G.; Angelici, R. J. *Organometallics* **1991**, *10*, 2436. (b) Choi, M. G.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 5651.
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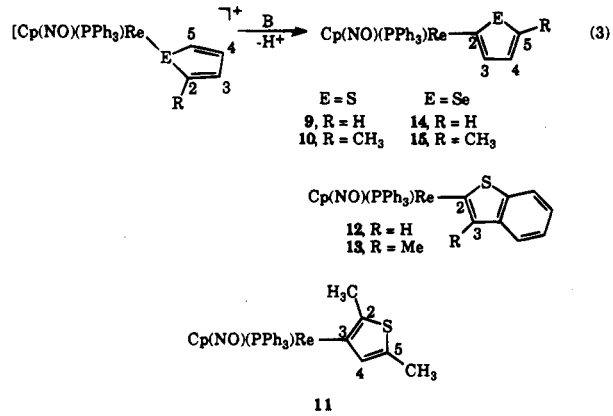
(23) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: NewYork, 1982, pp 96.

= 213 K), while the value is 44 kJ/mol (T_c = 225 K) for the 2,5-Me_2Sel complex. Coalescence in all of these complexes presumably occurs as a result of inversion at the S or Se atom. Such an inversion would be more favorable for S than Se because of greater π-bonding between the sulfur and the diene segment of the thiophene in the planar intermediate. In other organosulfur and selenium complexes [24] such as $Re(Cl)(CO)_3(EMe_2)_2$ and $Pt(Br)(Me)(EMe_2)_2$, the inversion barrier is also lower in the S than the Se analog. The low temperature ^1H NMR spectra of **1** and **6** in CD_2Cl_2 show only a slight broadening of the proton resonances at the freezing point (178 K) of CD_2Cl_2; this indicates that the T_c values for **1** and **6** are lower than 178 K. The lower T_c for **1** and **6** compared to **3** and **8** suggests that steric interactions between the methyl groups in the 2,5-positions of the thiophene or selenophene and the bulky triphenylphosphine ligand reduce the rate of inversion at the heteroatom in **3** and **8**.

Synthesis and Characterization of Cp(NO)(PPh$_3$)Re(L-yl) Complexes (9–15). Abstraction of a proton from the $\eta^1(S)$ complexes $[Cp(NO)(PPh_3)Re(\eta^1(S)$-Th-$)]BF_4$, where Th = T(**1**), 2,5-Me_2T (**3**), or BT (**4**), with KOH in methanol[6] gives the neutral thienyl complexes Cp(NO)(PPh$_3$)Re(2-Tyl) (**9**), Cp(NO)(PPh$_3$)Re(3–(2,5-Me_2Tyl)) (**11**), and Cp(NO)(PPh$_3$)Re(2-BTyl) (**12**) in moderate 28–60% yields. There is a side product in these reactions which is proposed to be Cp(NO)(PPh$_3$)Re(OH), based on its IR (ν(NO)(CH_2Cl_2): 1679 cm^{-1}) and ^1H NMR ((CD_2Cl_2): δ 7.52–7.30 (m, 15H, Ph), 5.22 (s, 5H, Cp), 4.9 (br)) spectra; this product results from the displacement of the thiophene ligand by OH^-. The use of a strong, non-nucleophilic, sterically hindered organic base avoids this competing reaction. The reaction of Proton Sponge (1,8-bis(dimethylamino)napthalene), DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), and Dabco (1,4-diazabicyclo[2.2.2]octane) with the cationic complexes **1**, **2**, **4**–**7** in CH_2Cl_2 rapidly gives (eq 3) the corresponding deprotonated Cp(NO)(PPh$_3$)Re(2-L-yl) complexes in greater than 90% yield.The cationic amine complex $[Cp(NO)(PPh_3)Re(amine)]^+$, resulting from displacement of the thiophene or selenophene ligand, is not observed in IR spectra of the reaction mixtures. Only $[Cp(NO)(PPh_3)Re(\eta^1(S)$-2,5-$Me_2T)]^+$ (**3**) cannot be converted to its L-yl complex Cp(NO)(PPh$_3$)Re(3-(2,5-Me_2-Tyl)) (**11**) with Dabco; however, KOH/methanol does effect this conversion.[6] Possible mechanisms for the reaction in eq 3 were discussed in the previous paper.[6]

The neutral L-yl complexes **9**–15 are remarkably stable (>10 days) to exposure to air in both the solid state and in solution. The ν(NO) values for the compounds **9**–**15** are ~70 cm^{-1} lower than those of their starting cationic complexes. The ^{77}Se NMR resonances for selenyl complexes **14** (2-Selyl: δ 705.1) and **15** (2–(5-MeSelyl): δ 719.2) are more than 300 ppm downfield of those of the cationic starting complexes **6**(Sel: δ 368.2) and **7**(2-MeSel: δ 386.5) and have chemical shift values similar to that of 2-cyanoselenophene (δ 709.3).[25]

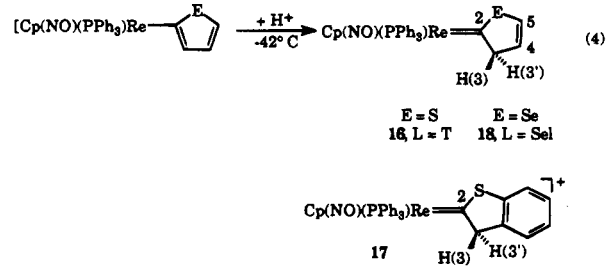
Deprotonation of 1, 4, and 6 with Bases of Varying pK_a. In order to determine the base strength required to cause the conversion (eq 3) of **1**, **4**, and **6** to



(3)

9, **12**, and **14**, respectively, a series of bases with a range of pK_a values was used in this reaction. The reactions were monitored by changes in the ν(NO) region of the IR spectrum of the solutions. The results are presented in Table 4. The pK_a of the bases required for deprotonation of the $\eta^1(S)$-thiophene complex (**1**) lies between that of 2,6-dimethylpyridine (2,6-Me_2py) (pK_a 6.99) and morpholine (pK_a 8.33). The $\eta^1(S)$-benzothiophene complex (**4**) requires a stronger base with a pK_a between Dabco (pK_a 8.7) and (n-Pr_3)N (pK_a 10.71). On the other hand, the $\eta^1(Se)$-selenophene complex (**6**) requires a base with a pK_a between pyridine (py) (pK_a 5.25) and 4-Mepy (pK_a 6.02). Thus the required base ranges are as follows: **4** (Sel) (pK_a 5.25–6.02) < **1** (T) (pK_a 6.99–8.33) < **4** (BT) (pK_a 8.7–10.71).

Synthesis and Characterization of L-yl Carbene Complexes 16–18. The reactions of Cp(NO)(PPh$_3$)Re(2-Tyl) (**9**) and Cp(NO)(PPh$_3$)Re(2-BTyl) (**12**) with HO_3SCF_3 to form the cationic carbene complexes, $[Cp(NO)(PPh_3)Re(2\text{-Tylcarbene})]^+$ and $[Cp(NO)(PPh_3)Re(2\text{-BTylcarbene})]^+$, respectively, were recently reported.[6] The L-yl complexes Cp(NO)(PPh$_3$)Re(2-Tyl) (**9**), Cp(NO)(PPh$_3$)Re(2–BTyl) (**12**), and Cp(NO)(PPh$_3$)Re(2-Selyl) (**14**) all react with one equivalent of $HBF_4{\cdot}Et_2O$ or HO_3SCF_3 to give the corresponding cationic carbene complexes $[Cp(NO)(PPh_3)Re(2\text{-Tylcarbene})]^+$ (**16**), $[Cp(NO)(PPh_3)Re(2\text{-BTylcarbene})]^+$ (**17**), and $[Cp(NO)(PPh_3)Re(2\text{-Selylcarbene})]^+$ (**18**) (eq 4). Isolation of the solid carbene



(4)

complexes was possible by conducting the reaction at low temperature (−42 °C) and in a solvent mixture of 2:1 Et_2O:CH_2Cl_2. The isolated bright yellow to bright orange solids are stable in air for greater than 3 weeks. In IR spectra of the three complexes the ν(NO) band is shifted to higher wavenumber **16** (1716 cm^{-1}), **17** (1720 cm^{-1}) and **18** (1716 cm^{-1}) from those of the starting L-yl complexes **9** (1653 cm^{-1}), **12** (1658 cm^{-1}) and **14** (1653 cm^{-1}). Assignments of the ^1H and ^{13}C NMR resonances were made using a combination of 2-D $^1H/^1H$ COSY, $^1H/^1H$ NOESY and $^1H/^{13}C$ HETCOR NMR techniques. Of the diastereotopic protons H(3) and H(3′), H(3′) is

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upfield of H(3) due to the shielding ring current of the nearby phenyl of the PPh_3 ligand. In the spectrum of **18**, coupling between ^{77}Se and the diastereotopic protons is not observed indicating that protonation is not occurring at C(5). In the room temperature spectrum of **16**, the signals for H(3) and H(3′) are slightly broadened and become sharper when the sample is cooled to −50 °C. The broadening of these peaks at room temperature could be due to rotation about the metal-carbene bond. Rotation about the metal carbene bond in the carbene $[Cp(NO)(PPh_3)Re(=C(H)(Ph))]^+$ occurs with $t_{1/2}$ = 60 min at 19.0 °C; the more stable rotational isomer is favored by a ratio of >99:1.[26] The ^1H NMR spectra of **17** and **18** also exhibit broadening of the H(3) and H(3′) resonances at room temperature, although evidence for the presence of a second isomer is not seen. For all three compounds, no metal hydride resonances are observed at high field (up to −30 ppm) even at −60 °C. The ^{13}C NMR spectra exhibit a carbene resonance (**16**, δ 267.96, d, $J_{C\text{-}P}$ = 7.4 Hz; **17,** δ 277.71, d, $J_{C\text{-}P}$ = 7.9 Hz; **18**, δ 274.83,d, $J_{C\text{-}P}$ = 6.8 Hz) that is coupled to the phosphorus; these chemical shifts are similar to those of related carbenes: $[Cp(NO)(PPh_3)Re(=C(H)(SCH_3)]^+$ (δ 274.4),[27] $[Cp(NO)(PPh_3)Re(=C(H)(Ph)]^+$ (δ 288.6).[26] The C(3) resonances of the starting material L-yl complexes (**9**, δ 135.76; **12**, δ 131.71; **14**, δ 138.33) all move upfield approximately 70 ppm upon protonation and formation of the carbene (**16**, δ 55.93; **17**, δ 66.21; **18**, δ 49.59) since this carbon becomes saturated in the reaction. At the same time, the C(4) and C(5) olefin carbons of **16** (δ 145.83 C(4), 149.24 C(5)) and **18** (δ 146.73 C(4), 152.81 C(5)) shift slightly downfield of those (**9**, δ 127.32 C(4), 128.34 C(5); **14**, δ 130.21 C(4), 132.42 C(5)) in the L-yl starting complexes.

Molecular Structure of $[Cp(NO)(PPh_3)Re(2\text{-}BTylcarbene)](O_3SCF_3)$ (17b). In the structure (Figure 1) of the cation in **17b**, the rhenium carbene carbon bond distance, Re-C(11) (1.992(7) Å), is slightly longer than previously determined Re=C bond distances in similar compounds: $[(Cp(NO)(PPh_3)Re=C(H)(Ph)]^+$ (1.949(6) Å),[26] $Cp^*(NO)(P(OPh)_3)Re(=CH_2)$ (1.898(18) Å).[28] The longer Re=C(11) bond is likely due to S-to-C(11) π-bonding which reduces the Re-to-C(11) π-bonding, as has been observed in other thiocarbene complexes.[29] In the closely related C-pyrrolyl complex, $[Cp(NO)(PPh_3)Re(\overline{C=NHCH_2CH=CH})]^+$ (2.046(3)Å),[30] the Re-C bond distance is somewhat longer than in **17b**. When compared to the rhenium-carbon single bond distance (2.178(6)Å) in $\{[(Cp)(NO)(PPh_3)Re\text{-}CH_2\text{-}]_2S^+\text{-}CH_3\}I$,[31] the distance in **17b** is significantly shorter. The torsion angles between P-Re-C(11)-S (86.8° (5)) and P-Re-C(11)-C(12) (−100.2° (6)) indicate that the π-accepting orbitals of C(11) are close to being parallel to the d orbital HOMO of the $Cp(NO)(PPh_3)Re^+$ fragment (Figure 2), which provides further evidence for some

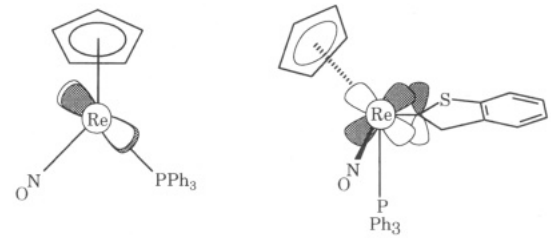
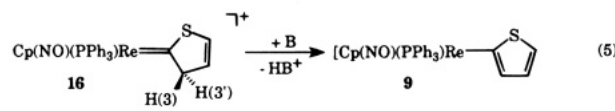


Figure 2. The HOMO (left) for the fragment $[Cp(NO)(PPh_3)Re]^+$ and its bonding with the carbene carbon in **17** (right).

Re=C(11) double bond character. The sum of the three angles about C(11) is 360° indicating a trigonal planar geometry. The benzothienyl carbene ligand retains the planarity of the original benzothiophene; the angle between the benzene ring and the thiophene ring is less than 1°. Disruption of the aromaticity of the thiophene ring is evident from the C(11)-C(12) (1.527(11) Å) distance which is ~0.20 Å longer than the corresponding bond distance (C(2)-C(3), 1.33(2) Å) in $(C_5Me_5)Re(CO)_2(\eta^1(S)\text{-}3\text{-}MeBT)$.[32] The C(11)-S (1.712(9) Å) bond is 0.066 Å shorter than the C(18)-S bond (1.778(7) Å) due to sulfur-to-carbene carbon π-bond donation; such short C-S bond distances are typical of thiocarbene ligands.[29] The benzene portion of the BTylcarbene ligand remains delocalized as indicated by the essentially equal C-C bond lengths (average 1.375Å).

Reaction of $[Cp(NO)(PPh_3)Re(2\text{-}Tylcarbene)]^+$ (16) with Nucleophiles. Nucleophiles typically react with carbene,[33] thiocarbene[34,35] and dithiocarbene[29] complexes by adding to the carbene carbon. Complex **16**, $[Cp(NO)(PPh_3)Re(2-Tylcarbene)]^+$, in a 5 mm NMR tube with a wide variety of nucleophiles either does not react (Me_2S, MeSH, $(Co(CO)_4)^-$) or undergoes deprotonation (Me_3N, Me_2HN, H_2MeN, Me_3P, MeS^- HS^-, H^-, $(Cp(CO)_2Fe)^-$) of C(3) to give the thienyl complex **9** at room temperature. Even warming at 40 °C for 48 h, **16** does not react with Me_2S or MeSH. The lack of carbene reactivity is probably due to two factors. First, relatively strong nucleophiles are also strong bases and deprotonation at C(3) is apparently a faster reaction than attack at the carbene carbon. Second, space filling models show that nucleophilic attack is greatly hindered by the PPh_3 on one side of the carbene plane, and nucleophilic attack from the less hindered side of the plane would force the Tylcarbene ligand into the region of the PPh_3, which is also unfavorable.

Deprotonation Studies of 16−18. The hydrogens on C(3) of the carbene complex $[Cp(NO)(PPh_3)Re(2\text{-}Tylcarbene)]^+$ (**16**) are acidic enough to protonate a variety of amines and phosphines to give the thienyl complex $Cp(NO)(PPh_3)Re(2-Tyl)$ (**9**) in quantitative yield (eq 5). The deprotonation of **16** occurs immedi-



(5)

ately, the color of the solution turning from bright yellow to orange. The ν(NO) of the carbene (1720 cm^{-1}) shifts

(26) Kiel, W. A.; Lin, G. Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.
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(30) Johnson, T. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 4728.
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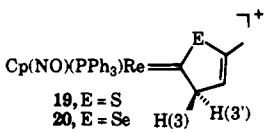
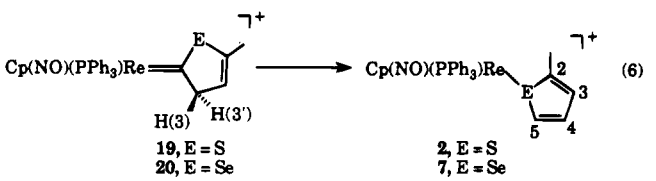
(32) Choi, M. G.; Angelici, R. J. *Organometallics* **1992**, *11*, 3328.
(33) Schubert, U. *Advances in Metal Carbene Chemistry*; Kluwer Academic Press: Dordrecht, 1989 and references within.
(34) Yu, Y. S.; Angelici, R. J. *Organometallics* **1983**, *2*, 1583.
(35) Yu, Y. S.; Angelici, R. J. *Organometallics* **1983**, *2*, 1018.

by ~70 cm^{-1} to the lower wavenumber of the thienyl complex (1654 cm^{-1}). The pK_a values of complexes **16**, **17**, and **18** were estimated from their reactions with a variety of bases; the results are given in Table 5. The benzothienylcarbene (**17**) is the most acidic with a pK_a between that of (p-FC_6H_4)$_3$P (pK_a 1.97) and Ph_3P (pK_a 2.73). The thienylcarbene (**16**) and the selenylcarbene (**18**) are less acidic than **17** and both have a pK_a between (m-MeC_6H_4)$_3$P (pK_a 3.30) and (p-MeC_6H_4)$_3$P (pK_a 3.84). Deuterated **16**, **17** and **18** were prepared by reaction of **9**, **12** and **14** with DO_3SCF_3; the isolated carbene solids contain equal amounts of D in both the H(3) and H(3′) positions as determined by integration of the ^2H and ^1H NMR spectra. Deprotonation with Dabco in CD_2Cl_2 gives the respective L-yl complex (**9**, **12**, and **14**) back with approximately equal amounts of the complexes with deuterium or hydrogen on C(3) based on integrations of the ^1H NMR spectra. When **17** and DO_3SCF_3 are dissolved in CD_2Cl_2, exchange of D into the H(3) or H(3′) positions is not observed.

Synthesis and Thermal Isomerism of the Carbenes 19 and 20. The reactions of Cp(NO)(PPh_3)Re-(2-(5-methylthienyl)) (**10**) and Cp(NO)(PPh_3)Re(2-(5−methylselenyl)) (**15**) in CD_2Cl_2 with triflic acid at −42 °C in 5 mm NMR tubes give the corresponding carbene compounds [Cp(NO)(PPh_3)Re(2-(5−methylthienyl)carbene)]$^+$ (**19**) and [Cp(NO)(PPh_3)Re(2-(5−methylselenyl)-carbene)]$^+$ (**20**) in quantitative yield. The IR, ^1H and



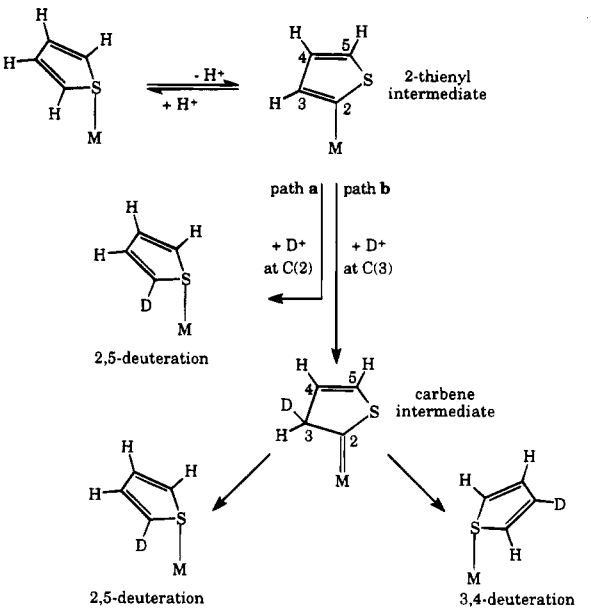
^{13}C NMR spectra closely resemble those of the isolated thienyl- and selenylcarbene complexes **16**, and **18**. However, upon warming the samples above −10 °C for **19** and −30 °C for **20**, the ^1H NMR resonances for the carbene complexes disappear and peaks for the $\eta^1(E)$ complexes **2** and **7** appear (eq 6). The reaction is



(6)

complete within 1 h with no evidence in the ^1H or ^{13}C NMR spectra for other products. Attempts to isolate **19** at low temperature (−78 °C) gave only the rearranged $\eta^1(S)$ isomer. The reaction of DO_3SCF_3 with **10** gives the deutero carbene (**19D**) with deuterium approximately equally distributed in the H(3) and H(3′) positions as determined by ^2D NMR studies. Upon warming, the isomerization reaction (eq 6) occurs, which yields **2** with deuterium not only in the 4- and 5-positions of the thiophene ring, but also in the ortho positions of the phenyl rings of the PPh_3. No evidence is found in the upfield region (up to −30 ppm) for a metal hydride intermediate in either the ^1H or ^2H NMR spectrum of the reaction mixture. The mechanism for the rearrangement (eq 6) is unclear at this time. However, the fact that it occurs demonstrates that the $\eta^1(E)$ isomers (**2** and **7**) are thermodynamically more stable than the carbene forms.

Scheme 1



While protonation of the Tyl complex **9** gives (eq 4) the stable Tylcarbene complex **16** and protonation of the 2-MeTyl complex **10** yields (eq 6) the unstable but detectable carbene **19**, protonation of Cp(NO)(PPh_3)Re(3-(2,5-Me_2Tyl)) (**11**) produces [Cp(NO)(PPh_3)Re($\eta^1(S)$-2,5-Me_2T)]$^+$ (**3**) in quantitative yield. An ^1H NMR study of the latter reaction at −60 °C shows no evidence for a carbene intermediate. If it were to form, it would likely be very unstable because the carbene carbon would not be stablized by an adjacent sulfur or selenium heteroatom, which undoubtedly contributes to the stabilities of the other carbene complexes (**16-20**).

Comments on the Mechanism of Deuterium Exchange of Thiophenes over HDS Catalysts. Catalytic reactor studies[36-40] of the deuterium exchange of thiophene with D_2 over HDS catalysts have shown that deuterium is readily incorporated into the 2- and 5-positions and to a lesser extent in the 3- and 4−positions. This exchange has been previously modeled in the η^5-thiophene complex CpRu(η^5−T)$^+$,[41,42] with the rate of deuterium incorporation into the 2,5−positions being much faster than into the 3,4-positions. These studies form the basis for a mechanism for deuterium exchange into thiophene that involves η^5-adsorbed thiophene.[41] An alternative mechanism[5,6] involves $\eta^1(S)$-adsorbed thiophene that is deprotonated by a basic oxide, sulfide or hydride species to give a surface bound thienyl group (Scheme 1); this step is similar to the reaction in eq 3. Transfer of D^+ from an acidic site on the surface to C(2) of the thienyl group would give the 2-deuterated $\eta^1(S)$-bound thiophene (Scheme 1, path **a**); the formation of 2−deutero-benzothiophene in the reaction[5] of Cp(CO)-(PPh_3)Ru(2-BTyl) with DO_3SCF_3 serves as an organometallic model for this step, which was originally

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proposed by Cowley.[43] The thienyl species could also undergo D^+ addition at C(3) to form the surface-bound carbene (Scheme 1, path **b**); this step is modeled by the reaction in eq 4. The carbene could then rearrange thermally to either the 2-deuterated or the 3-deuterated $\eta^1(S)$-bound thiophene as was observed (eq 6) for the 2-(5-methylthienylcarbene) (**19**) compound. Thus, the 2-thienyl intermediate is key to producing 2-deutero-thiophene via direct M-C(2) cleavage (path **a**)and to forming both 2- and 3-deutero-thiophene via the carbene intermediate (path **b**). Therefore, the new organometallic model reactions described in the present work provide new ways of thinking about deuterium exchange into thiophene and benzothiophene on HDS catalysts.

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Supplementary Material Available: A Fully labeled figure of **17b** and tables of atomic coordinates, bond distances and angles, anisotropic displacement coefficients, H atom coordinates, and least squares planes (11 pages). Ordering information is given on any current masthead page.

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